Experimental study on the ash behaviour in combustion of pelletized residual agricultural biomass

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ABSTRACT

Agricultural residual biomass presents a high potential for energy use around the world, often not utilized to a large extent due to its significant differences with respect to other biomass types, such as the one of forest origin. These differences are mainly related to the characteristics of its ashes (quantity and composition) which increase certain problematic phenomena during combustion, among them bottom ash sintering and fly ash deposition. The main goal of this paper is the experimental study of these issues for four different agropellets made of residual agricultural biomass (one woody and three blended with an herbaceous component) and a forest wood pellet (used as a reference), evaluated under different operating conditions in a laboratory fixed bed reactor. The influence of inlet air flow and temperature on the sintering degree and deposition ratio has been analyzed in a systematic way. For the five biofuels, under tested conditions, a clear relation inversely proportional between air excess ratio and deposition ratio has been determined. Deposition was more substantial for the four agropellets; meanwhile the sintering degree was more important for the three with an herbaceous component. The information obtained in this research work is intended to help researchers and technologists to make choices regarding the design and operation of conversion systems adapted for agricultural residual biomass, enhancing its market penetration.

KEY WORDS:

Biomass combustion; Agropellet; Fixed bed reactor; Ashes; Sintering; Deposition

1. INTRODUCTION

The main contribution of biomass to the renewable energy generation in the EU is found in the heating and cooling sector. The 2020 target is to reach 3785 PJ in the use of biomass for heating and cooling, and the contribution of solid biomass is the most important to this goal (in 2012, 2943 PJ had already been achieved with this resource) [1]. Solid biomass is largely used in households for heating, with an important presence of forest wood pellets. In 2012, the use of biomass in households already exceeded the target set for 2020 by 10% [1].

In order to satisfy this growing demand, forest biomass, whose main use is still energy production, is not enough [2]. The new uses foreseen in the medium term for these resources (e.g. biorefineries and new materials) will hinder their increased utilization for energy production [2], [3]. For this reason, it is necessary to look for new resources to satisfy the thermal energy sector. The biggest increase in supply should come from the agricultural sector, where an increase of more than 150% compared with 2006 is planned [1].

These new resources comprise mainly, apart from energy crops and some types of residual agro-industrial biomass, agricultural crops residues: herbaceous crop residues and pruning residues of permanent woody crops. In particular, the target of this paper are three residual agricultural biomasses: vineyard pruning, corn stover and barley straw. They were selected due to their potential as energy sources both in Europe and in the rest of the world. From FAOSTAT data (available at [4]), it can be seen that the cultivated surface of grape, maize and barley in the EU in 2016 was 24.5 Mha. Even using conservative availability indices (50% for vineyard pruning and corn stover, and 10% for barley straw), their attainable residual biomass amounts to an energy potential above 500 PJ/yr. Consequently, their use could contribute significantly to achieve the objectives set.

On the other hand, thermal conversion of agricultural biomass, mainly the herbaceous type, shows clear differences with respect to that of forest origin. This is mainly due to the characteristics of the ashes (quantity and composition) which give rise to certain phenomena in the conversion facility. The

use of a blend of woody and herbaceous biomass may reduce these problems (Zeng et al., 2016; Zeng et al., 2018).

During combustion, ashes undergo physical and chemical transformations which cause fractioning. Each of the fractions presents different problems:

- Part of the components of the ashes gives rise to a solid fraction which accumulates in the grate (bottom ash, mainly constituted by e.g. calcium and potassium silicates) and can cause sintering, affecting conversion in the bed, restricting the effectivity of the grate and negatively influencing proper control of gaseous emissions: carbon monoxide (CO), nitrogen oxides (NOx) and volatile organic compounds (VOC) [5]-[8].
- Other part is volatilized, so when it comes into contact with zones of lower temperature, it may condense in the form of small crystals (e.g., potassium chloride -KCl-, potassium sulfate -K_2SO_4- and potassium carbonate -K_2CO_3-) over the surfaces of the equipment used for heat exchange. An ash entrainment of solid particles in gas combustion flow from the bed to the convective areas also can be produced. This phenomenon together with volatilization are responsible for deposition, corrosion and erosion, which reduce performance and lifetime of the equipment.
- Additionally, some fractions of the finer particles (mostly those of size below 2.5 μm), instead of leading to deposits formation, can end up being emitted as aerosols to the atmosphere, causing respiratory diseases [9], [10].
- Finally, in the mass balance of the elements that constitute ashes it should be considered the compounds that remain in gaseous state, such as sulfur dioxide -SO_2- or hydrogen chloride -HCl- which are environmental pollutants [11]-[13].

During the last decades, several renowned research centers have been working towards identifying key factors in biofuels conversion, as well as the transformation of their ashes, in order to predict the problems generated by the latter. Although most of the published research so far concerns forest biomass (e.g., [14]-[20]), there are some studies addressing agricultural biofuels (e.g., [8], [21]-[23]). In all cases, it is recognized the critical influence of ash chemical composition, especially by the

77 concentration of Na, Mg, Al, Si, P, S, Cl, K and Ca [24], in the problems associated with thermal
78 conversion (e.g. sintering, deposition and emissions).
79 Notwithstanding, besides chemical composition, the ash behaviour (especially in grate boilers) is also
80 influenced by the combustion conditions in the bed, related with the design ([23]-[26]), as well as
81 with the operation mode [27].
82 In order to analyze these effects, tests can be made in commercial boilers adapted to carry them out
83 controlled [5], [8], [21], [22], [28]-[30]. However, due to the complexity of the phenomena
84 intervening in the fractioning of ashes, it is preferable to use laboratory reactors, most of them using
85 fixed bed technology, in order to have better control of combustion conditions [13], [23], [31]-[34].
86 This type of reactors makes possible to gather important information about the behaviour of fuels
87 under different operating conditions. It is possible to evaluate fuel reactivity (ignition front velocity
88 and ignition rate [35]), quantify bottom ash in the bed and determine its propensity to sintering as
89 well as quantify the amount of solid residue deposited in heat exchange surfaces (deposition ratio).
90 Furthermore, these reactors allow obtaining samples in order to characterize solid residues (bottom
91 ash and deposits), for a better understanding of the mechanisms driving ash fractioning and
92 quantifying the impact of corrosion phenomena in the heat exchange zones. In addition, carrying out
93 study of gaseous emissions (e.g. CO, NOx or volatile organic compounds) [36]-[39], as well as those of
94 particulate material [40]-[42], is possible.
95 The main goal of this work is the analysis of the three first points (reactivity, sintering and deposition)
96 for different mixed pellets made of residual agricultural biomass (agropellets), evaluated under
97 different operating conditions in a laboratory fixed bed reactor.

98 ## 2. MATERIALS AND METHODS

99 ### 2.1 Fuels

100 Five different biofuels are studied in this paper. One is a forest wood pellet and four are agropellets
101 (three mixed pellets and one wood pellet):

- Forest wood pellet:
  - Pine pellet (PP) -pellet A1, according to ISO 17225-2-: it will be used as a reference to record the differences from fuels of residual agricultural origin.
- Agricultural residual pellets (agropellets):
  - Wood agropellet: 100% Vineyard pruning pellet (PV)
  - Mixed pellet (with an herbaceous component):
    - 70% Vineyard pruning + 30% Barley straw (PVB)
    - 70% Vineyard pruning + 30% Corn stover (PVC)
    - 60% Vineyard pruning + 20% Corn stover + 20% Barley straw (PVCB).

Tables 1 and 2 show the main thermochemical properties of the selected fuels.

Table 1. Fuels properties

		PP	PV	PVB	PVC	PVCB
Bulk density (kg·m^{-3})[1]		674	599	562	556	546
Proximate analysis (% m/m d.b)	Volatile matter[2]	84.2	76.5	72.4	72.1	72.3
	Fixed carbon[8]	15.4	20.5	21.7	18.6	21.2
	Ash[3]	0.4	3.1	5.9	9.3	6.5
Total Moisture (% m/m w.b.)[4]		7.2	9.0	9.1	9.2	9.0
Ultimate analysis (% m/m d.b.)	Carbon[5]	50.9	48.9	46.36	46.01	46.36
	Hydrogen[5]	6.1	5.8	5.77	5.64	5.55
	Nitrogen[5]	0.09	0.55	0.56	0.55	0.60
	Sulfur[6]	< 0.01	0.09	0.055	0.050	0.094
	Chlorine[6]	0.01	0.03	0.047	0.080	0.090
	Oxygen[8]	42.49	41.6	41.29	38.33	40.58
HHV (d.b. at p=constant) (MJ·kg^{-1})[7]		20.43	19.11	18.54	18.06	18.36
LHV (w.b. at p=constant) (MJ·kg^{-1})[7]		17.55	16.01	15.48	15.06	15.40

[1] EN 15103:2009 [2] EN-ISO 18123:2016 [3] EN-ISO 18122:2016 [4] EN-ISO 18134:2016 [5] EN-ISO 16948:2015
[6] EN-ISO 16994:2015 [7] EN-ISO 14918:2011 [8] Calculated

121 Table 2. Ashes properties

		PP	PV	PVB	PVC	PVCB
Chemical ash composition (% m/m d.b.)[9]	Al_2O_3	2.1	0.91	2.72	2.19	2.30
	CaO	24	42.39	45.77	48.17	40.54
	Fe_2O_3	1.8	0.71	2.22	1.98	1.27
	K_2O	13	30.09	14.88	15.79	19.43
	MgO	9.9	10.45	8.64	7.64	11.01
	Na_2O	1.8	0.62	0.41	0.39	0.38
	P_2O_5	8.5	7.35	4.45	4.00	4.36
	SO_3	4.4	3.95	2.32	3.24	4.39
	SiO_2	15	2.65	17.70	15.31	15.22
	TiO_2	0.078	0.07	0.17	0.18	0.16
	Cl	-	0.12	0.21	0.57	0.54
Ash melting temperatures oxidant conditions (°C)[10]	Initial deformation temperature (DT)	> 1400	1240	1130	1310	1330
	Hemisphere temperature (HT)	> 1400	> 1500	1310	1460	1460
	Flow temperature (FT)	> 1400	> 1500	1370	1480	1470

122 [9] EN-ISO 16967:2015 [10] CEN/TS 15370-1:2006

123 ## 2.2 Reactor

124 As previously mentioned, it is very difficult to obtain accurate data using commercial equipment,
125 even a modified one. Thus, for research purposes, it is usual to resort to laboratory reactors. In the
126 case of fixed bed reactors simplified geometries are usually used, such that the behaviour is
127 considered one-dimensional [43].

128 The main variable in fixed bed commercial equipment is space, since by different means, biomass
129 moves through the grate while experiences several processes: heating and drying of the fuel,
130 volatiles release, and, finally, combustion of the char. However, in laboratory reactors, fuel
131 undergoes these processes successively [35]. Fuel is fed in batches, i.e., certain amount is introduced
132 in the reactor and after combustion, ashes are removed, to be added a new load of fuel. This
133 operation mode greatly simplifies design, facilitates data acquisition and allows better control of the
134 reactor.

135 In order to perform the tests, an experimental fixed bed reactor has been adapted (see Fig. 1). It was
136 designed and set up by CIRCE for a previous project [44]. It consists of a vertical cylindrical combustor
137 chamber made of stainless steel AISI-310S, with a height of 1700 mm and an inner diameter of 200

mm. There is an insulating material between the external side and the combustor chamber. At the bottom, there is a grate with 3 mm diameter holes separated equidistantly resulting in a porosity of 4.5%.

Combustion air is injected from the bottom, through the orifices in the grate, by means of a fan equipped with a variable-frequency drive that allows adjusting the air flow. Since tests are carried out at a controlled temperature of the combustion air, it is arranged to use a refrigerator or an electrical resistor at the inlet air, to cool down or heat up (see Fig. 1). Besides, a hot wire flow meter is located after the fan to measure the temperature and the velocity of the introduced air.

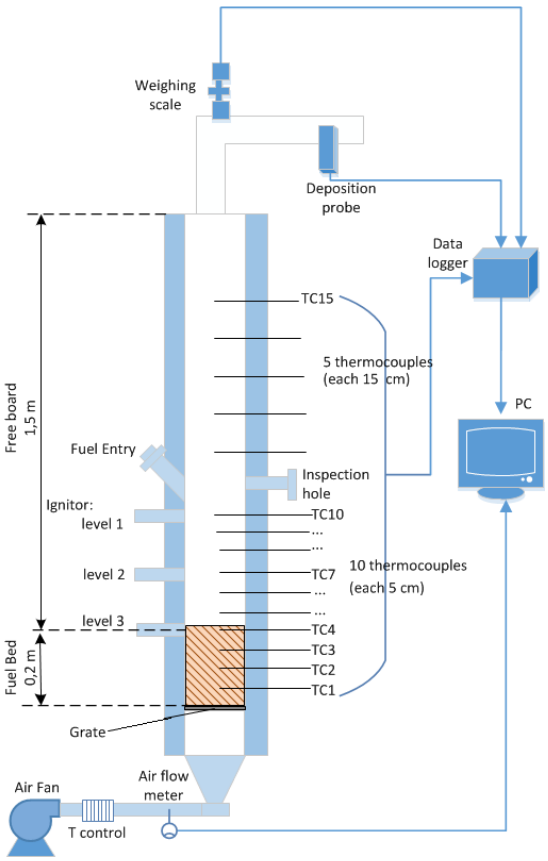


Fig. 1. Scheme of the experimental test facility

Combustion inside the reactor can be regarded as counter current, given the relative movement of the air flow and the ignition front. While the latter moves from the upper part of the reactor towards the base, the combustion air, as is already indicated, is injected from the grate located in the lower part of the reactor. In this configuration, radiation and conduction drive the ignition front in the opposite direction to the flow of combustion air. The latter, through convection, retains to some

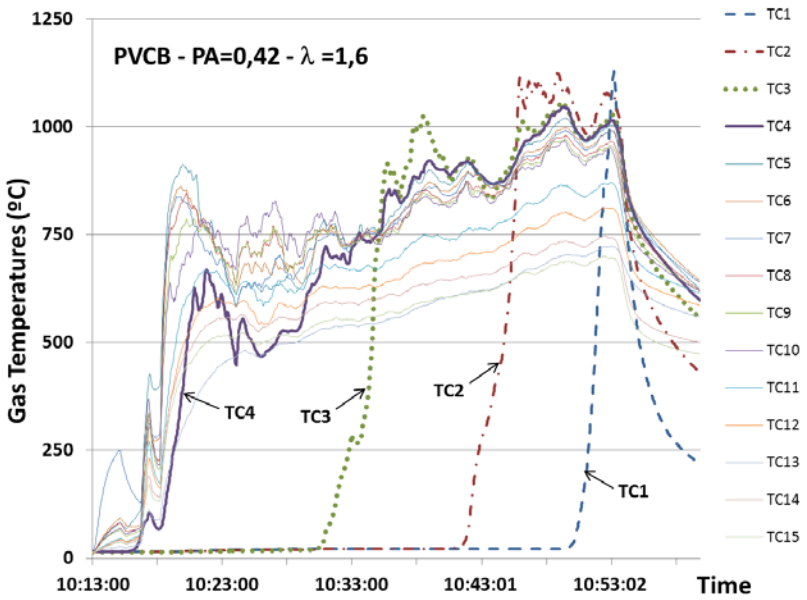
153 extent the advance of the ignition front [43]. Combustion gas exits through a pipe located near the
154 top.
155 Fifteen N-type thermocouples are inserted along the chamber wall. They perform the measurement
156 in the center of the combustion chamber and, as can be seen in Fig. 1, they are aligned. For
157 identification purposes, they are numbered from TC1, the closest to the grate, to TC15, located in the
158 upper part of the reactor. The first ten are located 5 cm from each other (from TC1 to TC10), and the
159 other five each 15 cm apart. The reactor is suspended from a weighting scale that allows monitoring
160 the mass loss of the fuel bed.
161 In addition, the facility has been completed by installing a deposition probe with a removable
162 sampling ring in the chimney of the reactor (see Fig. 1) [45]. This is a common device used to
163 simulate the deposition of ashes in furnace pipes and heat exchangers [46]. The sampling ring used
164 to extract samples of the deposits is cooled by compressed air, allowing to keep its surface at an
165 appropriate temperature for studying deposition [45]

166 **2.3 Test protocol**

167 In this section the relevant features of the tests performed with the laboratory reactor are
168 presented. A total of 82 tests have been carried out with the five fuels following the same protocol.
169 All of them were carried out with an excess air ratio in the range from 1 to 2.3 (over-stoichiometric
170 conditions), in order to reproduce the combustion conditions found in small, domestic equipment.
171 The parameters that have been varied in the tests, besides the fuel type, are:

172 - *Inlet air flow (PA, kg·m^{-2}·s^{-1})*, expressed as the air mass flow by unit area of the grate
173 - *Inlet air temperature (Ta, ^{o}C)*. According to this parameter, there are two types of test for
174 each fuel: without pre-heating (inlet air at 25 ^{o}C), and with pre-heating (inlet air at 80 ^{o}C).

175 The amount of biomass fed to the reactor in each test is such that the total bed height is 210 mm. In
176 this way, thermocouples TC1 to TC4 are initially set inside the bed. Fig. 2 shows the evolution of the
177 temperatures registered by the 15 thermocouples inside the reactor during one of the tests.



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179 Fig. 2. Temperature profiles. Reactor test with PVCB – PA=0.42 kg·m^{-2}·s^{-2} – Ta=25 ºC - λ=1.6.

180 The reaction is triggered by an ignitor placed above the fuel bed, which causes the temperatures of
181 the biomass to increase (upper thermocouples). Once combustion is initiated, and biomass is being
182 consumed, the temperature registered by thermocouples placed along the fuel bed rises, from TC4
183 to TC1 (Fig. 2). They represent the increase of the fuel temperature as the ignition front propagates.
184 Once all the fuel has been consumed, temperatures start to decrease. It is considered as stable
185 combustion period, to perform calculations, the time lapsed from TC3 reaching 500 ºC, so the fuel
186 above TC3 has been consumed and there has been enough time for the combustion to stabilize, until
187 TC1 reaches the same reference temperature, and the only remaining fuel is that between this
188 thermocouple and the grate.

189 During the stable combustion period, the deposition probe is inserted inside the chimney. The
190 removable sampling ring has been previously cleaned, dried and weighed. The compressed air for
191 refrigeration is adjusted so that the average temperature of the sampling ring is 335±25 ºC. Once
192 extracted (see Fig. 3) the dirty sampling ring is dried and weighed again to obtain the amount of mass
193 deposited. Using this weight value and the surface of the sampling ring it is possible to calculate the
194 deposition rate [REFERENCIAS], allowing to estimate the tendency to fouling of each studied fuel.

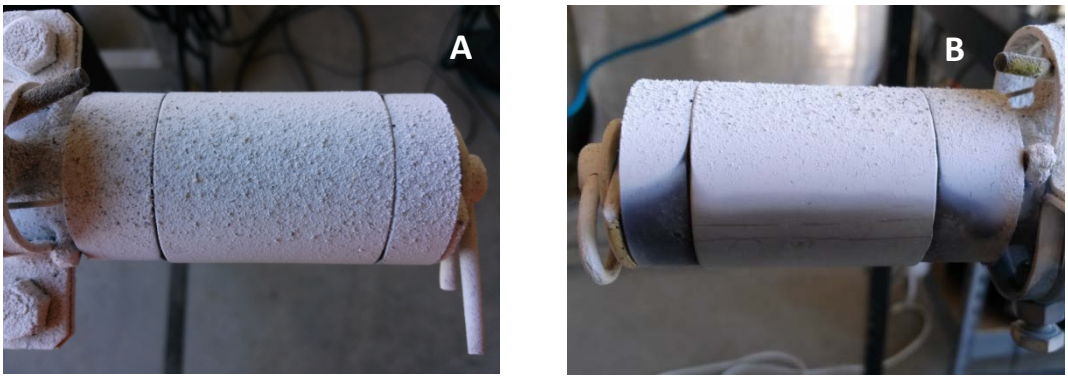


Fig. 3. Removable sampling ring. Reactor test with PVB – PA=0,40 42 kg·m^{-2}·s^{-2} – Ta=25ºC – λ=1.37 – DR = 26.1 g·m^{-2}·h^{-1} – A: Frontal view, B: Lateral view.

Besides the aforementioned variables, once combustion is complete and the reactor has cooled down, bottom ashes are collected from the top of the grate for weighing and classification (see Fig. 4). The determination of sintering degree with the sieving and weighting bottom ash fractions has been used in several studies to studies to determine the slag tendency of a fuel ([5], [47], [48]). In this case, the following categories, based on a revised classification of sintering degree defined in a previous work [21], are used: S1, pass through a 3.15 mm sieve and are considered as not sintered; S2, do not pass the 3.15 mm sieve, but are easily disaggregated by hand and present a low degree of sintering; S3, do not pass the 3.15 mm sieve, are difficult to disaggregate by hand and present a high degree of sintering. Since the difference between S2 and S3 is subjective, a fraction S2/3 encompassing both classes is used.

Fig. 4. Bottom ashes. Reactor test with PVC – PA=0.41 kg·m-2·s-1– Inlet Ta=25 ºC –λ =1.27

From the inlet parameters (PA y Ta), the measured variables, the geometrical data and the fuel analysis, the following parameters are calculated:

- **Air velocity in the grate (V_{PA}, $m \cdot s^{-1}$):** it is quantified from the mass flowrate of combustion air injected during the test (PA), its inlet temperature (Ta), and the inlet area (grate hole).
- **Velocity of the ignition front (v_{ir}, $m \cdot s^{-1}$):** it is a measure of how fast the flame progresses along the fuel bed height. It is calculated from the time that takes for consecutive thermocouples (TC3, TC2 and TC1) to reach a pre-determined temperature (reference value 500 °C) and the known distance between them (50 mm).
- **Ignition rate (m_{ir}, $kg \cdot m^{-2} \cdot s^{-1}$):** it is obtained by multiplying the velocity of the ignition front (v_{ir}) by the bulk density of the fuel, which allows comparing the combustion behaviour of different fuels [43]. It is expressed as mass loss per grate surface area (ignition front plane area) and time.
- **Excess air ratio (λ):** once the ignition rate (m_{ir}) has been determined, the excess air ratio for each test can be calculated from the mass flowrate of combustion air injected during the test (PA), and the stoichiometric air-to-fuel ratio of the studied fuel.
- **Mean flame temperature (TC3m, °C):** average value of the temperature registered by TC3 between the instant when TC2 and TC1 reach 500 °C.
- **Deposition rate (DR, $g \cdot m^{-2} \cdot h^{-1}$)):** it is obtained from the mass of ash deposits collected, the area of the ring surface and the duration of the exposition.

3. RESULTS AND DISCUSSION

Table 3 summarizes the main features of the tests performed. In the following section, the main characteristics and combustion behaviour differences among the fuels observed during the tests are presented regarding the different combustion parameters, the bottom ash and ash deposits collected by the probe.

Table 3. Summary of test features

		PP	PV	PVB	PVC	PVCB
Number of tests performed	**Without pre-heating (Ta=25 C°)**	9	10	10	9	11
	Pre-heated test (Ta=80 C°)	7	8	6	6	6
PA ($kg \cdot m^{-2} \cdot s^{-1}$)	**Min**	0.39	0.36	0.37	0.41	0.37
	Max	0.59	0.52	0.54	0.54	0.51
λ	**Min**	1.00	1.15	1.21	1.18	1.23
	Max	1.95	2.04	2.30	2.29	2.07
Fed fuel (kg)		4.40	4.03	3.78	3.74	3.67

3.1. Combustion parameters

One of the fundamental parameters used to characterize combustion is λ. In Fig. 5, this parameter is shown as a function of PA for all tests, including those in which Ta was 25ºC, and those in which this value was set at 80ºC (pre-heated test, namely, ph).

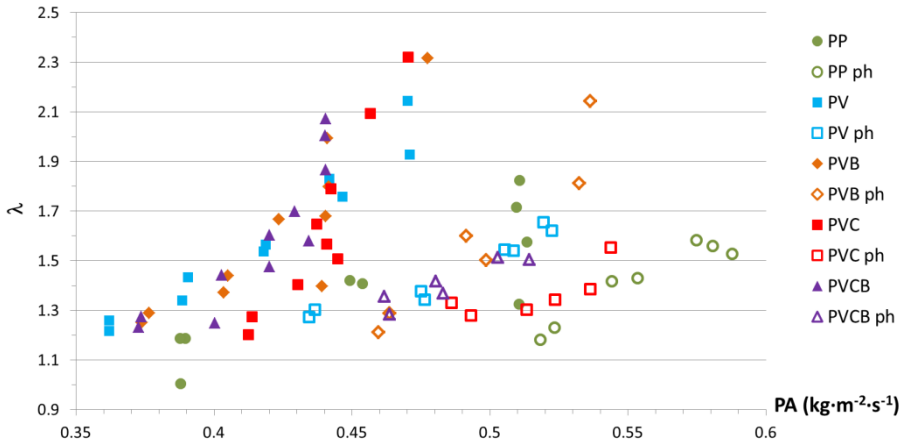


Fig. 5. Relation between excess air ratio (λ), inlet air flow (PA) and inlet air temperature (Ta).

As could be expected, for each fuel, given Ta (25ºC or 80ºC), λ increased with PA. PA supplied and, therefore, λ is the key parameter influencing the behaviour of the ignition front. Previous studies involving fixed bed reactors in literature have shown that, depending on PA supplied, different combustion regimens might appear [43], [49], [50]. There is a first regime, generally corresponding to λ values lower than 1 (sub-stoichiometric conditions), where the deficient amount of oxygen is the limiting parameter for combustion. In this case, an increase in PA supplied accelerates the propagation of the combustion front (higher m_{ir}) and causes that the reaction temperatures raise. If

PA supplied is increased further, generally corresponding to λ values higher than 1 (over-stoichiometric conditions), the behaviour is different. In this regime, as the air supplied increases, the fuel bed temperatures decrease and the flame propagation process slows down (lower m_{ir}) [43], due to the convective cooling. This general tendency is depicted for all the tested fuels in Fig. 6 and Fig. 7, where as λ values increase (higher than 1 in all the cases), m_{ir} and TC3m gradually decrease. This decrease in m_{ir} values means that the relation between λ and PA shown in Fig. 5 (for a constant Ta) is not exactly lineal.

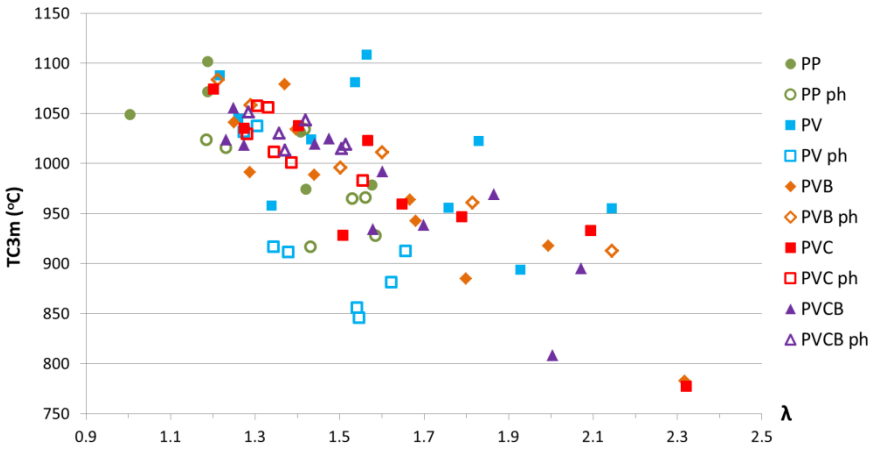


Fig. 6. Mean flame temperature (TC3m) versus excess air ratio (λ) for all fuels

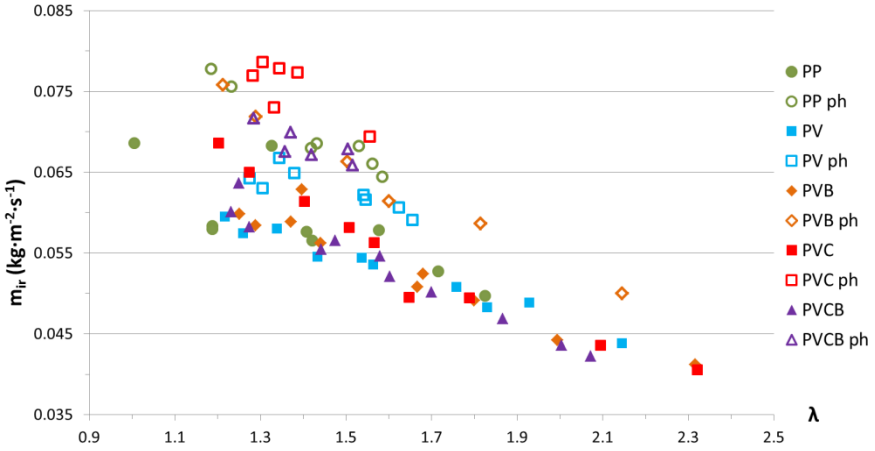


Fig. 7. Ignition rate (m_ir) versus excess air ratio (λ) for all fuels

In any case, given the interdependency for each fuel between m_{ir}, λ and TC3m, for purposes of clarity, in some of the following discussions it will be more interesting to use λ instead of PA as the parameter related to the amount of combustion air.

Regarding the influence of Ta, it can be seen in Fig. 5 that in order to attain a certain λ it is necessary to work with higher PA in the case of pre-heated air. This is because pre-heating primary air causes an increase in m_{ir} for all fuels and conditions tested, as can be seen in Fig. 7, due to a higher Ta does not lead to such a pronounced convective cooling, while it improves drying and ignition. The increase in m_{ir} achieved by pre-heating the inlet air is around 15-20% for the different fuels. However, the combustion temperatures in the bed (represented by TC3m) are not clearly influenced by Ta, except in the case of PV (see Fig. 6).

Concerning the comparison of the values of TC3m and m_{ir} among the tested fuels, there are not significant differences. All fuels reach similar TC3m values, except PV which shows a great variability. There is a wide variety of properties that influence the behaviour of a fuel during combustion, some are related to its composition (elemental composition, ash content, moisture, heating value or volatiles and fixed carbon ratio) and some are related to its physical characteristics (particle size and shape, particle durability or bed porosity). Previous studies in literature have tried to relate the behaviour of the propagation front with some characteristics of the fuel [41], [43], [49], [51]-[53]. As all the fuels tested in this paper are pelletized and present similar moisture values, no remarkable differences were expected in the m_{ir} and TC3m values and behaviour. It is very difficult to draw conclusions on the slight differences and tendencies observed as all the characteristics influence the parameters under study in a different and interrelated manner.

It has been also observed that for all test, PA and, therefore, V_{pa}, not only affects the combustion behaviour but also ash entrainment. In Fig. 8 the relationship between these two variables is depicted. As it was expected, the relationship between PA and V_{pa} is linear and clearly affected by the presence of pre-heating, due to this velocity is proportional to Ta. To attain similar λ values during tests with and without pre-heating, greater PA values were needed for the tests with higher Ta and, accordingly, higher values of V_{PA} are obtained in these cases.

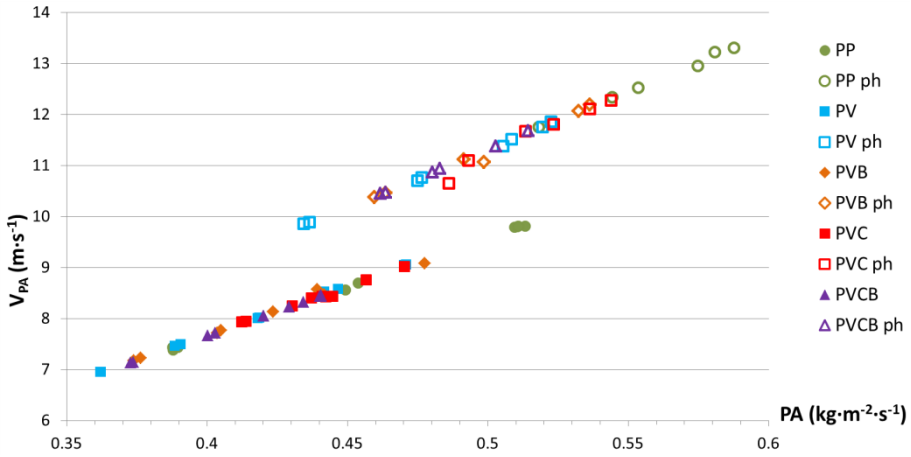


Fig. 8. Air velocity in the grate (V_{PA}) versus inlet air flow (PA) for all fuels.

3.2. Bottom ash

In terms of the bottom ash fraction and its sintering degree, important findings have been elucidated for all the tested fuels.

As it is depicted in Fig. 9, considering each fuel separately it can be noticed that the largest bottom ash proportion (% obtained with respect to the total amount of ash introduced with the fuel) is around 75% and corresponded to PVB, followed by PVCB and PVC pellets, with 60% and 50% respectively. On the contrary, the lowest proportion of gathered bottom ash (around 5-30%) is reached by PP and PV, in that order. Considering these results, it seems that tested pellets can be divided into two main groups: the first one is formed by wood pellets (PP and PV) whereas the second group corresponds to mixed pellets (PVB, PVC and PVCB).

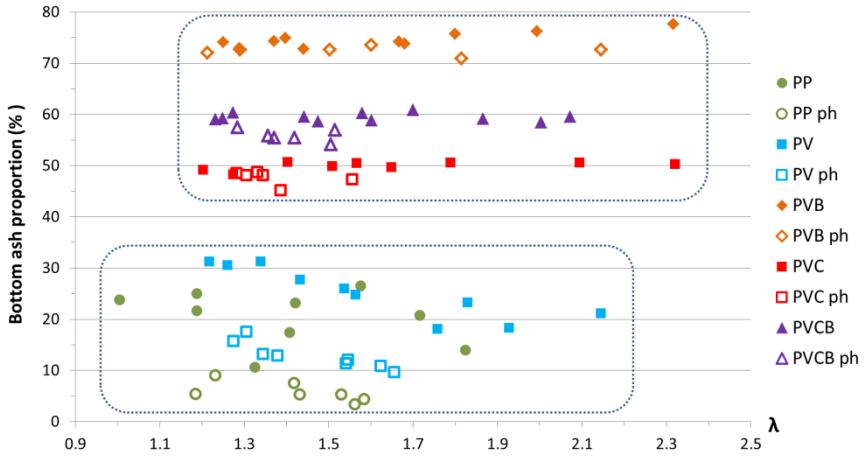
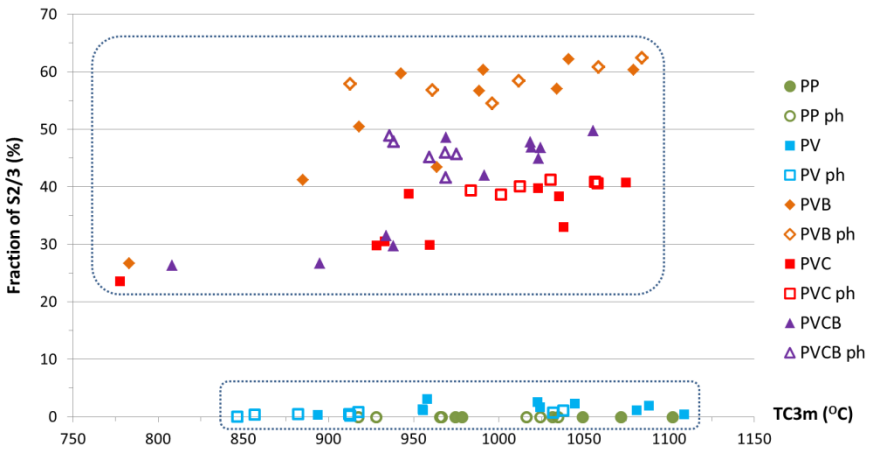


Fig. 9. Bottom ash proportion (% with respect the total amount of ash introduced with the fuel) versus excess air ratio (λ) for all fuels.

306 For the mixed pellets the proportion of bottom ash gathered is generally unaffected by λ. This trend
307 could suggest that for all combustion temperatures (from 775ºC) the expected ash fractioning is
308 reached, leading to the remaining bottom ash fraction on the grate whereas the more volatilized
309 components are released and carried out with the gases. However, it could also mean a decrease of
310 the quantity of volatilized ash, due to the lower combustion temperature, compensated with the
311 expected increase of ash entrainment, due to the larger air velocity.
312 With regard to woody fuels, both the low quantity of bottom ash, and its reduction upon increasing
313 λ, could be related to a high degree of particles entrainment.
314 Also, it is important to mention that almost all the fuels show a lower percentage of bottom ash for
315 tests with pre-heated air. These tests were carried out with a higher air velocity and a slightly higher
316 combustion temperature, and consequently a larger ash entrainment and vaporization, respectively,
317 could be expected. Nevertheless, this fact is much less clear in PVB case and much more in PV case.
318 The sintering degree of bottom ash is key to analyze the behaviour of the fuel, due to the problems
319 that these structures can generate during the development of combustion and for the equipment.
320 In Fig. 10 it is shown the ash fraction S2/3 found in the bottom ash (as a percentage respect to the
321 total amount of ash introduced) as a function of TC3m (with- and without pre-heating).



322

323 Fig. 10. Fraction S2/3 of the bottom ashes (% with respect the total amount of ash introduced with the fuel)
324 versus the mean flame temperature (TC3m) for all fuels.

325 Again the two groups of fuels show different behaviour: while wood pellets present low quantities of
326 S2/3 fraction (below 3% for PV and negligible for PP), in line with the high values of HT and FT

presented by these fuels (Table 2), for mixed pellets the percentages are much higher (between 24 and 63%). Among the mixed pellet, PVB stands out due its high sintering degree, which is also in line with its lower ash melting temperatures (Table 2).

From Fig. 9 and Fig. 10 is clear the relationship between the sintering degree and the percentage of retained ash, since the fuels with greater sintering degree show a greater amount of bottom ash as well. This could be because a high degree of sintering precludes particles entrainment.

In Fig. 10 can also be observed the clear increment of the sintering degree upon increasing TC3m, at least until 900-1000ºC depending on the fuel, from that point values are almost constant.

Concerning the effect of preheated air, it can be seen from Fig. 10 that not significant differences have been generally detected for the S2/S3 proportion.

It is difficult to completely explain the differences in the behaviour of fuels, especially in the case between the PV and the rest of residual agricultural pellets, relying only in the chemical composition of the ashes shown in Table 2., because the phenomenon of sintering and slagging depends not only on chemical composition but also on its mineral origin [54]. Nevertheless, some important characteristics can be analyzed considering molar ratios presented in Table 4., based on earlier research studies [22].

Table 4. Molar ratios

Ratio label	Ratios	PV	PVB	PVC	PVCB
I	Si/P	0.43	4.70	4.52	4.12
II	(K+Na+Ca+Mg)/(Si+P)	11.34	3.81	4.49	4.51
III	(Ca+Mg)/(K+Na)	1.54	3.13	3.01	2.35

Considering molar ratio I, Si/P, it is evident that bottom ash is Si-dominated for all mixed pellets (PVB, PVC and PVBC). For PV, besides Si-compounds expected to be retained in bottom ash, P interactions might result into a P-compounds distribution among bottom and fly ashes. Furthermore, comparison of molar ratio II suggests that there is a surplus of alkali components compared to (Si+P) for all the four agricultural fuels. According to molar ratio III, this surplus is formed by a larger fraction of alkaline earth elements (Ca+Mg) than the one for the alkali metals (K+Na).

It is generally expected that presence of alkaline earth oxides will rise the melting temperatures of alkali silicates, which largely will contribute to overcome occurrence of severe sintering. The excess of alkaline earth elements will remain in the residual ash limiting the sintering tendency whereas the alkali metal fraction will be volatilized and, consequently, will contribute to the formation of fine particulate emissions and deposits. Nevertheless, this beneficial effect to limit sintering behaviour is surely minimized for the mixed pellets due to the surplus of Si (see ratio I). Consequently, silicates of lower melting temperature (K/Ca/Silicates) are formed contributing to the achieved sintered ashes. This was not the case of PV, due to its low value of molar ratio I.

3.3. Deposition

Deposits were settled chiefly on the upstream side of the probe, with only a very marginal portion downstream (see Fig. 3), similarly to other results found in literature [35], [54].

In Fig. 11 it is shown DR as a function of λ (with- and without pre-heating).

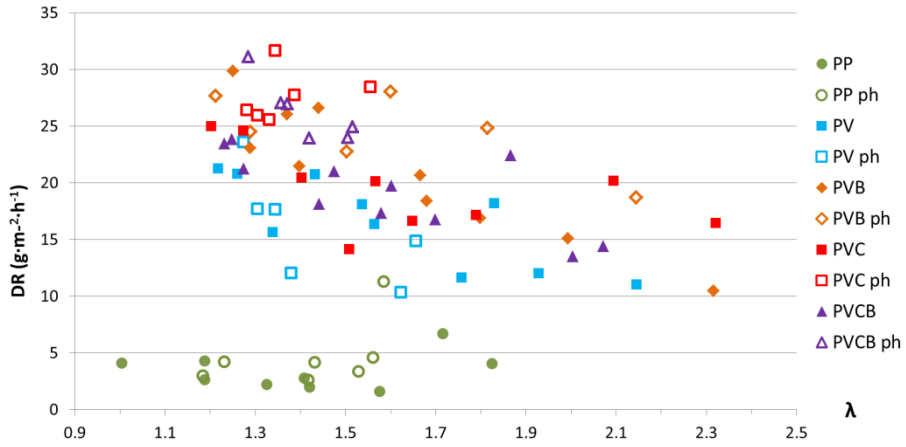


Fig. 11. Deposition ratio (DR) versus excess air ratio (λ) for all fuels.

As expected, DR for PP is very small (around 5 $g \cdot m^{-2} \cdot h^{-1}$), mostly due to the reduced amount of ash this fuel shows (lower than 1 wt-% d.b.). This fact, positive regarding ash behaviour, makes it difficult to find trends for this fuel.

For agropellets, the worst conditions are attained for the lower values of λ (around 1.2) corresponding to DR in the range of 20-32 $g \cdot m^{-2} \cdot h^{-1}$. Although it is difficult to compare these ratios with those obtained in other tests found in the literature due to differences in conversion

371 technology, fuel composition, placement of the probe, surface temperature, etc., it can be suggested
372 that these values are of the same order of magnitude of those obtained in the experiments and
373 simulations gathered for similar fuels and combustion conditions [56].
374 Despite no significant differences are identified among agropellets, based on the quantitative results
375 comparison of their deposition tendency might be according to the following order:
376 PVC>PVCB>PVB>PV. This suggests that the fuels with an herbaceous component are the more
377 troublesome ones.
378 It may be surprising the lower DR of PV compared to the rest of agricultural fuels, given the high
379 concentration of K in its ash (i.e., 30.09 wt-% d.b. expressed as K_2O, compared to 14.88 wt-% d.b. %-
380 20.54 wt-% d.b. % for the others), and considering that K is one of the elements that might
381 contribute to a greater tendency of fouling [57]-[59]. However, it is necessary to take into account
382 that the percentage of ash for PV is much lower than for mixed pellets (3.1 wt-% d.b. % compared to
383 5.9 wt-% d.b. %- 9.3 wt-% d.b.%), which implies that the amount of K per fuel unit mass is
384 significantly lower. In addition, it should be considered its very different content of Cl and S in PV
385 compared to the mixed pellets (see Table 2):
386 • The content of Cl is lower in the case of PV, which does not facilitate the transfer of K in the
387 flue gas [57], [60], [61].
388 • The content of S is relatively high, which implies a low value for the Cl/S molar ratio in the
389 feed ash that might facilitates formation of K-sulphates. These compounds can be retained in
390 the bottom ash fraction in the temperature range of 850–1000ºC [23].
391 For all the agropellets it is clearly observed that upon increasing λ there is less deposition in the
392 probe. To analyze this result is necessary to take into account that the ash transformation reactions
393 may be influenced by a lot of factors: temperature, residence time, air supply, flue gas velocity, etc.
394 [24]. In spite of the complexity of the deposition process, it can be stated that, as observed in section
395 3.2, a larger flow of combustion air might contribute to a larger ash entrainment, which in certain
396 circumstances (particles composition, velocity and temperature of the gas, temperature of the

surfaces, etc.) can be deposited on the exchange surfaces, increasing deposition. Likewise, this increase in the air flow causes a reduction of the mean flame temperature, which may limit the volatility degree of main reactive ash elements that participate on the deposition mechanisms (e.g., K, Cl, S) and consequently, a lower DR can be obtained [64], [65]. Hence, the reduction of DR upon increasing λ suggests that volatilization of reactive elements was the dominant effect in the deposition phenomenon, compared to a possible contribution of the entrained of ash.

It is worth noting that for mixed pellets it is perceptible a slightly increase in DR when using pre-heating. This may be mostly due to an increase in the particles entrainment since, as already discussed, the pre-heated tests were carried out with higher PA, which causes a higher speed in the bed without significantly increasing TC3m. This rise in DR with pre-heating can be quantified (for the same λ) in approximately a 10% for PVB, a 20% for PVCB and 30% for PVC. The amount in which different herbaceous fuels are affected is clearly related to the sintering tendencies (see Fig. 10 and Fig. 11), reflecting the fact that a higher sintering degree tendency implies a lower amount of ash available to be dragged, in spite of an increase in the air velocity.

Notwithstanding, in the case of PV it is not observed an increase of DR in the tests with preheating, which is apparently at odds with the noticeable increase of particle entrainment with pre-heating, as shown in Fig. 11. In other words, pre-heating produces, for PV, a rise in ash entrainment but not in deposition. Although it is necessary to study this effect more carefully, it could be related to a great predominance for this fuel of the mechanism of condensation (condensed deposits) in the deposition against the inertial impact.

In any case, both in the case of sintering (section 3.2) and in the case of deposition (section 3.3), the complexity of the combustion processes makes it difficult to draw clearer conclusions as it is also mentioned in [25]. Nevertheless, additional information to support these trends will be obtained from the ash characterization to be carried out by SEM-EDS and P-XRD as the continuation of this research study.

4. CONCLUSIONS

This study provides systematical experimental results on five biomass pellets combustion in a laboratory fixed bed reactor, regarding the influence of inlet air flow and temperature on combustion parameters, bottom ash characteristics, and ash deposition.

The work carried out has confirmed that for all fuels analyzed, as the excess air ratio increases (higher than 1 in all the cases) the velocity of the ignition front (and therefore the ignition rate) and the combustion temperature gradually decrease. Also it has been observed that the influence of the inlet air temperature is greater on the ignition rate than on the combustion temperature.

Important differences in the quantity and sintering degree of bottom ash among the five fuels have been observed. Tested pellets can be divided into two main groups: the first one is formed by wood pellets (PP and PV) with low bottom ash proportion and low quantity of S2/3 fraction (around 5-30% and 0-3%, respectively, with respect to the total amount of ash introduced with the fuel), whereas the second group corresponds to mixed pellets (PVB, PVC and PVCB) with much higher values of these parameters (around 50-75% and 24-63%, respectively).

Concerning deposition, a clear relation inversely proportional between air excess ratio and deposition ratio has been determined for the four agropellets (PV, PVB, PVC and PVCB). Thus, the worst conditions were attained for the lower values of λ (around 1.2) corresponding to deposition ratios in the range of 20-32 $g \cdot m^{-2} \cdot h^{-1}$.

The data provided in this paper is intended to complement the existing knowledge of the influence of excess air ratio on efficiency and emissions (mainly CO and NO_x), in order to support the decision making process concerning the design and operation of conversion systems suitable for agropellets.

Only a preliminary evaluation of the mechanism involved into the sintering and deposition phenomena and their relation with fuel composition has been carry out. In order to gain a better understanding on these issues, additional information will be obtained from the bottom ash and deposits chemical characterization, as part of further research studies.

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6. REFERENCES

[1] Scarlat N., Dallemand J.F., Monforti-Ferrario F., Banja M. Renewable energy policy framework and bioenergy contribution in the European Union – An overview from National Renewable Energy Action Plans and Progress Reports. Renewable and Sustainable Energy Reviews 2015; 51: 969-985.

[2] Scarlat N., Dallemand J.F., Monforti-Ferrario F., Nita V. The role of biomass and bioenergy in a future bioeconomy: Policies and facts. Environmental Development 2015; 15: 3-34.

[3] Bozell J.J., Black S.K., Myers, M., Cahill, D., Miler W. P. Park, S. Solvent fractionation fo renewable woody feedstocks: Organoslv generation of biorefinery process streams for the production of biobased chemicals. Biomass Bioenergy 2011; 35(10): 4197-208

[4] Food and Agricultural Organization of the United Nations – FAOSTAT - http://www.fao.org/faostat/ , accessed in October 2018

[5] Carvalho L., Wopienka E., Pointner C., Lundgren J., Verma V.K., Haslinger W., Schamidl C. Performance of a pellet boiler fired with agricultural fuels. Applied Energy 2013; 104: 286-296.

[6] Sippula O., Hytönen K., Tissari J., Raunemaa, T., Jokiniemi, J. Effect of Wood Fuel on the Emissions from a Top-Feed Pellet Stove. Energy & Fuels 2007; 21 (2): 1151-1160.

[7] Houshfar E., Lovas T., Skreiberg, O. Experimental Investigation on NOX Reduction by Primary Measures in Biomass Combustion: Straw, Peat, Sewage Sludge, Forest Residues and Wood Pellets. Energies 2012; 5 (2): 270-290.

[8] Díaz-Ramírez M., Sebastian F., Royo J., Rezeau A. Influencing factors on NOX emission level during grate conversion of three pelletized energy crops. Applied Energy 2014; 115 (0): 360-373.

[9] Junemann A., Legarreta G. Inhalación de humo de leña: una causa relevante pero poco reconocida de Enfermedad Pulmonar Obstructiva Crónica. Revista Argentina de Medicina Respiratoria 2007 - Nº 2, 51-57.

[10] Tian D., Hu Y., Wang Y., Boylan J.W., Zheng M., Russell A.G. Assessment of Biomass Burning Emissions and Their Impacts on Urban and Regional PM2.5: A Georgia Case Study. Environmental Science Technology 2009; 43: 299–305

[11] Christensen K.A., Stenholm M., Livbjerg H. The formation of submicron aerosol particles, HCl and SO2 in straw-fired boilers. Aerosol Science 1998; 29 (4): 421-444.

[12] Saud T., Mandal T.K., Gadi R., Singh D.P., Sharma S.K., Saxena M., Mukherjee A. Emission estimates of particulate matter (PM) and trace gases (SO2, NO and NO2) from biomass fuels used in rural sector of Indo-Gangetic Plain, India. Atmospheric Environment 2011; 45 (32): 5913-5923.

[13] Fernández-Llorente M.J., Escalada-Cuadrado R., Murillo-Laplaza J.M., Carrasco-García J.E. Combustion in bubbling fluidised bed with bed material of limestone to reduce the biomass ash agglomeration and sintering. Fuel 2006; 85 (14-15): 2081-2092.

[14] Johansson L.S., Leckner B., Gustavsson L. Cooper D., Tullin C., Potter A. Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets. Atmospheric Environment 2004; 38 (25), 4183-4195.

[15] Obernberger I., Biedermann F., widmann W., Riedl R. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. Biomass and Bioenergy 1997; 12 (3), 211-224.

[16] Wierzbicka A., Lillieblad L., Pagels J., Strand M., Gudmundsson A., Gharibi A., Swietlicki E., Sanati M., Bohgard M. Particle emissions from district heating units operating on three commonly used biofuels. Atmospheric Environment 2005; 39 (1), 139-150.

[17] Wiinikka H., Gebart R., Boman C., Boström D., Öhman M. Influence of fuel ash composition on high temperature aerosol formation in fixed bed combustion of woody biomass pellets. Fuel 2007; 86 (1-2), 181-193.

[18] Wiinikka H., Gebart R. Experimental investigations of the influence from different operating conditions on the particle emissions from a small-scale pellets combustor. Biomass and Bioenergy 2004; 27 (6), 645-652.

[19] Brunner T., Obernberger I., Scharler R. Primary measures for low-emission residential wood combustion-Comparison of old with optimised modern systems. Proceedings of 17th European Biomass Conference and Exhibition, Hamburg, Germany, 2009, 1319-1328.

[20] Obernberger I., Brunner T., Bärnthaler G. Chemical properties of solid biofuels--significance and impact. Biomass and Bioenergy 2006; 30 (11): 973-982.

[21] Díaz-Ramírez M., Boman C., Sebastian F., Royo, J., Xiong S., Boström D. Ash Characterization and Transformation Behavior of the Fixed-Bed Combustion of Novel Crops: Poplar, Brassica, and Cassava Fuels. Energy & Fuels 2012; 26 (6): 3218-3229.

[22] Díaz-Ramírez, M., Sebastian F., Royo J., Rezeau A. Combustion requirements for conversion of ash-rich novel energy crops in a 250 kWth multifuel grate fired system. Energy 2012; 46 (1): 636-643.

[23] Díaz-Ramírez M., Frandsen F.J., Glarborg P., Sebastian F., Royo J. Partitioning of K, Cl, S and P during combustion of poplar and brassica energy crops. Fuel 2014; 134 (0): 209-219.

[24] Boström D, Skoglund N, Grimm A, Boman C, Ohman M, Brostrom M, Backman R. Ash transformation chemistry during combustion of biomass. Energy & Fuels 2012; 26: 85–93.

[25] Becidan M, Houshfar E, Khalil RA, Skreiberg Ø, Løvås T, Sørum L. Optimal Mixtures to Reduce the Formation of Corrosive Compounds during Straw Combustion: A Thermodynamic Analysis. Energy & Fuels 2011; 25: 3223-3234

[26] Khor A, Ryu C, Yang Y-b, Sharifi VN, Swithenbank J. Straw combustion in a fixed bed combustor. Fuel 2007; 86: 152-160

[27] Magdziarz A, Dalai AK, Koziński JA. Chemical composition, character and reactivity of renewable fuel ashes. Fuel 2016; 176: 135-145

[28] Tissari J., Hytönen K., Sippula O., Jokiniemi J The effects of operating conditions on emissions from masonry heaters and sauna stoves. Biomass and Bioenergy 2009; 33 (3): 513-520.

[29] Lamberg H., Sippula O., Tissari J., Jokiniemi J. Effects of Air Staging and Load on Fine-Particle and Gaseous Emissions from a Small-Scale Pellet Boiler. Energy & Fuels 2011; 25 (11): 4952-4960.

[30] Tissari J., Sippula O., Kouki J., Vuorio K., Jokiniemi J. Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. Energy & Fuels 2008; 22 (3): 2033-2042.

[31] Knudsen J.N., Jensen P. A., Dam-Johansen K. Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. Energy & Fuels 2004; 18 (5): 1385-1399.

[32] van Lith S.C., Alonso-Ramírez V., Jens P. A., Frandsen F.J., Glarborg P. Release to the gas phase of inorganic elements during wood combustion. Part 1: Development and evaluation of quantification methods. Energy & Fuels 2006; 20 (3): 964-978.

[33] Theis M., Skrifvars B.J., Hupa M., Tran H. Fouling tendency of ash resulting from burning mixtures of biofuels. Part 1: deposition rates. Fuel, 2006; 85: 1125–1130.

[34] Li G., Li S., Xu X., Huang, Q., Yao Q. Dynamic behavior of biomass ash deposition in a 25 kW one-dimensional down-fired combustor. Energy & Fuels, 2013; 28: 219-227

546 [35] Ryu C., Yang Y.B., Khor A., Yates N. E., Sarifi V.N., Swithenbank J. Effect of fuel properties on
547 biomass combustion: Part I. Experiments – fuel type, equivalence ratio and particle size. Fuel,
548 2006; 85 (7-8): 1039-1046
549 [36] Houshfar, E., Khalil R.A., Lovas T., Skriberg O. Enhanced NOx Reduction by Combined Staged
550 Air and Flue Gas Recirculation in Biomass Grate Combustion. Energy & Fuels, 2012. 26(5):
551 3003-3011.
552 [37] Zhou, H., Jensen A.D., Glarborg P., Kavaliauskas A. Formation and reduction of nitric oxide in
553 fixed-bed combustion of straw. Fuel, 2006; 85 (5-6): 705-716
554 [38] Andzi-Barhe T., Rogaume T., Richard F., Torero J.L. Numerical characterisation of the
555 mechanisms of NOx formation during MSW incineration.MCS6. 2009. Ajaccio (France).
556 [39] Brunner T., Biedermann F., Kanzian W., Evic N., Obernberger I. Advanced Biomass Fuel
557 Characterization Based on Tests with a Specially Designed Lab-Scale Reactor. Energy & Fuels,
558 2013; 27 (10): 5691-5698.
559 [40] Wiinikka, H. and Gebart, R. Experimental investigations of the influence from different
560 operating conditions on the particle emissions from a small-scale pellets combustor. Biomass
561 and Bioenergy, 2004. 27(6): p. 645-652.
562 [41] Zhou, H., Jensen A.D., Glarborg P., Jensen P.A., Kavaliauskas, A. Numerical modeling of straw
563 combustion in a fixed bed. Fuel, 2005; 84: 389-403.
564 [42] Wiinikka, H. and Gebart, R. Critical Parameters for Particle Emissions in Small-Scale Fixed-Bed
565 Combustion of Wood Pellets. Energy & Fuels, 2004. 18(4): p. 897-907.
566 [43] Porteiro J., Patiño D., Collazo J., Granada E., Moran J., Miguez J.L. Experimental analysis of the
567 ignition front propagation of several biomass fuels in a fixed-bed combustor. Fuel, 2010; 89:
568 26-35
569
570

[44] Rezeau A., Royo J., Ribas Cruells J., Masot A., Díaz-Ramírez M., Sala S., Yescas N. Advanced characterization of non-conventional biomass (from emerging markets) in a fixed-bed reactor. Proceedings of 24th European Biomass Conference and Exhibition, Amsterdam, The Netherlands (2016) 801-806

[45] Díaz-Ramirez M., Maraver D., Rezeau A. Royo J., Sala S., Sebastian F., Sin A. Estimation of the deposition on trigeneration system components fueled by ash rich biomass. Proceedings of 20th European Biomass Conference and Exhibition, Milan, Italy (2012) 774-780

[46] Nunes L.J.R., Matias J.C.O., Catalao J.P.S. Biomass combustion systems: A review on the physical and chemical properties of the ashes. Renewable and Sustainable Energy Reviews, 2016; 53: 235-242.

[47] Zeng T., Pollex T., Weller N., Lenz V., Nelles M. Blended biomass pellets as fuel for small scale combustion appliances: Effect of blending on slag formation in the bottom ash and pre-evaluation options. Fuel 2018; 212: 108-116

[48] Öhmana M., Bomana C., Hedmanb H., Nordina A., Boström D. Slagging tendencies of wood pellet ash during combustion in residential pellet burners. Biomass and Bioenergy 2004; 27: 585–596

[49] Horttanaimen M. V. A., Saastamoinen J. J., Sarkomaa P. J. Operational limits of ignition front propagation against airflow in packed beds of different wood fuels. Energy & Fuels, 2002; 16: 676–686.

[50] Regueiro A., Patiño D., Granada E., Porteiro J. Experimental study on the fouling behaviour of an underfeed fixed-bed biomass combustor. Applied Thermal Engineering, 2017; 112: 523-533.

[51] Ryu C., Yang Y.B., Khor A., Yates N.E., Sharifi V.N., Swithenbank J. Effect of fuel properties on biomass combustion: Part I. Experiments—fuel type, equivalence ratio and particle size. Fuel, 2006; 85: 1039–1046.

[52] Saastamoinen J. J., Taipale R., Horttanainen M., Sarkomaa P. Propagation of the ignition front in beds of wood particles. Combustion and Flame, 2000; 123: 214–226.

[53] Shin D., Choi S. The combustion of simulated waste particles in a fixed bed. Combustion and Flame, 2000; 121: 167–180.

[54] Folgueras M.B., Díaz R. M., Xiberta J., García M. P., Pis J.J. Influence of sewage sludge addition on coal ash fusión temperaturas. Energy&Fuels, 2005; 19:2562-70

[55] Madhiyanon T., Sathitruangsak P., Sungworagarn S., Pipatmanomai S., Tia S. A pilot-scale investigation of ash and deposition formation during oil-palm empty-fruit-bunch (EFB) combustion. Fuel Processing Technology, 2012; 96:250–264.

[56] Kleinhans U., Wieland C., Frandsen F.J., Spliethoff H. Ash formation and deposition in coal and biomass fired combustion systems: Progress and challenges in the field of ash particles ticking and rebound behavior. Progress in Energy and Combustion Science, 2018; 68:68-168

[57] Niu Y., Tan H., Hui S. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. Progress in Energy and Combustion Science, 2016; 52: 1-61

[58] Baxter L.L., Miles T.R., Jenkins B.M., Milne T., Dayton D., Bryers R.W., Oden L.L. The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. Fuel Processing Technology, 1998; 54: 47–78.

[59] Teixeira P., Lopes H., Gulyurtlu I., Lapa N., Abelha P. Evaluation of slagging and fouling tendency during biomass co-firing with coal in a fluidized bed. Biomass and Bioenergy, 2012; 39: 192–203.

[60] Thy P, Jenkins BM, Grundvig S, Shiraki R, Lesher CE. High temperature elemental losses and mineralogical changes in common biomass ashes. Fuel, 2006; 85:783–95.

[61] Theis M., Skrifvars B.-J., Zevenhoven M., Hupa M., Tran H. Fouling tendency of ash resulting from burning mixtures of biofuels. Part 2: deposit chemistry. Fuel, 2006; 85: 1992–2001.

[62] Skrifvars B-J, Laure´n T, Hupa M, Korbee R, Ljung P. Ash behavior in a pulverized wood fired boiler – a case study. Fuel 2004; 83:1371–9.

622 [63] Robinson AL, Junker H, Baxter LL. Pilot-scale investigation of the influence of coal-biomass
623 cofiring on ash deposition. Energy Fuels 2002; 16:343–55.
624 [64] van Lith S. C., Jensen P. A., Frandsen F. J., Glarborg P. Release to the Gas Phase of Inorganic
625 Elements during Wood Combustion. Part 2: Influence of Fuel Composition. Energy & Fuels,
626 2008; 22: 1598–1609
627 [65] Johansen J. M., Aho M., Paakkinen K., Taipale R., Egsgaard H., Jakobsen J. G., Frandsen F. J.,
628 Glarborg P. Release of K, Cl, and S during combustion and co-combustion with wood of high-
629 chlorine biomass in bench and pilot scale fuel beds. Proceedings of the Combustion Institute,
630 2013; 34: 2363–2372.