



Full Length Article

Combustion of poultry litter and mixture of poultry litter with woodchips in a fixed bed lab-scale batch reactor

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A B S T R A C T

Experiments have been conducted in a batch fixed bed lab-scale reactor to investigate the combustion behaviour of three different biomass fuels, poultry litter (PL), blend of PL with wood chips (PL/WC) and softwood pellets (SP). Analysis of the data gathered after completion of the test runs, provided useful insights about the thermal decomposition behaviour of the fuels, the formation of N gaseous species, the release of ash forming elements and the estimation of aerosol emissions. It was observed that the N gaseous species are mainly produced during the devolatilisation phase. Hydrogen cyanide (HCN) was the predominant compound in the case of SP combustion, whereas ammonia (NH₃) displayed the highest concentration during the combustion of PL and blend (PL/WC). With reference to ash forming elements, the release rates of potassium (K) and sodium (Na) range between 15–50% and 20–37% respectively, whereas the release rate of sulphur (S) falls between 54–92%. Chlorine (Cl) presents very high release rate for all tested fuels acquiring values greater than 85%, showing the volatile nature of the specific compound. The maximum potential of aerosol emissions was estimated based on the calculation of ash forming elements. In particular, during PL combustion the maximum aerosol emissions were observed, 2806 mg/Nm³ (dry flue gas, 13 vol% O₂), mainly influenced by the release rate of K in the gas phase. Fuel indexes for the pre-evaluation of combustion related challenges such as NO_x emissions, potential for aerosols formation, corrosion risk, and ash melting behaviour have also been investigated.

1. Introduction

Fossil fuels are still the predominant means for satisfying the global energy demand, whereas the share of renewable resources is still limited (Fig. 1). However, depletion of fossil fuels along with the associated emission of greenhouse gases considered as the root cause of global warming and climate change, make urgent the need for further exploration of renewable energy resources. The Paris Agreement 2015 signed by 195 countries across the world, show the collective commitment to combat the global climate change with the ultimate goal to limit the global warming to well below 2 °C above pre-industrial levels. Particularly, EU countries have set an ambitious target that by 2030, 32% of total energy consumption will be covered from renewables with a consequent reduction of 40% greenhouse gases emissions compared to 1990 levels [1].

Amongst the various renewable resources, bioenergy is the main contributor, accounting for more than 10% of the gross primary energy consumption, within EU-28 in 2017 [3]. Bioenergy results from the utilisation of biomass fuels which are considered ideally CO₂ neutral,

since they are produced during photosynthesis process. However, there is always some net addition of CO₂ released in the atmosphere, stemming from the utilisation of fossil fuels during the phases of production, handling and transportation of biomass. Other associated problems with the use of bioenergy that need to be further investigated are the release of fine particulate matter and NO_x emissions in the atmosphere.

Approximately 70% of the biomass consumed for bioenergy production is derived from wood. The rest is covered by biomass originating from agriculture (18%) and the organic fraction of municipal waste (12%) [4]. The main categories of woody biomass are forest main products (stem wood, short rotation wood), primary forest residues (tops, branches, and leaves), by-products from forest industries (sawdust, wood chips, and mill residues), wood pellets, and waste wood resulting from construction and demolition sites. However, increased production cost of woody biomass, regional availability mainly to areas close to forests or relevant industries, along with high transportation cost from the forest or industrial area to the end-users, have risen the research interest on alternative biomass types such as the agricultural residues. Agricultural residues can be categorised as follows: a) residues resulting from food crops after processing (husks, shells and kernels), b)

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Nomenclature			
<i>Symbols</i>		O ₂	Oxygen
C	Carbon	Pb	Lead
Ca	Calcium	PM ₁	Particulate matter with diameter < 1 μm
CH ₄	Methane	P ₂ O ₅	Phosphorus pentoxide
Cl	Chlorine	S	Sulphur
CO	Carbon monoxide	Si	Silica
CO ₂	Carbon dioxide	SO _x	Sulphur oxides
H ₂ O	Water	Zn	Zinc
HCl	Hydrogen chloride	ZnO	Zinc oxide
HCN	Hydrogen cyanide	<i>Abbreviations</i>	
K	Potassium	BEST	Bioenergy and Sustainable Technologies
KCl	Potassium chloride	EPC	Electrostatic precipitator
K ₂ SO ₄	Potassium sulphate	EU	European Union
K ₂ CO ₃	Potassium carbonate	FID	Flame ionisation detector
Mg	Magnesium	FTIR	Fourier-transform infrared spectroscopy
N	Nitrogen	ICP	Inductively coupled plasma
Na	Sodium	LCV	Lower calorific value
NaCl	Sodium chloride	mg	Milligram
Na ₂ CO ₃	Sodium carbonate	min	Minutes
NH ₃	Ammonia	PL	Poultry litter
N ₂ O	Nitrous oxide	sec	Seconds
NO _x	Nitrogen Oxides	SP	Softwood pellets
Na ₂ SO ₄	Sodium sulphate	TFN	Total fuel nitrogen
		WC	Wood chips

residues left on the field after the crop harvesting (straw after cereal production) and c) animal husbandry [5].

Focusing on the latter category, meat production shows a continuous upward trend over the past decades. Population increment, rising income, urbanisation, along with the growing need for high value proteins, have shifted society’s patterns from plant based to animal food diets. In 2013 the global market of meat production amounted 315 million tonnes. Pig meat constituted the highest share of the global production, approximately 112 million tonnes, followed by 109 million tonnes of poultry and 68 million tons of beef and buffalo [6]. Among the different meat segments, poultry is predicted to have the highest development. Poultry production has grown substantially throughout

the years, transforming poultry to a very popular commodity. Particularly in EU-28, the production of poultry meat reached a new high of 15.2 million tonnes in 2018 [7].

Growing demand for poultry meat consumption has shifted poultry meat production from a traditional farming-based approach on small installations, to intensive livestock farming units. Intensive farming, although being more efficient and cost effective than traditional farming, results in the accumulation of a large amount of litter within confined areas [8]. However, the available arable land nearby the intensive poultry farming unit for litter application as nutrient source, is limited. Overapplication of animal manure on agricultural land would result in environmental issues such as surface water contamination

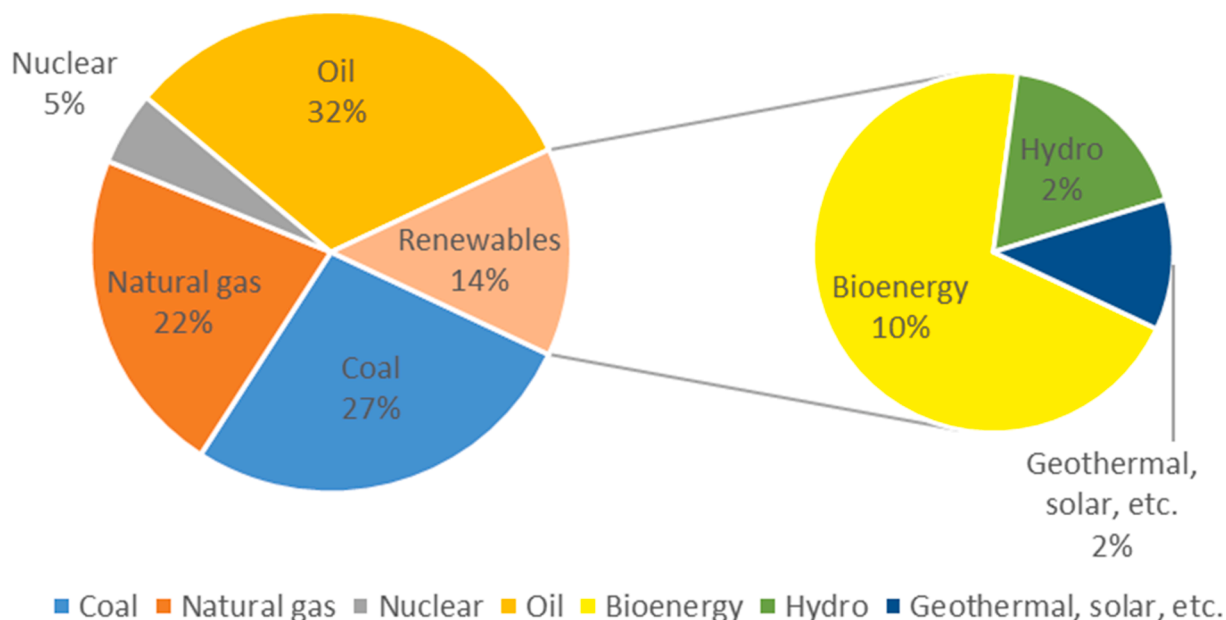


Fig. 1. Global primary energy production by source [2].

(eutrophication), ground water contamination (nitrate and heavy metals leaching), crop toxicity, odour problems, heavy metal contamination, pathogens, and air pollution (NH_3 , NO_x , N_2O) [9–12]. Excess nitrogen is one of the main causes of water pollution in Europe, forcing member states to implement Nitrates Directive (1991) in order to prevent this phenomenon.

Environmental concerns associated with the excessive application of animal manure on cropland, demands the development of alternative methods pertaining to the sustainable disposal of animal waste. As an example, thermochemical conversion seems a promising option for PL treatment, since it can reduce its volume significantly (80–95%), upgrade PL to higher value products (bio-oil, synthetic natural gas), destruction of pathogens in high operating temperature regimes, whilst electricity, heat generation and biofuel production are also possible [13,14]. Among the different thermochemical conversion technologies, combustion is the most mature technology for biomass utilisation having reached already a commercialisation level.

Although combustion of woody biomass is considered well developed, this is not the case for PL when applied as a fuel in combustion units. The reasons are the distinct differences in its composition compared to woody biomass, which may pose challenges during the pre-processing and combustion stages [15]. More specifically, PL contains high amounts of ash consisting of alkali elements (silica, potassium, sodium etc.) forming compounds with low eutectic temperatures that can melt on the grates causing agglomeration and system malfunction [16,17]. Additionally, volatile and semi-volatile elements contained in the ash such as S, Cl, K, Na, Zn, Pb, are partly released during the combustion process into the gas (flue gas) phase. These elements are taking part in homogeneous reactions and form aerosols (particles with a diameter less than $1 \mu\text{m}$ known also as PM_{10}). These fine particles may condense in the cooler surfaces of the combustion unit and form deposits, causing reduced heat transfer capacity, corrosion and fouling issues [9,18]. Among the various compounds found in ash, K has the highest impact on aerosol formation, since it is usually found in higher concentrations compared to the other ash forming elements [9,18].

Moreover, a high nitrogen content in PL originating mainly from animal feed, leads to elevated NO_x (NO , NO_2) emissions, which are linked to serious environmental pollution (acid rain and photochemical smog). Additionally the formation of N_2O is also favoured in presence of high nitrogen content, contributing to the greenhouse effect and ozone layer depletion in the stratosphere [19]. Three different pathways exist as regards NO_x formation, namely thermal- NO_x , prompt- NO_x and fuel- NO_x . The first two become important when the operating temperature exceeds 1300°C . However, this is not the case for biomass combustion, where the temperatures normally range between 900 and 1000°C . Therefore the predominant mechanism for NO_x emissions is the conversion of fuel nitrogen to NO_x , depending on the initial concentration of nitrogen in the fuel and the process conditions [20,21]. Release of nitrogen during fuel decomposition involves complex chemistry but generally fuel nitrogen is released mostly during the devolatilisation phase, and is converted into HCN , NH_3 , NO and small percentages of N_2O and NO_2 . Some part of nitrogen is converted also during charcoal burnout, mainly as NO [22].

The Cl and S concentrations found in PL are significantly higher than in wood and may pose emission issues during combustion (see Table 2 in the following sections). The specific compounds can vaporise and form gaseous emissions such as HCl , Cl_2 , SO_x (SO_2 or SO_3). According to EU commission regulations [23] the emissions limits for SO_x during on farm combustion must not exceed 50 mg/Nm^3 (dry gas, 11% O_2). Limitations for HCl emissions are in place in certain countries, e.g. in Germany, HCl emissions for the combustion of agricultural residues are limited to 30 mg/Nm^3 (dry gas, 11% O_2). Alternatively, Cl and S compounds can mobilise the inorganics contained in the ash (mostly potassium) to form aerosols (KCl , K_2SO_4), through the vaporisation-condensation mechanism of ash formation [24–27]. This can lead to increased ash deposition in the combustion plant, especially on cooled surfaces such as the boiler.

Moisture content is another decisive factor related to combustion behaviour of PL, especially when pre-treatment measures are not available. Moisture in PL varies considerably and when found in high values, it affects negatively fuel homogeneity, energy content and system sizing. A moisture content below 10 wt% is recommended for an efficient PL combustion [24,26].

These challenges associated to PL combustion show the need to investigate the detailed combustion behaviour of the specific fuel, which has not been done so far or reported in the scientific literature. For this purpose, a batch lab-scale reactor especially designed for simulating thermal decomposition of biomass under fixed-bed conditions has been utilised. The study compares the decomposition behaviour, release of N gaseous species, ash-forming elements and the maximum potential for aerosol emissions resulting from PL combustion, with the traditional biomass (SP) and the blend (PL/WC).

2. Methods

2.1. Experimental setup and measurement methods

The lab-scale reactor presented in Fig. 2 is especially designed for simulating thermal decomposition of biomass under fixed-bed conditions. It consists of a cylindrical retort (height 35 cm, inner diameter 12 cm) and the fuel is loaded in a cylindrical sample holder (100 mm height and 95 mm inner diameter) prior being fed to the reactor. The material used in the reactor wall and sample holder is reinforced silicon carbide, which is inert under reducing and oxidising conditions, thus avoiding any reactions between the wall and the fuel, ash, or flue gases.

The following measurements/analyses were performed during each of the combustion test runs: a) Weight loss of the fuel sample over time, b) Concentrations of flue gas species over time (CO_2 , H_2O , CO , CH_4 , NH_3 , HCN , N_2O and basic hydrocarbons), c) O_2 detection, d) Total amount of hydrocarbons (C_xH_y), e) Temperature measurements over time and f) Fuel and ash analysis. A summary of the analytical methods and the instruments used is given in Table 1. Gas analysis was performed by FTIR method and by using a multicomponent gas analyser. Similarly, oxygen concentration was measured with the multicomponent gas analyser and a lambda sensor. The goal of applying different methods was to check the consistency of the resulted data. Since data were very comparable among the different methods, the results from multicomponent gas analyser were considered.

2.2. Materials

PL consists of poultry excreta, waste feed, feathers and bedding material such as straw, peat, or sand. PL was collected from a local company in Austria and it was partially dried and pelletised at a particle size range of 6 mm before being fed into the reactor. WC and SP were provided by the research institute BEST - Bioenergy and Sustainable Technologies, where the experiments took place. Compared to woody biomass (in this case SP), PL is characterised by lower concentrations of C and H, whereas N, Cl and S, are present in higher fractions. It also contains significantly higher amount of ash, consisting of minerals and metals like phosphorus (P), potassium (K) and sodium (Na). Tables 2 and 3 report the ultimate and proximate analysis, and the ash composition of the three tested fuels, respectively. The oxygen content was determined by the difference from the elements presented in ultimate analysis.

2.3. Test procedure

Before the start of an experiment, fuel was dried at $\leq 10\%$ moisture on a wet basis (a.r) and a sub-sample was sent for chemical analysis. Afterwards the fuel was inserted into the cylindrical holder, while the reactor's lower and upper parts were preheated by electrical means at 450°C and 750°C , respectively. When the preset temperatures were achieved, the fuel sample was inserted in the reactor where rapid

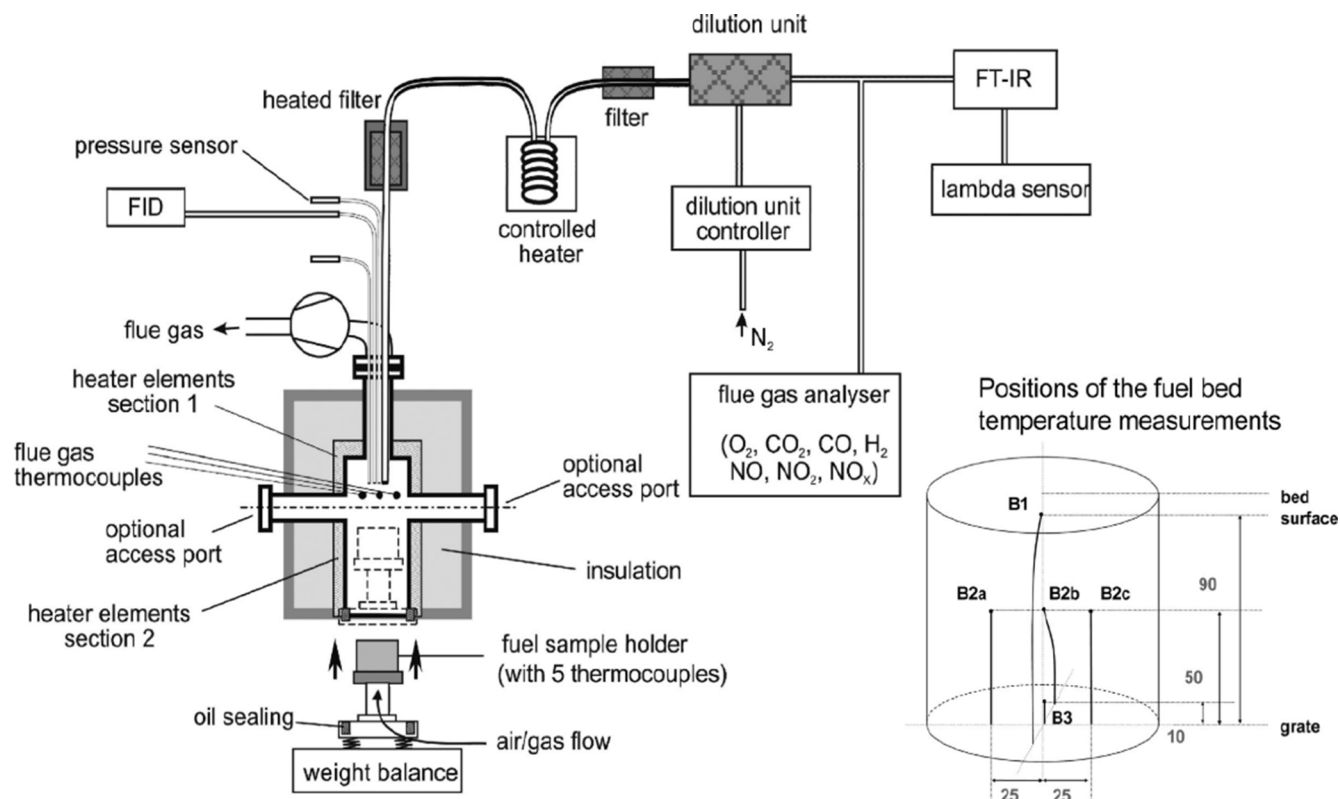


Fig. 2. Scheme of the lab-scale reactor, including measurement setup and positions of the thermocouples [28].

Table 1

Analytical methods.

Analysis	Method	Instrument
Weight loss of the sample	Gravimetric method	Radwag PS 6000/C/2
Concentrations of flue gas species over time	Gas analyser/ FTIR spectroscopy	Ansyco Series DX 4000
O ₂ detection	Gas analyser/Lambda sensor	ABB EL 3020
Total amount of hydrocarbons (C _x H _y)	Flame ionisation detector	Messer Griesheim Austria Model VE 7
Temperature measurements	Thermocouples	5 Type K thermocouples (NiCr-Ni)
Fuel composition	C, H, N contents according to ÖNORM CEN/TS 15,104	Elementar vario EL cube
	Ash content according to CEN/TS 14,775	
	Cl according to ÖNORM CEN/TS 15,289	Shimadzu LC 20
Chemical analysis of ash	Major and minor elements according to ÖNORM CEN/TS 15,290 and 15,297	Anton Paar Multiwave PRO Spectro Arcos
	Multi-step pressurised digestion with HNO ₃ (65%) / HF (40%) / H ₃ BO ₃ (saturated).	
	Measurement by ICP-OES	

heating occurred, similar to conditions of a real scale fixed bed combustion systems. Dry air (21% O₂ and 79% N₂ by volume basis) was supplied as an oxidising medium through the grate at a constant flow rate of 30 l/min. Three tests of identical conditions for all the fuels were performed to ensure repeatability. Measurements were taken at 2 sec intervals and the total duration of the experiments ranged between 25 and 65 min depending on the fuel density and moisture content. At the end of each experiment, residual ash was removed and sent for chemical analysis.

The weight loss of the fuel sample was continuously monitored

Table 2

Ultimate and proximate analysis of feedstock.

Type of feedstock	PL	PL/WC	SP
<i>Proximate analysis (% w/w)</i>			
Moisture (a.r.)	10	9.2	7.1
Ash (d.b.)	21.98	13.01	0.33
<i>Ultimate analysis (% w/w, d.b.)</i>			
C	38.03	43.22	49.53
H	4.86	5.08	6.13
N	3.72	2.84	0.05
Cl	0.58	0.42	0.01
S	0.47	0.29	0.02
O*	30.36	35.15	45.35
LCV (MJ/kg d.b.)	17.21	19.44	17.59

a.r.: as received, d.b.: dry basis, *calculated by difference.

Table 3

Chemical composition of ash for the three fuels.

Ash composition (mg/kg d.b.)	PL	PL/WC	SP
Calcium	74,600	43,700	950
Silicon	1860	1800	300
Magnesium	9450	355	122
Potassium	22,700	14,600	507
Sodium	4820	2850	15
Phosphorus	16,900	10,400	38
Aluminium	377	358	n.d.
Zinc	550	328	12.5
Lead	2	3	0.1
Iron	766	1010	n.d.
Manganese	548	355	n.d.
Copper	93	63	n.d.

n.d.: not detected.

during the experimental process (drying, devolatilisation, gasification and charcoal combustion). The concentration of the produced gases and the formation of N gaseous species were also measured. Furthermore, the data derived from the chemical analysis of fuel and residual ash, as well as the weight loss measurements of the fuel and the ash sample, were used to calculate the elemental release rate into the gas phase by calculating the mass balances of relevant elements (S, Cl, K, Na, Zn, Pb). Since the chemical analysis is robust, any observed deviation in the mass balance of the elements was considered to result from the entrainment of the ash particles with the flue gases. The formula used to calculate the release rate is given below.

$$\text{Release rate}(\%) = 1 - \left(\frac{\text{mass of element in the residual ash}}{\text{mass of element in the fuel}} \right) * 100 \quad (1)$$

Once the release rate of aerosol-forming elements has been determined, it is possible to estimate the aerosol formation potential. In particular, it is considered that elements K, Na, P and Zn form K_2SO_4 , KCl , Na_2SO_4 , $NaCl$, P_2O_5 , and ZnO . Moreover, if there is not enough S and Cl to bind K and Na, the formation of carbonates K_2CO_3 and Na_2CO_3 is also possible [28,29]. If it is assumed that the whole S reacts with K and Na to form sulfates, the maximum aerosol formation potential can be estimated, whereas if all the Cl is assumed to be bound with K and Na, the minimum aerosol emission can be determined. The difference is attributed to the fact that sulfates have higher molecular weight than chlorides. However, it is imperative to state that the particle losses due to condensation and subsequent deposit in reactor walls as well as gaseous emissions of S (SO_x) and Cl (HCl) were not considered in the analysis. Therefore, the results might be overestimated; however, they can provide a proximate evaluation of aerosol emissions potential.

2.4. Fuel indexes

Fuel indexes were applied as a pre-evaluation step regarding typical combustion related problems when new fuels are introduced. Their

determination is based on fuel chemical analysis, chemical reactions between ash forming elements and interactions between different group of elements. Moreover, their validation was performed via dedicated combustion tests on lab, pilot and real scale facilities [28,30]. The indexes being considered in this work are as follows: a) N content in the fuel as indicator for NO_x emissions potential b) $K + Na + Zn + Pb$ to estimate the potential of aerosol emissions, c) molar ratio $(Si + P + K)/(Ca + Mg)$ for determining the ash melting behavior and d) molar ratio $2S/Cl$ for the prediction of corrosion on boiler surfaces.

$$Index_{PM1} = K + Na + Zn + Pb \text{ (mg/kg d.b.)} \quad (2)$$

$$Index_{Ashmelting} = \frac{Si + P + K}{Ca + Mg} \text{ (mole/mole)} \quad (3)$$

$$Index_{Corrosion} = \frac{2 * S}{Cl} \text{ (mole/mole)} \quad (4)$$

3. Results and discussion

3.1. Combustion behaviour during lab-scale experiments: case study of SP

This section thoroughly describes the test runs conducted on the SP in order to have a complete overview of the experimental procedure, before summarising the relevant results of the combustion of PL and blend of PL/WC. Fig. 3 shows the combustion behaviour of SP related to fuel mass decrease, temperatures at different positions in the bed and the release of gaseous compounds, over time. A fuel mass of 410 g was inserted in the preheated reactor and the total duration of the experiment lasted approximately forty minutes. Initially the drying process occurred which can be identified by moderate mass decrease, low temperatures in the fuel bed and the release of H_2O . After approximately 11 min (652 sec) the devolatilisation phase started taking place. During this phase, the reaction front propagates from the top of the bed to the

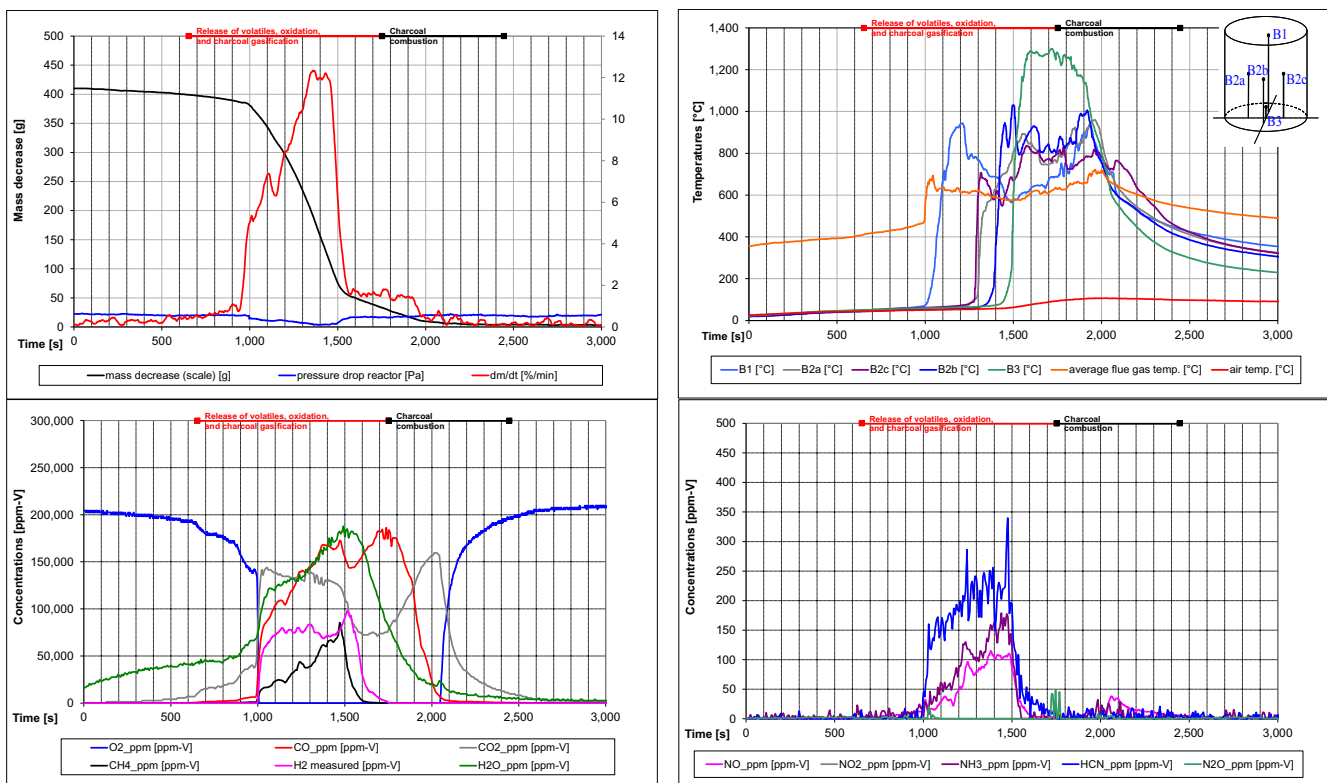


Fig. 3. Mass loss (top left), fuel bed temperatures (top right), and release of main gaseous (bottom left), and nitrogen compounds (bottom right), during SP combustion.

bottom. This causes an intensive mass loss and a sharp increase in the temperature, especially when the main devolatilisation phase starts at ~ 1000 sec, as observed from the thermocouple's values (Fig. 3, top right). The main gaseous compounds produced are CO, CO₂, H₂O, CH₄ and smaller amounts of other hydrocarbons. After approximately 30 min (1752 sec) from the beginning of the experiment, the devolatilisation front reaches the grate and the concentration of CH₄ drops to zero, indicating the end of this phase and the initialisation of charcoal combustion. The latter phase occurs at the bottom of the bed close to the grate and the main product during this phase is CO₂, produced either directly from carbon oxidation or from partial oxidation of CO. It should be noted that the highest temperature is observed in this stage, and in the case of SP test run the maximum temperature reached 1301 °C. The N gaseous species are mostly released during devolatilisation phase (Fig. 3 bottom right), with the dominant compounds being HCN, NH₃ and NO. Moreover, a second peak in volatiles release is observed during charcoal combustion, with an increase in NO concentration, implying the partial oxidation of N bounded in charcoal.

In Fig. 4 the profile of air ratio and flue gas flow rate over time is illustrated. At the start of the devolatilisation phase oxygen concentration decreases; however high values of air ratio are still present. When the main devolatilisation phase starts (~ 1000 sec), a sharp reduction in the values of air ratio is observed, implying the rapid consumption of oxygen in the oxidation of the devolatilisation products (refer Fig. 3 bottom left). On the contrary, during charcoal combustion phase, air ratio rises again acquiring values higher than one and keeping the same trend until the end of the experiment. Similarly, the amount of flue gas increases during the release of the devolatilisation products, following a downward trend afterwards.

Figs. 5 and 6 show the combustion behaviour of PL and PL/WC blend. The initial mass of PL inserted in the reactor was 400.5 g. Compared to SP test run, the drying phase of PL combustion lasted longer (1698 sec) due to comparatively higher moisture content in the PL. The maximum temperature was observed during the beginning of charcoal combustion phase, reaching 1228 °C and the total duration of

PL combustion was 65 min. Among the N gaseous species, NH₃ is the compound with the highest concentration followed by NO, both released mainly during the devolatilisation phase, with a small peak in NO concentration observed also during charcoal combustion. On the other hand, during combustion of PL/WC blend, drying lasted approximately 60 sec since the initial mass was smaller (240.6 g), due to density differences between the tested fuels. The maximum bed temperature during charcoal combustion was 1041 °C and the total duration of the PL/WC experiment lasted 1560 sec (26 min). NH₃ appeared to be the dominant compound released during devolatilisation phase, in line with the combustion of PL. In contrast to PL and SP, the PL/WC charcoal combustion didn't show a peak of NO concentration. It should be highlighted that the residual ash after combustion of SP was 1.43 g (0.35% of the initial fuel mass), whereas in the case of PL and the PL/WC residual ash was 69.7 g (17.4% of the initial fuel mass) and 27.7 g (11.5% of the initial fuel mass) respectively. The latter fact clearly implies the associated challenges due to high ash content when combusting PL compared to traditional biomass. Representation of ash residues after the combustion of PL and PL/WC is given at Fig. 7. From the residual ashes of tests with PL (see Fig. 7) no sintered ash particles have been obtained, while the pellet structure was still intact, whereas for PL/WC a similar result has been observed.

3.2. N gaseous species and aerosols formation

Initially the conversion rate of fuel bound N into gaseous species is depicted in Fig. 8. Total fixed nitrogen (TFN) stands for the sum of fuel bound N in NH₃, NO, HCN, NO₂ and N₂O. As observed N contained in PL is converted by $\sim 40\%$ into NH₃, less than 10% into NO, while the rest (50%) remains in the charcoal. In the case of PL/WC, NH₃ amounts slightly more than 30%, followed by NO ($\sim 6\%$). On the other hand, TFN for the SP reads almost 100%, since N is converted into HCN by 50%, $\sim 30\%$ into NH₃, and $\sim 20\%$ into NO. As observed, NH₃ and HCN are the main nitrogen products released during devolatilisation phase. Their ratio varies depending on the fuel characteristics, reactor set-up and

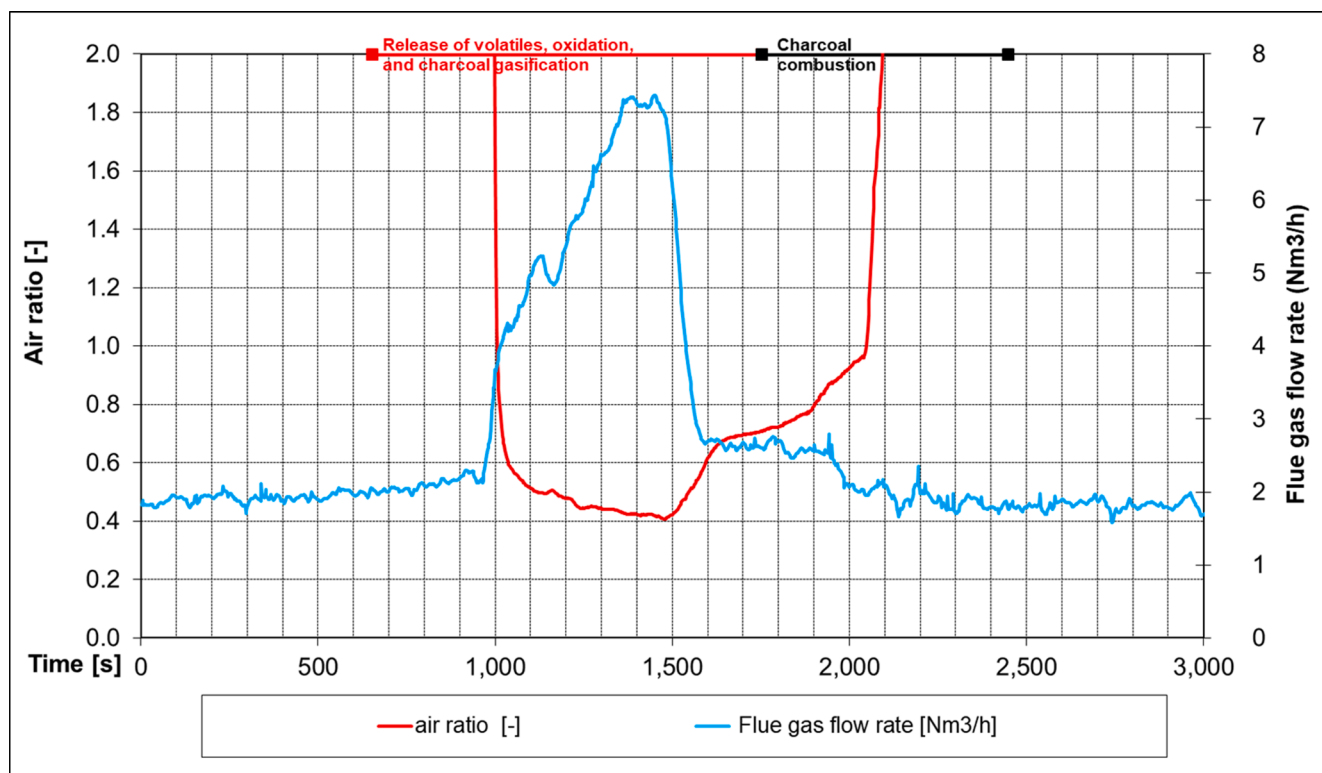


Fig. 4. Air ratio and flue gas flow rate during SP combustion vs time.

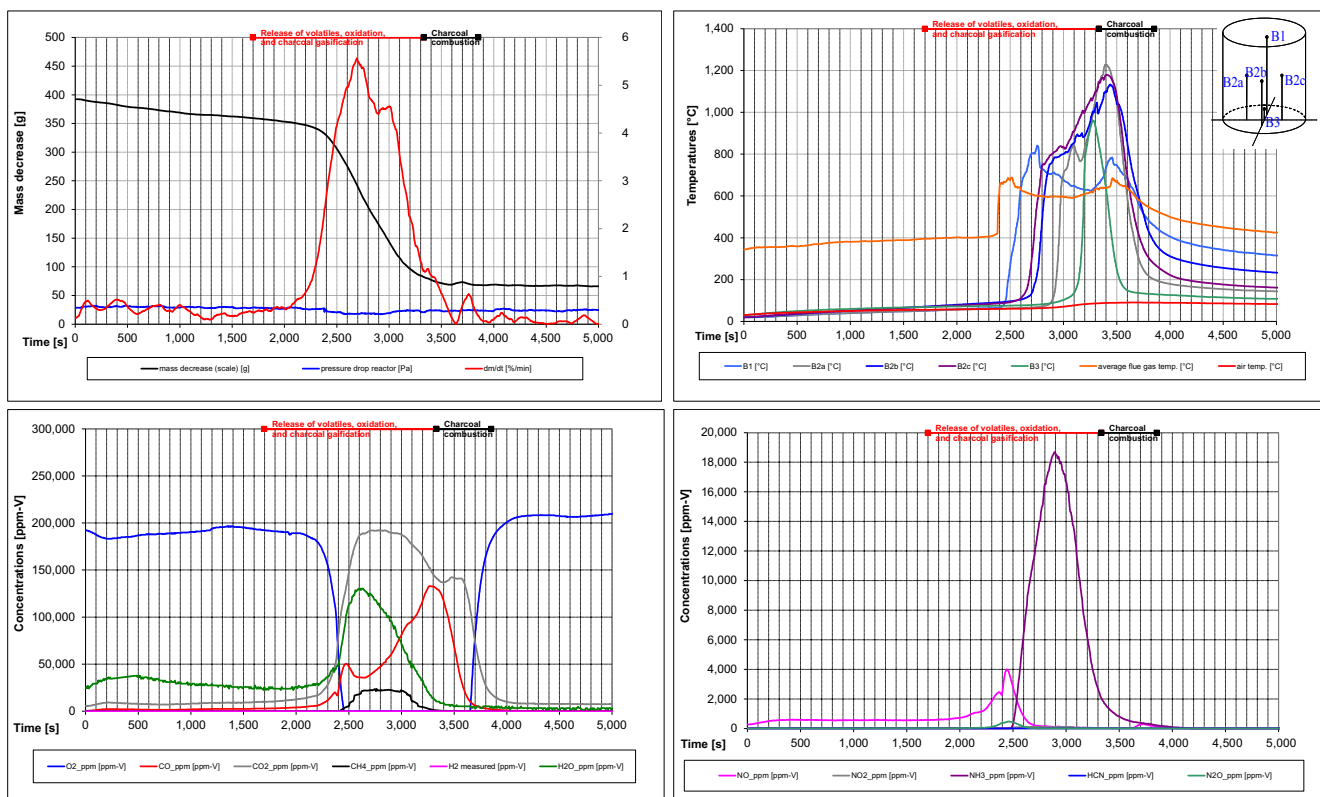


Fig. 5. Mass loss (top left), fuel bed temperatures (top right), and release of main gas (bottom left), and nitrogen compounds (bottom right), during PL combustion.

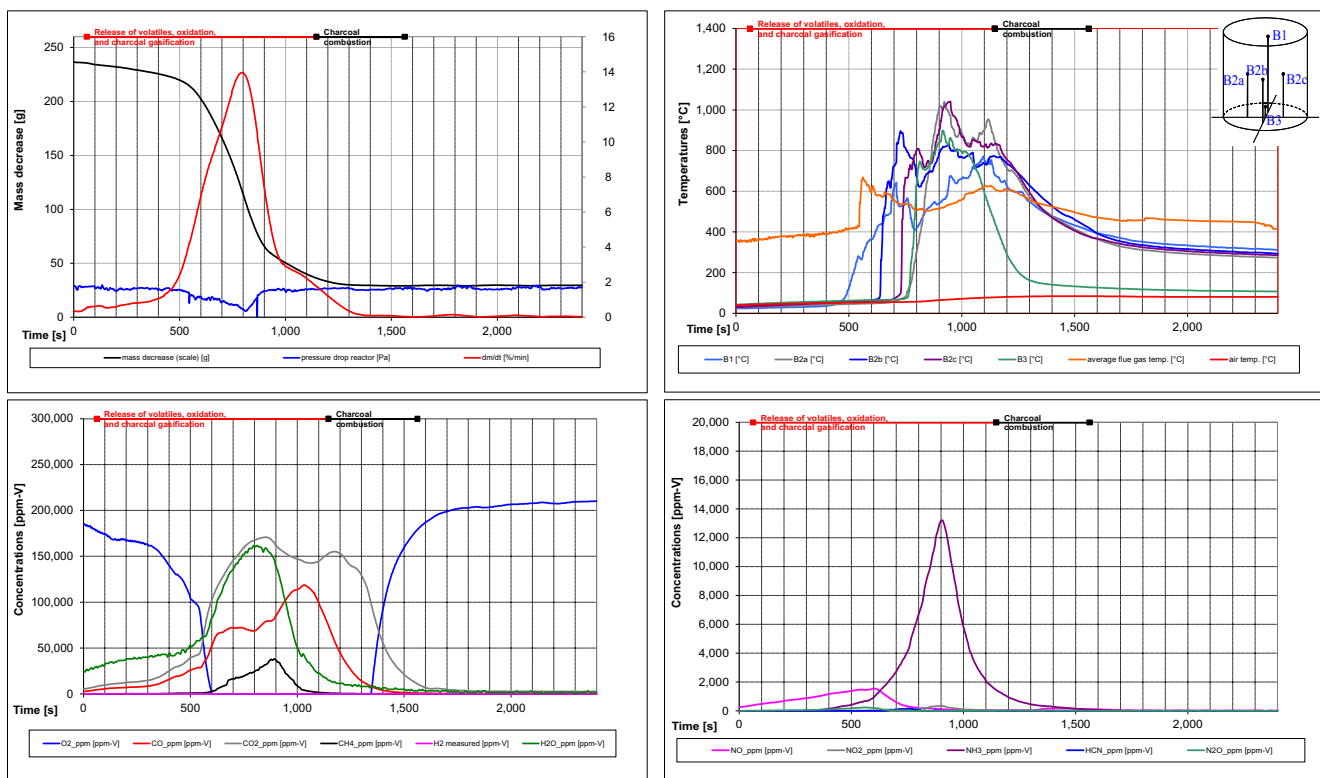


Fig. 6. Mass loss (top left), fuel bed temperatures (top right), and release of main gas (bottom left), and nitrogen compounds (bottom right), during PL/WC combustion.



Fig. 7. Ash residues after combustion. PL (left) and PL/WC (right).

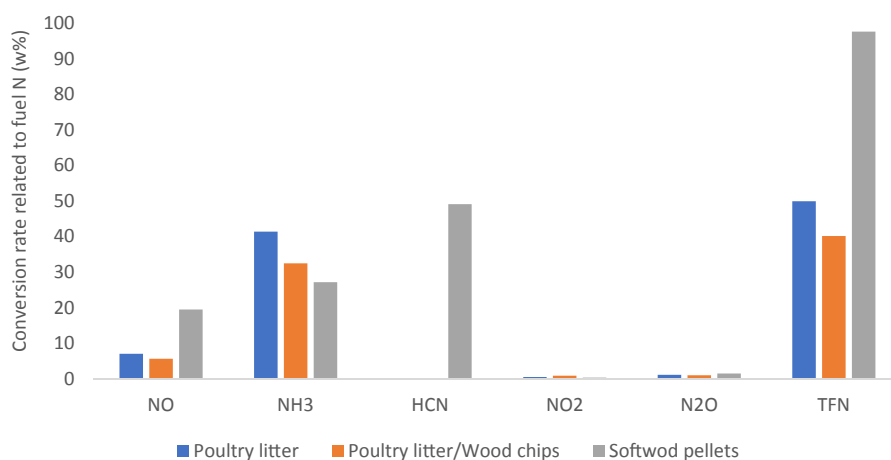


Fig. 8. Release of N gaseous species related to nitrogen content of the fuel.

operating conditions. The fate of fuel nitrogen from biomass residues and biowastes was investigated and the authors have concluded that N in heterocyclic compounds mostly decompose into HCN, while N found

in amino acids and proteins decompose into NH₃ [31]. Indeed, most of the N in the PL derives from the animal feed, excreta and feathers rather than from the bedding material and this N is chemically incorporated

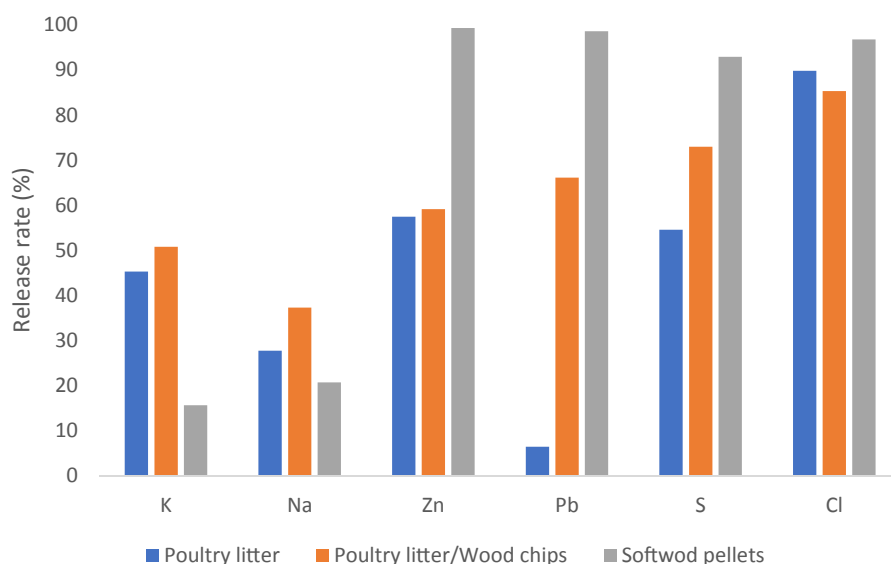


Fig. 9. Release rate of volatile and semi-volatile elements in the gas phase.

into protein molecules and urea. Therefore, it could be a possible explanation for NH_3 being the dominant compound during PL combustion. However, due to the complex structure of nitrogen, it's not yet possible to draw definite conclusions regarding the ratio NH_3/HCN . In the study of Anca-Couce et al. [20], the authors tested 32 different biomass fuels (woody biomass, agricultural, etc.) in the same reactor of the present study. The authors have reported similar amounts of HCN and NH_3 for woody biomass characterised by low N content, while in some cases (hardwood and stem softwood) HCN showed the highest concentration. Furthermore, in the study of Brunner et al. [29], the authors tested beech woodchips also in the same reactor utilised in the present study and the findings revealed HCN as the compound with the highest concentration (44.5%) during devolatilisation, followed by NH_3 (~20%). Beechwood pellets in the study of Brunner et al. [29] had similar composition with the softwood pellets (SP) tested during the present study, and the findings from both studies are in qualitative agreement regarding the concentration of the N gaseous species during devolatilisation. In both studies the authors reported two different peaks for NO concentration, one in the beginning of the devolatilisation phase and the second one during char oxidation, similarly to the present study.

Fig. 9 shows the release rates of the aerosol forming elements in the gas phase, based on their concentrations in the fuel (see Table 3) and residual ashes (see Table 4). Fig. 10 illustrates the maximum potential of aerosol emissions from all tested fuels. The blend of PL/WC shows the highest release rate of alkali metals K and Na, reaching 50% and 37% respectively. Furthermore, Zn was almost completely released in the case of SP, whereas in the case of the other two tested fuels (PL and PL/WC), Zn release rate was ~60%. Pb was present in minor concentrations, reaching an almost 100% release rate into the gas phase for SP. Pb is categorised as a highly volatile element at higher temperatures which can get re-absorbed on the carbon/char particle if available when temperature drops [32]. It has shown the same behaviour in the combustion phase for SP. However, an opposite trend is found in the case of PL. Therefore, the drop in Pb release rate could be linked with the relatively higher ash content in PL and PL/WC compared to SP. Cl displayed high release rates (>80%) for all tested fuels. S illustrated the lowest release rate in the case of PL combustion (54%) whilst the highest release rate was reported during SP combustion (92%).

The maximum estimated aerosol emissions result from the combustion of PL, reaching the value of $2806 \text{ mg}/\text{Nm}^3$ (dry flue gas, 13 vol% O_2), whereas for PL/WC a value of $2584 \text{ mg}/\text{Nm}^3$ (dry flue gas, 13 vol% O_2) was determined. As expected, the estimated aerosol emissions from SP combustion are negligible with $16.5 \text{ mg}/\text{Nm}^3$ (dry flue gas, 13 vol% O_2), due to the low presence of aerosol forming elements initially contained in the fuel. Moreover, it should be highlighted that the aerosol emissions are mainly influenced by the release of potassium in the gas phase. The findings are in line with the work of Sommersacher et al. [28].

Table 4
Chemical composition of residual ashes after the test runs.

Ash composition (mg/kg d.b.)	PL	PL/WC	SP
Calcium	328,000	305,000	277,000
Silicon	12,700	28,400	81,600
Magnesium	45,300	42,200	36,400
Potassium	66,300	70,800	114,000
Sodium	18,600	17,600	3170
Phosphorus	78,700	73,500	11,600
Aluminium	2540	4360	n.d.
Zinc	1250	1320	22.8
Lead	10	10	0.5
Iron	3980	4720	n.d.
Manganese	2240	2180	n.d.
Copper	404	381	n.d.

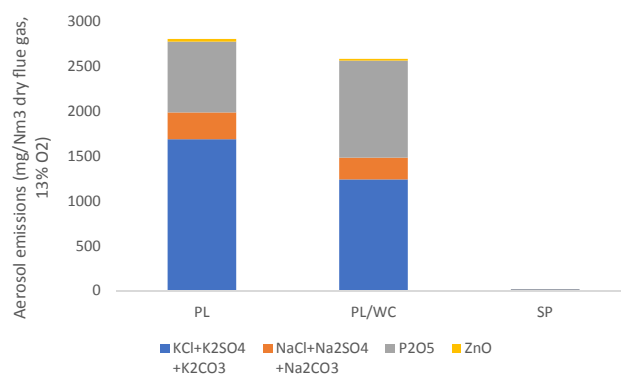


Fig. 10. Amount and concentration of estimated aerosol emissions.

3.3. Fuel indexes

Generated NO_x emissions are an important factor to be addressed during the operation of biomass combustion plants. Pre-evaluation of a particular fuel can be proven a very effective measure, since it can provide a good estimation if its utilisation in a combustion plant will exceed the emission limits imposed from European regulations, and the consequent mitigation measures that need to be considered. In the study of Sommersacher et al. [30], data has been derived from test runs of different biomass fuels in grate combustion plants equipped with air staging technology. According to their observations, NO_x emissions are increasing with the N content in the fuel and that fuels with N content > 1 wt% (d.b.) tend to produce NO_x emissions > $200 \text{ mg}/\text{Nm}^3$ (dry gas, 13% O_2). Therefore, based on the fuel index, combustion of PL is expected to generate $\sim 400 \text{ mg}/\text{Nm}^3$ (dry gas, 13% O_2) at 3.7 wt% (d.b.) nitrogen content. The index is considered valid only for the specific type of plant, and furthermore, there is a possibility that the expected NO_x emissions can be lower due to the fact that the main N gaseous compound released during devolatilisation phase is NH_3 (See Fig. 8). It is very likely that the NH_3 will reduce the NO_x emissions and therefore this index cannot be directly applied. However, the index delivers a maximum range of expected NO_x emissions. It should be highlighted that under Commission Regulation (EU, 142/2014), NO_x emissions derived from on-farm PL combustion must not exceed $200 \text{ mg}/\text{Nm}^3$ (dry gas, 11% O_2) [23].

A correlation between the production of aerosol emissions and the concentration of aerosol forming elements (K, Na, Zn, Pb) in the dry fuel is depicted in Fig. 11. Sommersacher et al. tested the fuel indexes of

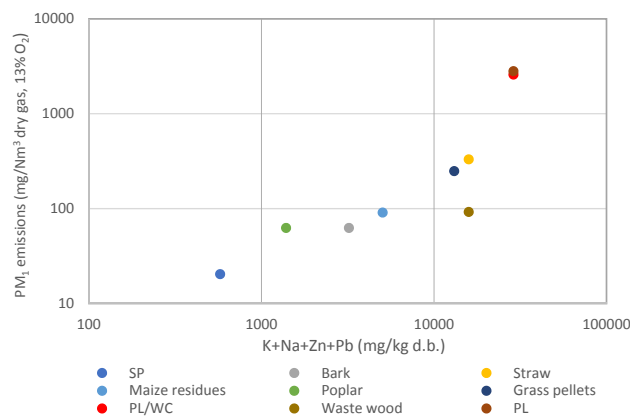


Fig. 11. Particulate emissions (PM_1) vs concentration of aerosol forming elements present in the fuel. PM_1 emissions for Bark, Straw, Maize residues, Poplar, Grass pellets, Waste wood result from tests in real scale plants and have been taken from Sommersacher et al. [30]; PM_1 emissions of PL, PL/WC, and SP, tested in this work are estimated values.

different types of biomass fuels [30] and classified the level of aerosol emission as follows: a) Low PM₁ emissions range for an index with value < 1000 mg/kg d.b., b) medium PM₁ emissions range for index with value ranging between 1000 and 10000 mg/kg d.b. and c) high PM₁ emissions range if the index exceeds 10000 mg/kg d.b.

In the current study, index acquires values >10000 mg/kg d.b. in the cases of PL and PL/WC combustion, therefore aerosol emissions above 500 mg/Nm³ (dry gas, 13 vol% O₂) should be expected. This estimation has been confirmed by the test runs with the lab-scale reactor, where maximum estimated aerosol emissions of 2806 mg/Nm³ (dry gas, 13 vol% O₂) for PL and 2584 mg/Nm³ (dry gas, 13 vol% O₂) for PL/WC were determined, as shown in Fig. 11. The index related to SP combustion is low (535 mg/kg d.b.) and consequently the aerosol emissions are estimated to be in negligible quantities 16.5 mg/Nm³ (dry gas, 13 vol% O₂). The high aerosol emissions formed can cause high deposition rates on cooled surfaces in a plant (e.g. the boiler) and show the need to consider this aspect when designing a plant. An effective measure to tackle this issue is the installation of an automatic boiler cleaning system. Additionally, the limit of particulate matter emissions stemming from on-farm PL combustion shouldn't exceed 10 mg/Nm³ (dry gas, 11vol% O₂) according to European regulations [23]. Therefore, high aerosol emissions determined from PL combustion show the need to equip a plant with flue gas cleaning devices such as electrostatic precipitators (ESPs) or bag filters, that remove the aerosols from the flue gas with high efficiency before it is emitted into the atmosphere.

Ash melting behaviour is determined by the molar ratio of Si/(Ca + Mg). It is generally accepted that the presence of Si in combination with K decreases the ash melting temperature, while the opposite is observed when there is an increased concentration in Ca and Mg [18,33–35]. However, for fuels with high concentration in P and K, the index is not valid. Therefore, another index is used, Si + P + K/(Ca + Mg), considering also the presence of P and K. In the work of Sommersacher et al. [36], a correlation was developed according to which ash melting temperatures decrease with rising values of the index. The indexes for PL and PL/WC have low values, 0.53 and 0.57 (mol/mol) respectively, and thus high ash melting temperatures should be expected. Indeed, the estimated melting temperatures based on the correlation were found to be ~1335 °C for both fuels, a fact that comes into agreement with the lab-scale experimental observations. Similarly, the estimated melting temperature of the SP was 1315 °C.

Regarding the fuel index 2S/Cl (mol/mol), it is known that the presence of Cl is very crucial with reference to corrosion of boiler surfaces. Chlorine induced corrosion is usually realised by the direct attack of gaseous Cl in the form of Cl₂ and HCl, or the deposition of alkali chlorides on the boiler surfaces. The former corrosion mechanism is favoured mainly in high temperature combustion environment, whereas the latter causes the reduction of melting temperature range. Presence of sulphur in the fuel composition, along with adequate residence time and high enough combustion temperature is reported to limit the corrosion effect since alkali chlorides are converted into sulphates, characterised by higher melting temperatures compared to chlorides. On the contrary, if there is not enough time for alkali chlorides to convert into sulphates, then their deposition on the surfaces release Cl which becomes available for corrosion reactions. This mechanism is known as active oxidation [30,37]. If the molar ratio <4, then high corrosion risks should be expected. Furthermore, if the value is >8, Cl concentration in boiler deposits is considered to be negligible, therefore minimising corrosion risks [30,38]. Based on the description above, corrosion risk is much higher in case of PL (fuel index 1.82) and blend of PL/WC (fuel index 1.53) compared to SP (fuel index 6.85).

4. Summary and conclusions

The combustion behaviour of PL, blend of PL/WC and SP, was experimentally studied in a discontinuous lab-scale fixed bed reactor. After the completion of the test runs data were gathered related to the

thermal decomposition behaviour of the three fuels, the release of N gaseous species and aerosol forming elements, as well as the potential of aerosol emissions and ash melting behaviour. As regards the N gaseous species, NH₃ showed the highest concentration in cases of PL and the blend, while HCN was the most abundant compound during SP combustion. Almost all N initially bound with the SP was converted into N gaseous species, whereas the corresponding conversion for PL and the blend amounted around 50% and 40% respectively. Easily volatile elements Cl and S illustrated higher release rates, while 15–50% was the range for the release rate of alkali metals K and Na for all tested fuels. Furthermore, the maximum estimated aerosol emissions were estimated during PL combustion, reaching the value of 2806 mg/Nm³ (dry flue gas, 13 vol% O₂), followed by 2584 mg/Nm³ (dry flue gas, 13 vol% O₂) in the case of blend (PL/BW). On the contrary, the estimated aerosol emissions for SP combustion were very low.

Performed evaluation of the tested fuels based on fuel indexes revealed the associated challenges of PL during combustion. Initially, presence of nitrogen in high concentrations in the PL composition, implies that primary measures may not be sufficient, and therefore secondary measures (Selective Non-Catalytic Reduction) will be needed for effective control of NO_x emissions. Moreover, increased concentration of aerosol emissions is closely related to ash deposition and corrosion in the heat exchangers, and thus proper dust cleaning equipment will be essential, as well as a careful selection of materials resilient to corrosion. Ash melting is another decisive factor regarding the efficient operation of a plant running on PL. In this particular study ash melting temperatures of PL and blend are estimated to be high and thus it wouldn't be expected to create any significant problem associated to ash melting. However, given the fact that composition of PL varies considerably, a pre-evaluation of the ash melting temperature is recommended prior to utilisation. Possible low ash melting temperatures will lead to lower operating temperatures in the combustion chamber, a fact that could affect considerably the efficiency of the combustion process.

Despite the challenges described above, combustion of PL and blend of PL/WC on-farm seems to be a promising option. Their utilisation as fuels can contribute to the energy demand coverage of the farm without the need for fossil fuels, while on the same time avoiding the disposal costs from a farm owner's perspective. Furthermore, the significant volume reduction during combustion, eliminates the need for land-filling, which is considered as the last option in terms of a sustainable waste management.

CRediT authorship contribution statement

Giannis Katsaros: Conceptualization, Data curation, Methodology, Writing - original draft. **Peter Sommersacher:** Conceptualization, Data curation, Methodology, Writing - review & editing. **Stefan Retschizegger:** Conceptualization, Data curation, Methodology, Writing - review & editing. **Norbert Kienzl:** Methodology. **Savvas Tassou:** Writing - review & editing. **Daya Shankar Pandey:** Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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