

# Chemometric analysis for the relationship between mineral contents, particle matter and bottom ash distribution during pellets combustion

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## Abstract

This paper aims to identify the correlation between the mineral contents in agropellets and particle matter and bottom ash characteristics during combustion in domestic boilers. Four agrifood residues with higher mineral contents, namely grape marc (GM), tomato waste (TW), exhausted olive mill solid waste (EOMSW), olive mill wastewater (OMWW), were selected. Then, seven different pellets were produced from pure residues or their mixture and blending with sawdust. The physico-chemical properties of the produced pellets were analyzed using different analytical techniques and a particular attention was paid to their mineral contents.

Combustion tests were performed in 12 kW domestic boiler. The particle matter (PM) emission was characterized through the particle number and mass quantification for different particle size. The bottom ash composition and size distribution was also characterized. Chemometric analyses were performed to identify the correlation between the mineral contents and PM and bottom ash characteristics. The performed analyses indicate that K, Na, S and Cl are released partially or completely during combustion tests. In contrast, Ca, Mg, Si, P, Al, Fe and Mn are retained in the bottom ash. The chemometric analyses indicate that, in addition to the operating conditions and the pellets ash contents, K and Si concentrations have a significant effect on the PM emissions as well as on the agglomeration of bottom ash.

**Keywords :** Pellets, Combustion, PM emissions, bottom ash, size distribution, chemometric analysis

## 1-Introduction

The growth of the energy demand in combination with the high fossil fuel prices and environmental concerns incites many governments to support biomass energy development [1]. Therefore, the domestic and industrial demand of wood for heat and power production is rising in all over Europe [2]. Wood is a very adaptable fuel and can be combusted in many different forms in a wide range of heating equipment. The most common forms are wood logs and chips which could be used at different scales [3]. However, these fuel forms have several drawbacks in terms of quality, logistics and fuel supply. Hence, a rapid growth in the wood pellet production is observed during the last decades [4]. Such increasing interest for pellets is mainly due to their homogeneity, the high energy density and the low ash content [5]. These characteristics facilitate the automatic operation and improve the boiler efficiency. Currently, the main raw materials used for pellets production are wood derived fuels (sawdust, wood shavings and chips). However, the increasing demand on wood residues has led to unbearable pressure on the forest [6]. In order to lighten this pressure, the use of agriculture and agri-food industry residues for the production of fuel pellets seems to be a promising issue [7].

Several investigations showed that these alternative biomass fuels have a considerable potential to be used in the combustion systems [8-13]. Gonzalez et al. have obtained boiler efficiencies ranging between 89.7% and 91.6% for a 12 kW mural boiler fuelled with tomato, forest, olive stone and cardoon pellets [8]. Verma et al. have evaluated the performance of different pellets from agriculture residues namely apple pomace, reed canary grass, pectin waste, sunflower husk, wheat straw during combustion tests in a 40 kW boiler [9]. Authors found that the used boiler satisfied efficiency requirements of the European standard EN-303-5 for all the tested pellets. Limousy et al. have performed combustion tests in domestic boiler using spent coffee grounds/sawdust pellets [10]. Authors noted the possibility of the partial substitution of wood sawdust by spent coffee grounds without a significant decrease in the boiler performance. This substitution may alleviate the current pressure on wood sawdust which became rare and expensive [10]. Elmay et al. have found that date palm residues presented a good potential for energy recovery in residential boiler [11]. However, they have noted that moisture content should be controlled carefully during the combustion optimization. Cardozo et al. have evaluated the direct combustion of several agricultural residues such as sunflower husks, Brazil nut shells and sugar cane bagasse at small-scale heat and power generation [12]. The authors pointed out the importance of the biomass properties and the operating conditions on the conversion efficiency. Lajili et al. have examined the combustion of agropellets produced from olive solid waste blended with pine sawdust [13]. The authors claimed that it is recommendable to use blends with 50% of olive solid waste [13]. They found also the importance of the adjustment of the primary and secondary air flow to increase the boiler efficiency.

Although the promising results obtained previously for pellets prepared from agriculture and agrifood residues, their low quality comparing to wood pellets leads to considerable amount of gaseous and particulate matter emissions during combustion in the available boilers on the European market. In fact, agriculture residues have a high ash, nitrogen and sulphur contents compared to wood pellets which may be the origin of higher NO<sub>x</sub>; SO<sub>x</sub> and PM emissions as observed by Garcia-Maraver et al. during the combustion of olive pruning residues in a domestic boiler [14]. In addition, several operational problems in combustion systems including undesired effects in the equipments such as slagging, fouling or corrosion were observed with these low quality pellets [8-9, 15-16]. As an example, Gonzalez et al. suggested a continual removal of ash from the fireplace fuelled with cardoon pellets due to their high content and low melting point of ashes [8]. Similar behaviour was observed by Verma et al. for the straw pellets. Authors have noted that the high ash content with low melting temperature makes unsuitable for domestic heating applications [9].

Several attempts have been performed to identify the relationship between the fuel properties and PM emissions. Wiinikka et al. showed that inorganic PM emissions were correlated with both the fuel ash content and composition [17]. Verma et al. observed that biomass fuels with higher Si content in the ashes produced the lowest total PM emissions [18]. Garcia-Maraver et al. observed that PM emission is significantly affected by the amount of volatile inorganic elements K and Na in the ash composition [14]. The effect of alkali metals on ash related problems such as deposition, corrosion and emission of fine particulate matter (PM) was already observed by Baxter et al. in biomass-fired electric power boilers [19]. Other investigations were performed on the transformation of these inorganic species during the combustion of solid fuels [20-21]. Although information could be found on the behaviour some inorganic elements during biomass combustion, further investigations are requested to identify the correlation between the mineral contents and PM and residual ash characteristics especially during pellets production. Hence, the purpose of this work is to identify the correlation between the pellets characteristics and the particle matter (PM) distribution as well as bottom ash size and composition during combustion tests in domestic boiler.

## **2. Materials and methods**

### **2.1. Raw Materials**

Different agrifood industry residues were used in this study, namely : Grape marc (GM), tomato waste (TW), exhausted olive mill solid waste (EOMSW) and olive mill wastewater (OMWW). GM was provided from a winery company named “Cooperative Viticole de BouArgoub“ located in Nabeul (North-East, Tunisia). TW was collected from a tomato processing company, named “Jouda“, located in Kairouan (Center, Tunisia). OMWW and EOMSW were collected from olive mill (three-phase centrifugal olive mill) at the seed oil factory “Zouila” located in Mahdia (Center-East, Tunisia). These residues were blended with pine sawdust (PS) provided by a sawmill located in Alsace (North-East, France) in order to respect the French and the European Standards for Biofuels.

### **2.2. Pellets Production**

#### **2.2.1. Pellets Formulation**

The densification process was carried out using a pelletizer KAHL 15/75 type (Amandus Kahl GmbH & Co, Reinbek, Germany) containing a die diameter of 6 mm and a length of 30 mm. The specifications of the used pelletizer are : Die diameter (mm) : 175, Diameter/length of roller (mm) : 130/29, Number of rollers : 2, Control motor (kW/min-1) : 3, Roller speed (m/s) : 0.5-0.8. The capacity of the pelletizer depend on its properties (frequency, temperature, ..) and sample characteristics (composition, moisture content..) and controlled manually. Generally, it is about 2-3 kg/h. Based on the raw materials characteristics, seven types were produced from these residues, namely : IS (Impregnated sawdust by OMWW), IEOMSW (Impregnated EOMSW by OMWW), 100% PS, 100% EOMSW, 100% TW, 50% TW/50%PS, 50% GM/50%PS.

#### **2.2.2. Pellets Characterization**

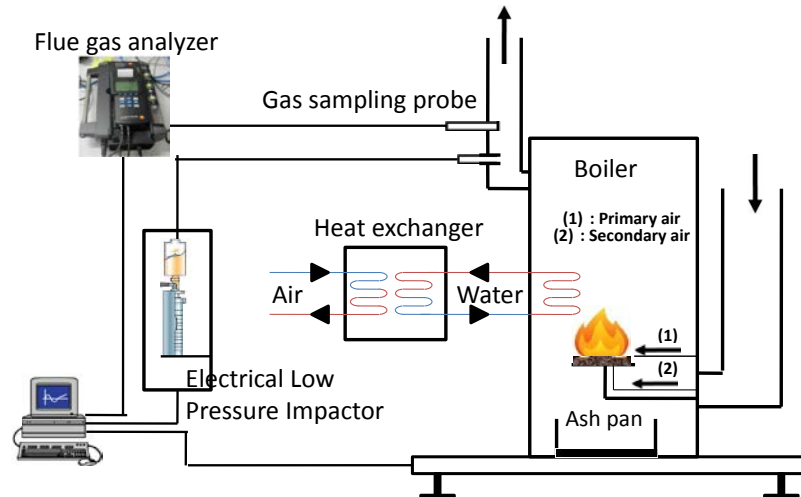
The characteristics of pellets were determined using different analytical techniques based on the available European standards. The moisture content was evaluated according to EN 14774-2. The ash content was determined according to EN 14775 using a muffle furnace. Nitrogen (N) determination was carried out according to EN 15104 by means of a CHONS elemental analyser. Sulfur (S) and chlorine (Cl) contents were determined following EN 15289. The major inorganic elements analysis of the produced pellets was performed according to EN 15290 using an inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The high heating value (HHV) was determined using an adiabatic oxygen bomb calorimeter (IKA C200). Low heating value (LHV) is estimated from HHV by calculating the thermal heat losses coming from water vaporization (both moisture and hydrogen content are considered). The energetic potential of the different biomasses was estimated basing on the calculation of low heating values (LHV), bulk density (BD) and energy density (ED).

### **2.3. Combustion tests**

#### **2.3.1. Experimental Bench**

The experimental bench is shown in Figure 1. Combustion tests were performed in a 12 kW boiler (Pellematic PES12 – PVB 2000) supplied by Ökofen (Barberaz, France) specifically equipped for combustion studies (see Figure 1).



**Figure 1 – Combustion installation.**

This boiler is equipped with the RCB system (Recycling Combustion system), which improves the combustion efficiency, and with a combustion plate of volcano firebox type. It was used at nominal power, using a draught of 0.08 mbar, which induced a medium exhaust gas flow of 28.6 m<sup>3</sup>/h. Heat of combustion is evacuated by a hydraulic circuit composed of a four way melting gate, a variable speed water pump, a water flow meter and a heat exchanger (32 kW). This external exchanger connected to the hydraulic circuit was used to evacuate calories. The boiler was fitted in a pan (Sartorius, France) with an accuracy of 50 g, and the hydraulic circuit was connected to the boiler with flexibles in order to avoid the disruption of mass variation. Inlet and outlet temperatures of the heat exchanger were monitored as well as exhaust gas temperature, fuel mass loss and hydraulic circuit water flow.

### 2.3.2. Gaseous and Particles Matters Analysis

Gaseous emissions were monitored with a portable analyzer (TESTO 350XL/TESTO454) for 20 minutes when the boiler was operating at constant rate. According to French standards the following gases were analyzed during the combustion: Carbon monoxide (CO) and volatile organic compounds (VOC). Gaseous compounds such as O<sub>2</sub>, CO<sub>2</sub>, NO and NO<sub>2</sub> were also monitored during combustion. Gas sampling was performed through the exhaust gas manifold with respect to the NF EN 304 standard at constant flow (close to 1L/min).

An Electrical Low Pressure Impactor (ELPI) manufactured by Dekati Ltd. (Tampere, Finland) was used to collect particles from 29 nm to 10 μm into 12 size fractions. Mass concentration, number concentration and number size distribution of particles were determined using 1 g/cm<sup>3</sup> of density value.

### 2.3.3. Bottom Ash Characterization

At the end of combustion tests, the residual ashes were carefully collected in the ash pan under the grate of the domestic boiler. The bottom ash composition, particles size and slagging tendency were analyzed. The particle size distribution was performed using a laser granulometer CAMSIZER-XT. This technique is based on the optical particle measurement for particle sizing varying from 1 μm 3 mm. During this measurement, bottom ash was feed in the instrument as powders.

The bottom ash composition was evaluated by X-ray fluorescence using a spectrometer Magix (PHILIPS). During these analysis samples were shredded and then disks were manufactured under a mass of 2 tons during two minutes.

## 3. Results

### 3.1. Pellets characteristics and performance

The main characteristics of the prepared pellets are given in Table 1. A higher variability is observed in the properties of the different pellets. In particular, the low heating value varies from 16.3 MJ.kg<sup>-1</sup> for EOMSW to 19.8 MJ.kg<sup>-1</sup> for IEOMSW. These values are in the range available in litterature for pellets [8-15]. The ash content varies from 0.6 wt% for PS pellets to 11 wt% for the TW pellets. The high values obtained for TW and GM-PS prevent these pellets to obtain the French agropellets standard (≤7%). The latter standard could not also be reached for TW, TW-PS, EOMSW, IEOMSW and IS due to the higher chlorine (≤0.2 %) and sulphur (≤0.2%) contents.

The analysis of the inorganic elements shows that, as expected, K, Cl and Ca are the main elements present in the different fuels, while Na, P, Fe, Mg and Si contents depend strongly on the nature of the biomass. Mn and Al are also present, but at trace levels. In addition, it is seen that Na is highly concentrated in the IS, EOMSW and IEOMSW samples, which is mainly due to the initial amount of Na in EOMSW but also to the high concentration of Na in olive mill wastewater.

The higher concentrations of inorganic elements as well as the high sulphur content are very interesting in this present investigation. These values will help to assess the effect of inorganic elements on the particles emission and ash composition. In fact, the available investigations in the literature on mineral contents effect have examined essentially woody biomasses. These latter have few mineral contents and it was difficult to establish molar balance and to identify strong correlation.

Parameter	Unit	TW	TW-PS	GM-PS	EOMSW	IEOMSW	PS	IS
Moisture	(%, wb)	10	11	9	12	7	13	9
Ash	(%, db)	11	4	9	3	7	0.6	4
$\rho_{\text{apparent}}$	( $\text{kg}\cdot\text{m}^{-3}$ )	522	473	569	626	690	601	550
LHV <sup>wb</sup>	( $\text{MJ}\cdot\text{kg}^{-1}$ )	19.5	17.6	16.6	16.3	19.8	16.4	18.5
ED <sub>pellets</sub>	( $\text{GJ}\cdot\text{m}^{-3}$ )	10.2	8.3	9.4	10.2	13.7	9.8	10.2
N	(%, wb)	1.5	0.8	1.4	0.8	1.8	0.2	1.0
S	( $\text{g}\cdot\text{kg}^{-1}$ )	2.96	2.08	1.43	1.99	2.55	0.12	1.55
K	( $\text{g}\cdot\text{kg}^{-1}$ )	30.48	5.14	5.15	3.67	7.53	0.36	3.40
Cl	( $\text{g}\cdot\text{kg}^{-1}$ )	5.75	3.42	0.70	3.44	6.28	0.31	6.12
Ca	( $\text{g}\cdot\text{kg}^{-1}$ )	1.45	1.22	1.28	1.13	1.45	0.36	0.87
Si	( $\text{g}\cdot\text{kg}^{-1}$ )	0.19	0.18	0.21	0.09	0.21	0.01	0.16
Na	( $\text{g}\cdot\text{kg}^{-1}$ )	0.35	0.29	0.23	0.78	1.79	0.01	1.15
P	( $\text{g}\cdot\text{kg}^{-1}$ )	0.93	0.64	0.36	0.13	0.23	0.08	0.18
Mg	( $\text{g}\cdot\text{kg}^{-1}$ )	0.59	0.45	0.22	0.12	0.22	0.02	0.16
Al	( $\text{g}\cdot\text{kg}^{-1}$ )	0.12	0.11	0.20	0.05	0.13	0.01	0.09
Fe	( $\text{g}\cdot\text{kg}^{-1}$ )	0.10	0.10	0.12	0.04	1.00	0.02	0.90
Mn	( $\text{g}\cdot\text{kg}^{-1}$ )	0.09	0.01	0.01	0	0.01	0.05	0.02

**Table 1.** Chemical and physical parameters of the prepared pellets

The energetic and the environmental performance of the different pellets were evaluated during combustion tests in domestic boiler. The combustion and boiler efficiencies as well as gaseous and particles emissions are presented in Table 2. The calculation details are given in previous investigations [22, 23].

Sample	$q$ ( $\text{kg h}^{-1}$ )	$\lambda$	$\eta_{\text{combustion}}$	$\eta_{\text{boiler}}$	[O <sub>2</sub> ]	[CO <sub>2</sub> ]	CO	NO <sub>x</sub>	VOC	PM
			(%)	(%)	(%)	(%)				
TW	2.60	2.10	88.9	80.6	12.1	8	495	428	566	2719
TW-PS	2.40	2.90	87.3	81.1	13.7	7	809	537	515	2279
GM-PS	2.30	4.70	90.4	80.2	16.6	5	631	456	602	966
EOMSW	2.70	2.40	88.4	83.7	12.3	8	993	384	777	558
IEOSW	2.00	2.07	91.5	84.9	10.9	9	631	223	491	1038
PS	2.1	2.61	91.0	83.4	15.0	6	346	116	914	143
IS	2.3	2.35	88.2	81.8	12.1	8	1022	255	1207	659

$q_{\text{comb}}$  is the fuel mass flow ( $\text{kg h}^{-1}$ ),  $\lambda$  is the air factor, [O<sub>2</sub>] is the mean oxygen proportion in fumes (%),  $\eta$  is the efficiency, [O<sub>2</sub>] and [CO<sub>2</sub>] are the mean oxygen and carbon dioxide concentrations in fumes, CO, NO<sub>x</sub>, VOC, PM are the concentrations of carbon monoxide, nitrogen oxides, hydrocarbons and particle matter in  $\text{mg}/\text{Nm}^3$  calculated at 10% O<sub>2</sub>

**Table 2.** Combustion parameters and pollutants emissions

Table 2 shows that the combustion efficiency varies from 87.3% for TW-PS to 91.5% for EOMSW. These values are in the same order of magnitude than those found in literature [8-15]. These obtained values are higher than the minimum value required by the European Standard EN 303-5 (77%). The difference values between the samples may be attributed to several parameters such as primary and secondary air supply adjustments and the high ash contents [22, 23]. In addition, ash contents seem to have a significant effect on PM emissions. In fact, TW pellets have the highest ash content (11 wt%) and the highest PM emissions ( $2719 \text{ mg.Nm}^{-3}$ ) while PS pellets have the lowest ash content (0.6 wt%) and the lowest PM emissions ( $143 \text{ mg.Nm}^{-3}$ ). However, GM pellets have lower PM emissions comparing to TW-PS although their ash content (9 wt%). Such results indicate that the ash composition and more precisely the mineral elements composition in the pellets play a fundamental role in the PM emissions. Hence, these aspects will be assessed further in the next section to identify the relationship between mineral contents and PM emissions.

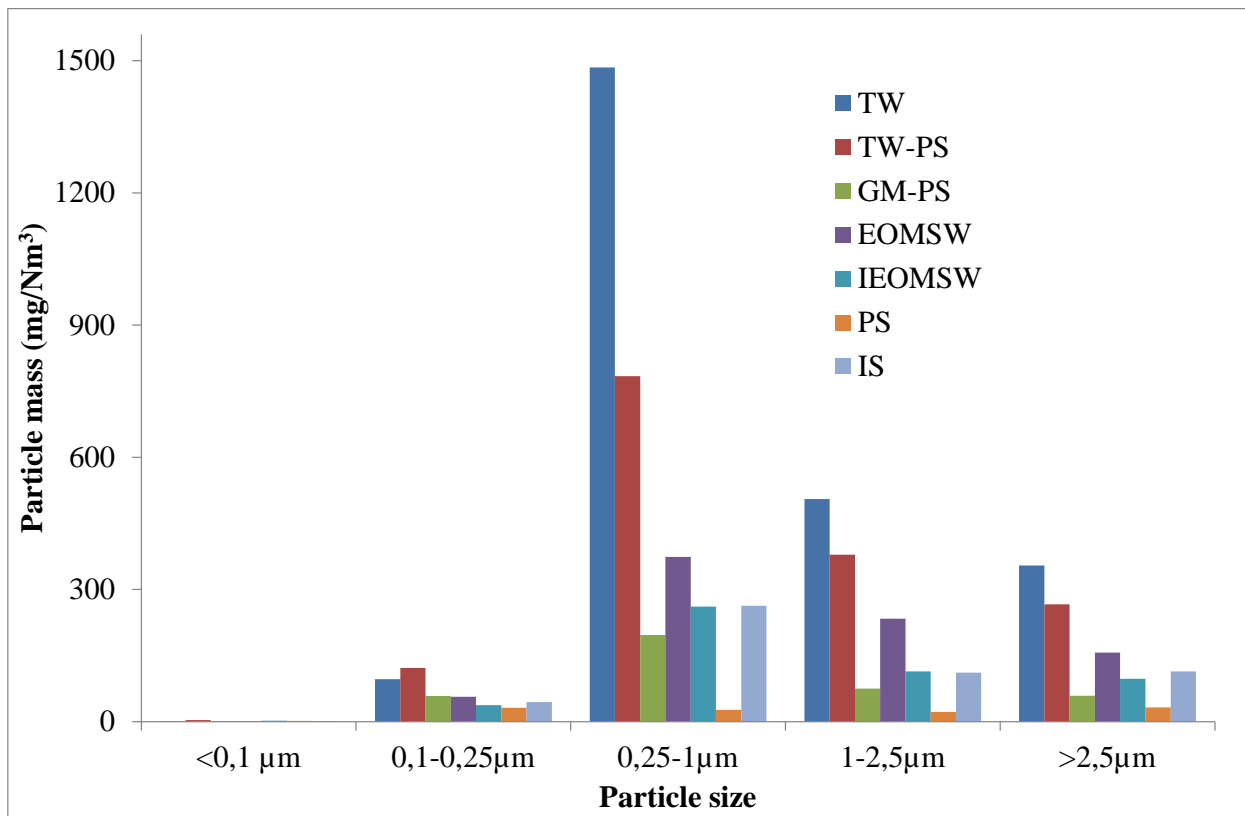
### 3.2. Characterization of the PM emissions

The PM emissions were analysed according to their mass and number for different size range. Table 3 shows the percentage of the different PM particle size during the combustion of the different pellets in the domestic boiler. Table 3 indicates that 99% in number of PM emissions consisted primarily of fine submicron particles with a diameter lower than  $0.1 \mu\text{m}$  during the combustion of the different pellets. Similar results were obtained by Johansson et al. during the combustion of wood pellets briquettes [24]. Furthermore, it seems that the blending with PS and impregnation of OMWW lead to the nanoparticles emissions with a diameter lower than  $0.1 \mu\text{m}$ . The increase of nanoparticles emissions may be attributed to two different reasons. For PS blending, the increase of nanoparticles emissions is expected since PS pellets generated a significant fraction on nanoparticles (39.4%) during combustion. For the impregnated samples, the increase of nanoparticles is attributed to the addition of minerals during OMWW impregnation. Some minerals could be found in the nanoparticles while other minerals may play a catalytic role for the fractioning of the agglomerate soot or condensable organic vapours. Such observations are in agreement with the percentage of carbon (40%) found in the composition of nanoparticles collected during the olive pruning pellets combustion [14].

Sample	PM 0.1	PM 0.1-0.25	PM 0.25-1	PM1-2.5	PM 2.5-10
	(% )				
TW	0.33	46.11	53.07	0.45	0.03
TW-PS	19.58	55.37	24.74	0.28	0.02
GM-PS	13.21	65.14	21.51	0.13	0.01
EOMSW	0.52	59.53	39.46	0.46	0.03
IEOSW	67.70	17.52	14.65	0.11	0.01
PS	39.40	56.22	4.32	0.05	0.01
IS	35.57	39.07	25.19	0.17	0.01

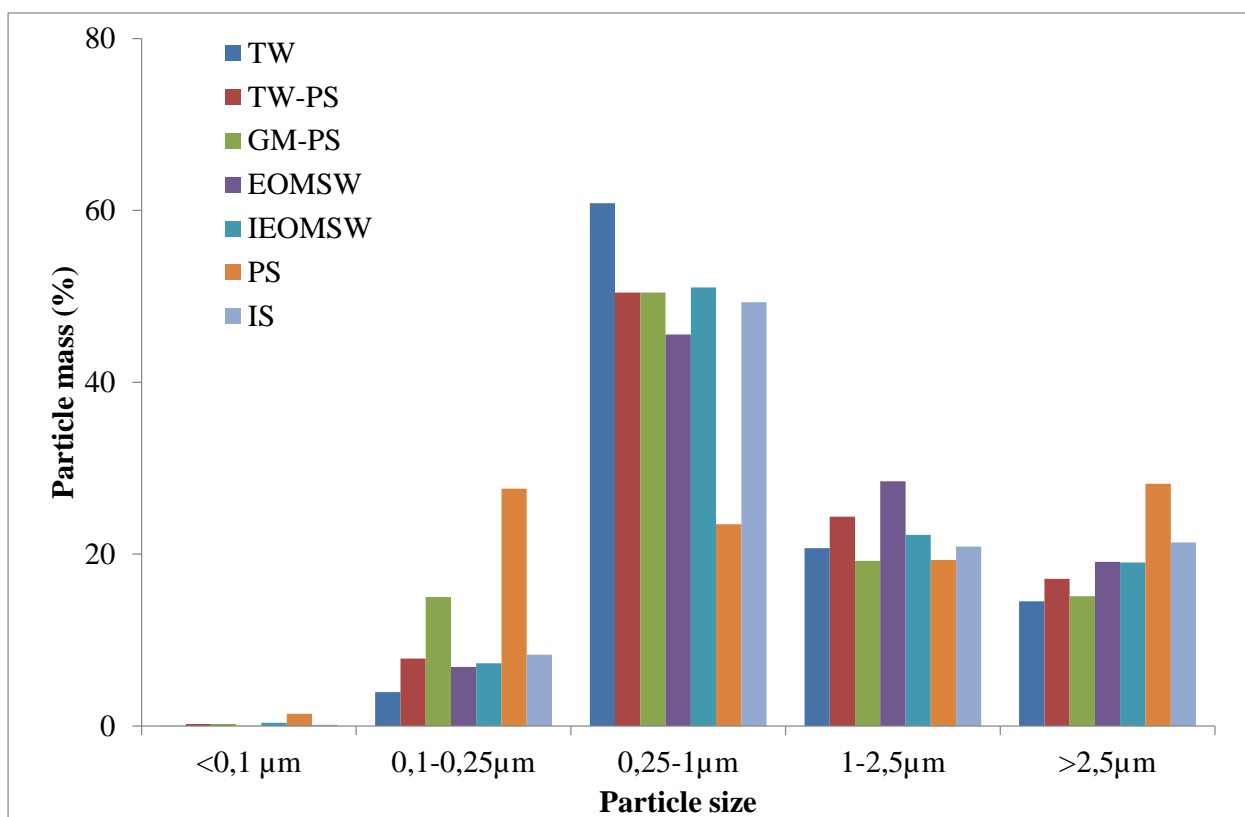
**Table 3.** Percentage of PM number for different particle size fractions

In addition to the particle number, the mass particle distribution could bring further information of the effect of mineral contents on the PM emissions. Figure 2 and Figure 3 show a comparison of the particle size distribution according to their concentration ( $\text{mg.Nm}^{-3}$ ) and percentage from the total mass particles (%), respectively.



**Figure 2.** PM concentrations versus particle size fractions during pellets combustion

As mentioned previously in section 3.1, Figure 2 shows that the PM concentrations vary strongly between the different pellets. This variability is mainly due to the minerals concentrations in the pellets. However, a similar trend is observed for the particle mass percentage shown in Figure 3. In particular, it is clearly shown that, except for PS, the higher particle mass percentage is ranging between 0.25 and 1 μm.



**Figure 3.** PM mass percentage versus particle size fractions during pellets combustion

### 3.3. Characterization of the bottom ash

The chemical composition of the bottom ash collected under the grate during combustion tests were characterized by X-ray fluorescence (XRF). The obtained data for the different oxides (normalized to 100%) are presented in Table 4. The major 3 oxides present in the bottom ash are CaO, K<sub>2</sub>O and SiO<sub>2</sub> representing between 54 wt% and 76 wt% from the total composition. In addition, Table 4 indicates the presence of P<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, which concentrations vary between the different pellets. Comparison between the different ash compositions shows that CaO is the major oxide found in the bottom ash of PS pellets while SiO<sub>2</sub> is the major oxide for GM-PS pellets. K<sub>2</sub>O is present at higher concentration (> 25 wt%) except for PS pellets. Such values are typical for agri-food residues. Furthermore, high concentrations of P<sub>2</sub>O<sub>5</sub> and MgO are observed for TW and TW-PS pellets due to a significant P and Mg content in TW (see Table 1) while the impregnation of OMWW leads to an increase in the Fe<sub>2</sub>O<sub>3</sub> concentration.

Element	PS	IS	EOMSW	IEOMSW	TW	TW-PS	GM-PS
K <sub>2</sub> O	18.68	30.99	27.35	28.27	26.84	26.00	25.32
SiO <sub>2</sub>	8.62	6.93	19.44	21.97	9.42	12.64	32.50
CaO	40.03	15.34	29.81	18.33	17.88	22.19	18.26
Fe <sub>2</sub> O <sub>3</sub>	7.52	10.65	2.09	9.64	1.86	2.11	2.30
SO <sub>3</sub>	1.99	3.60	4.47	5.08	3.56	3.64	2.42
P <sub>2</sub> O <sub>5</sub>	3.22	3.81	5.01	4.23	16.22	16.03	5.39
Na <sub>2</sub> O	2.04	4.05	3.75	4.09	2.32	2.50	1.81
MgO	3.31	2.68	3.43	2.85	10.10	11.08	3.69
Cl	1.18	7.90	2.39	2.72	1.51	0.75	0.19
Al <sub>2</sub> O <sub>3</sub>	1.84	1.54	1.57	2.23	1.88	2.54	5.97
TiO <sub>2</sub>	0.20	0.13	0.18	0.25	0.06	0.07	0.16
SrO	0.11	0.02	0.25	0.15	0.13	0.14	0.07
CuO	-	0.12	0.11	0.07	-	-	-
Cr <sub>2</sub> O <sub>3</sub>	-	-	0.12	0.05	-	-	-
ZrO <sub>2</sub>	0.01	-	-	0.04	-	-	-
ZnO	0.04	0.03	-	0.03	-	0.03	-
Rb <sub>2</sub> O	0.04	0.02	0.01	0.01	-	0.01	-
MnO <sub>2</sub>	0.88	0.48	-	-	0.22	0.23	-
Br	-	0.02	-	-	-	-	-
Other oxides	-	-	-	-	-	-	-
Sum	-	-	100	100	100	100	100

**Table 4** – Bottom ash analysis (%wt).

The particles size distribution of the bottom ash was also analysed. Figure 4 shows the percentage of particle below to 50µm while Figure 5 presents the cumulated percentage versus particle size. Both figures bring significant information on the effect of mineral contents on bottom ash deposition and agglomeration. In particular, it is clearly shown that the bottom ash collected during PS pellets is very homogenous and contains the smallest particles size. In fact, 48.7% of bottom ash size of PS pellets is lower than 10 µm. Moreover, Figure 4 shows that blending with PS generates the presence of the smallest particle size in the bottom ash. In contrast, GM-PS pellets generate the biggest particle size in bottom ash with 44.7% higher than 500 µm.

Figure 5 shows that the combustion of EOMSW and IEOMSW pellets generates a heterogeneous bottom ash size with close percentage for the different particle size range. Similar trend is also observed for the bottom ash of TW and TW-PS pellets with 40% of the bottom ash size in the range 50-500 µm.

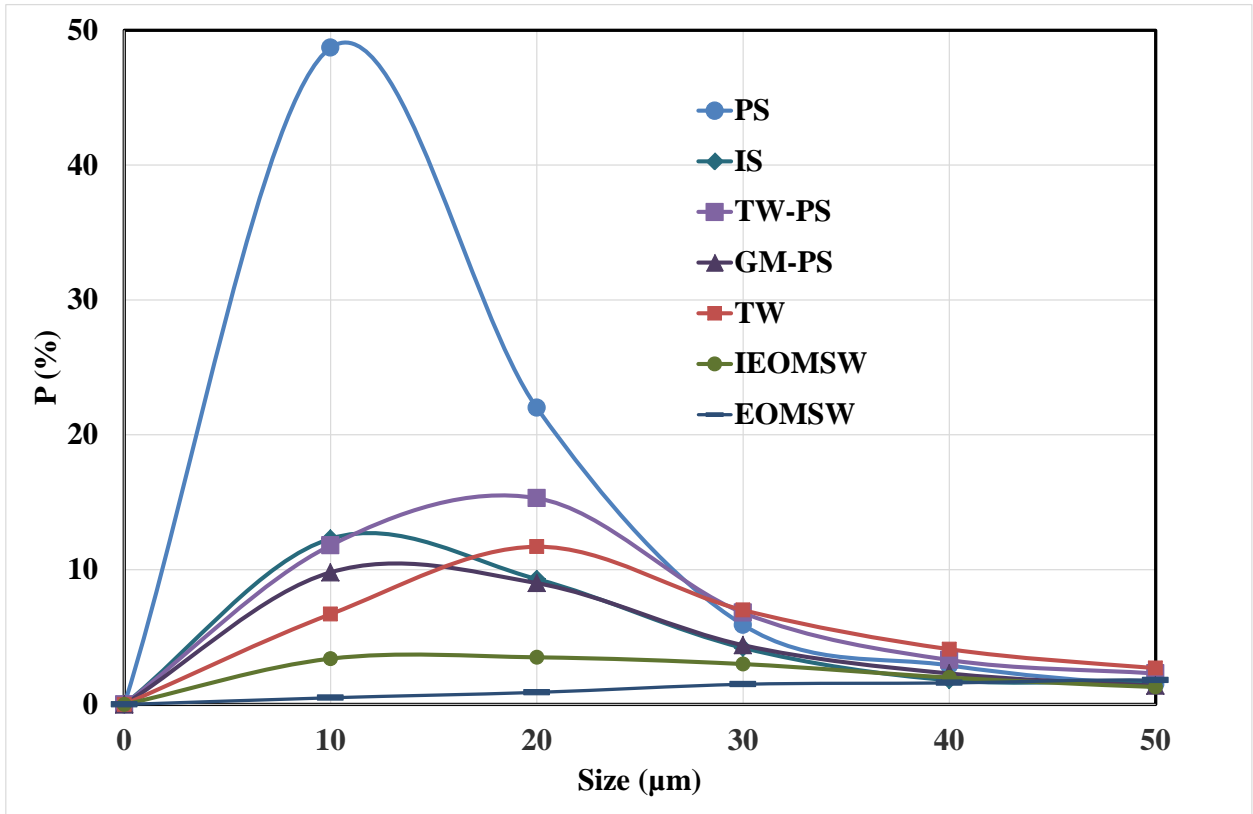


Figure 4. Percentage of particle size distribution in the bottom ash for the fraction below 50µm

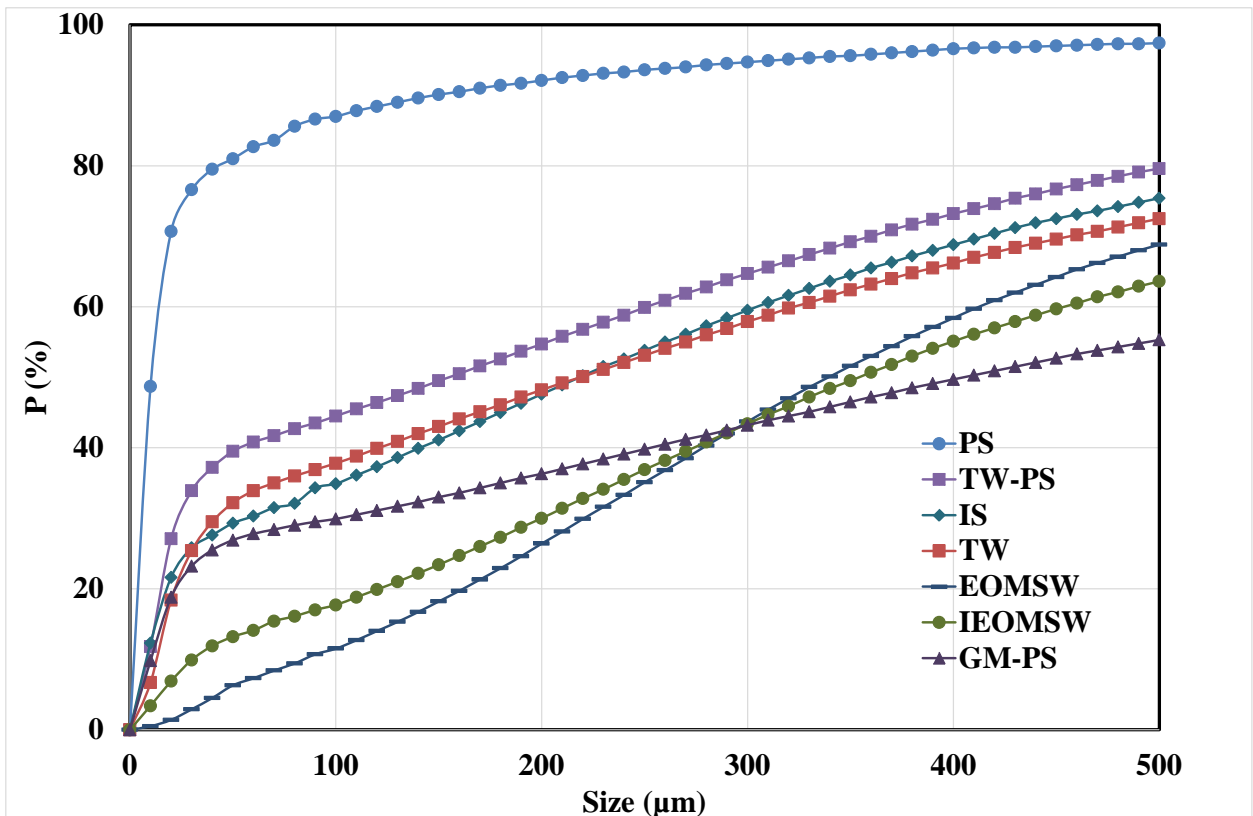


Figure 5. Cumulated percentage of particle size distribution in the bottom ash

#### 4. Effect of the biomass mineral contents on the PM distribution and bottom ash composition

Previous analyses of the PM and bottom ash distribution shows a significant variability between the different pellets. Such difference may be attributed, in addition to the operating conditions, to the mineral contents pellets. Hence, the



main purpose of this section is to identify the correlation between the mineral concentrations and the characteristics of PM emission and bottom ash.

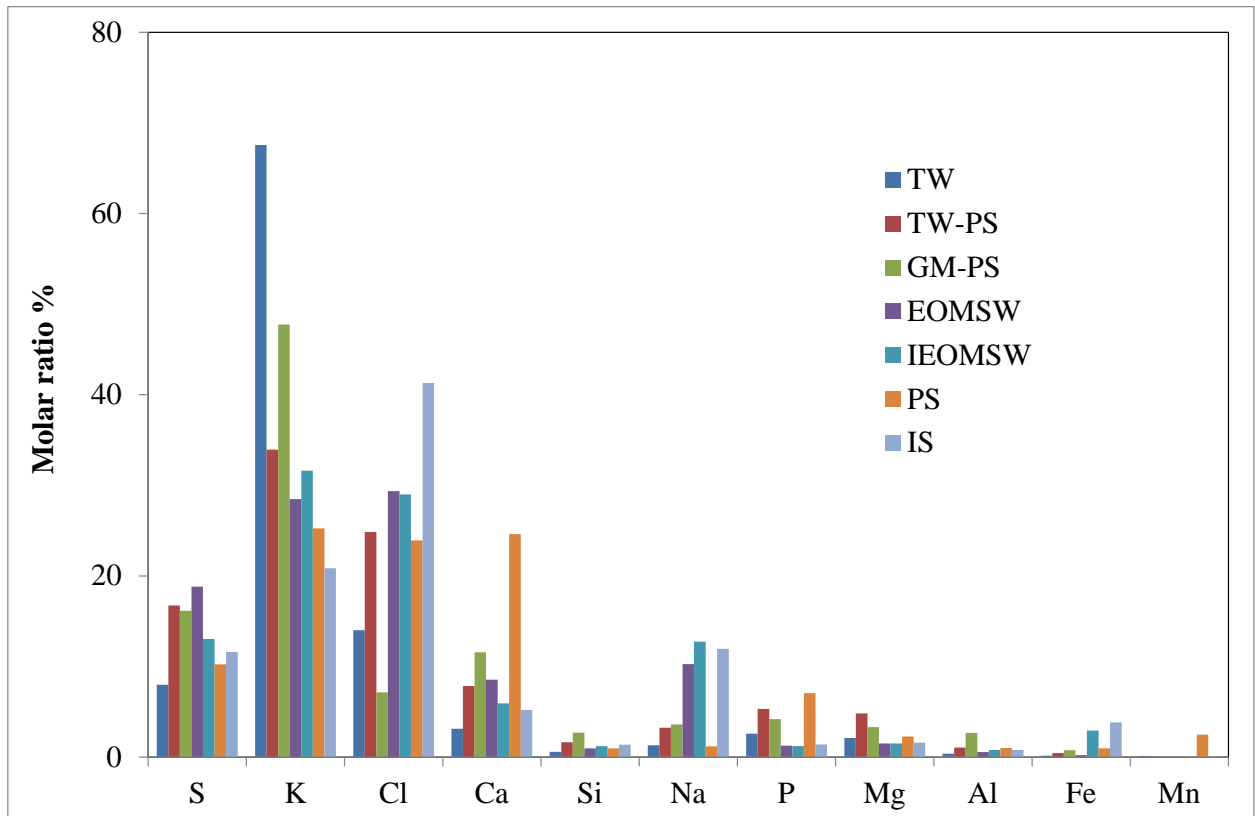


Figure 6. Molar ratio of each mineral in pellets before combustion tests

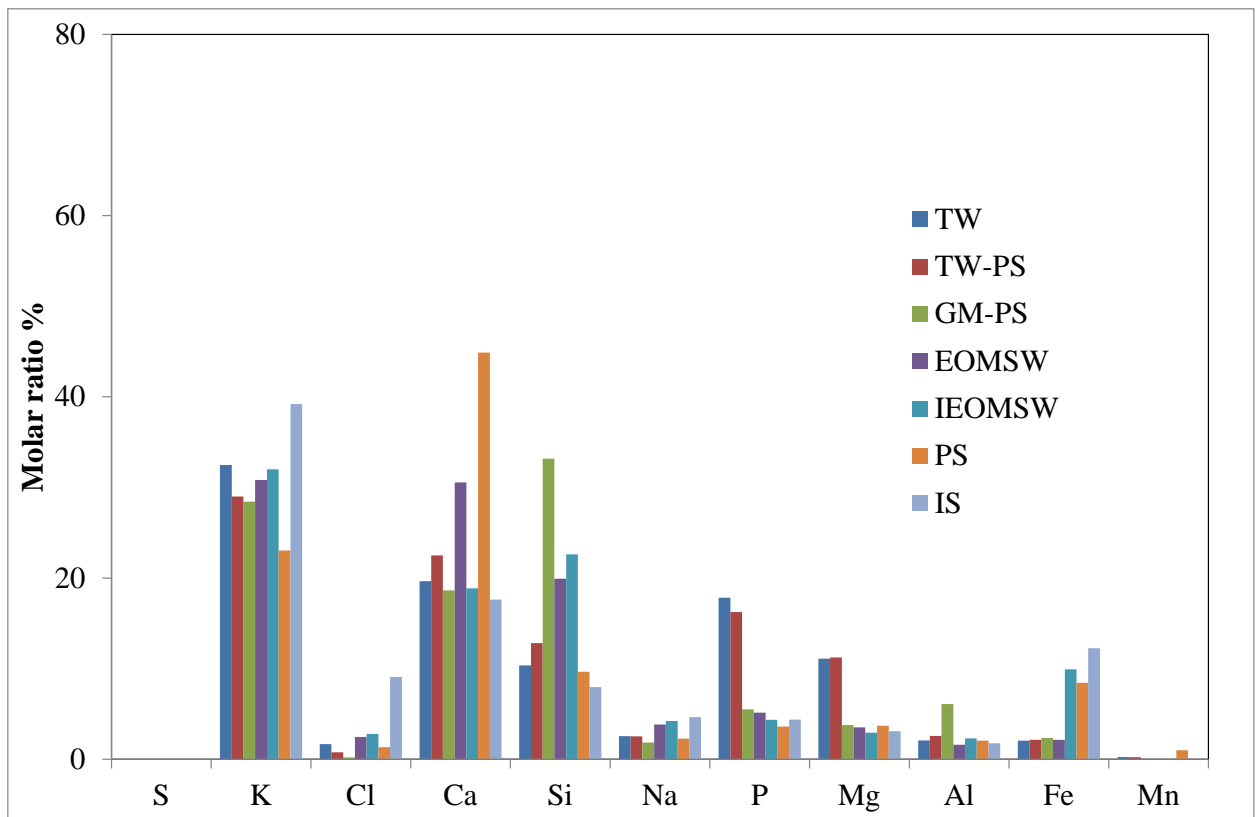


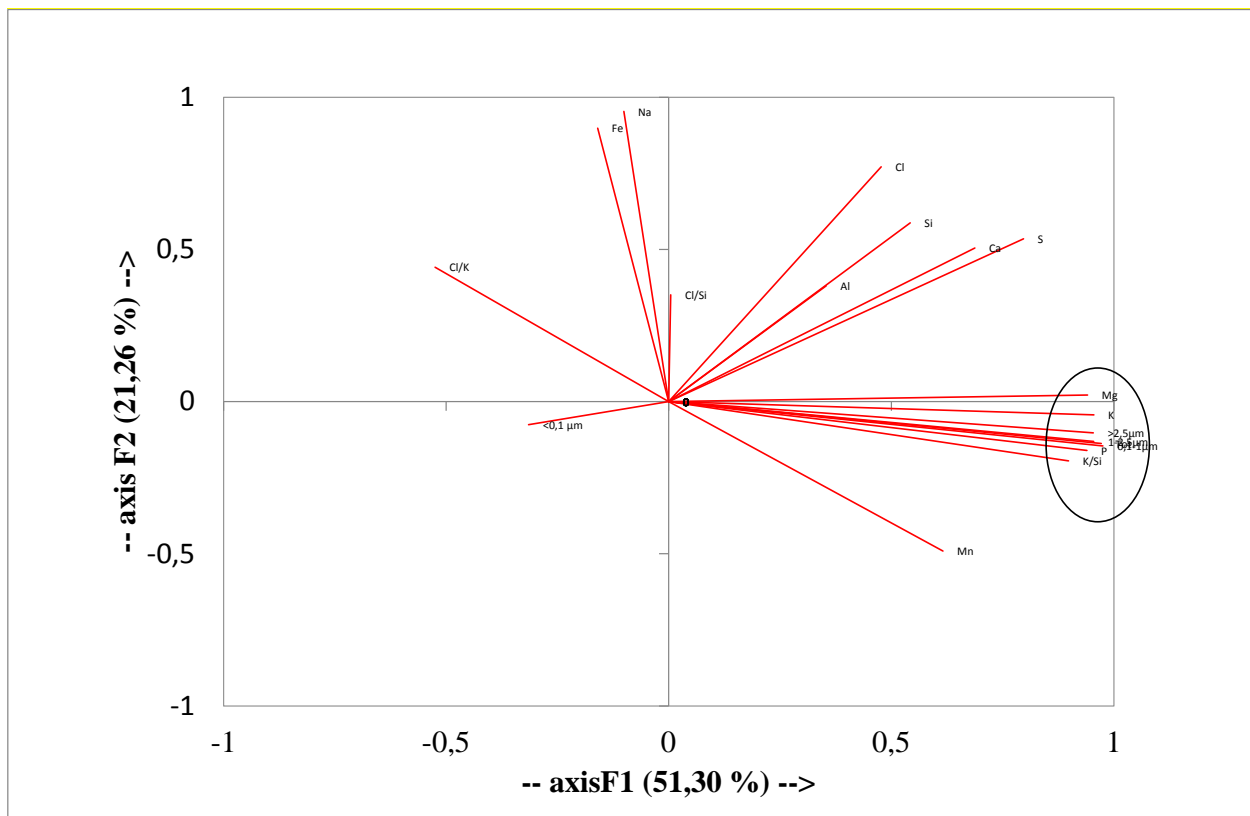
Figure 7. Molar ratio of each mineral in the bottom ash content after combustion tests

As a first approach, the molar ratio of the different minerals in the pellets and the bottom ash, before and after the combustion process are analysed in Figures 6 and 7, respectively. This dimension is more adapted to compare and also to describe the behavior of minerals in that case, because the scale of concentrations and the chemical forms of the minerals present in ash and in fuels may differ significantly. The molar ratios were normalized in both cases, to obtain a proportion of 100% for the eleven considered elements. The comparison of the ratios before and after the combustion process allows understanding the evolution of minerals during the combustion process. Among the 11 elements, the molar ratios of K, Na, Cl and S decrease in the bottom ash. It means that these elements are partially emitted in the flue gas as flying ash or gases, and this fact is noticed especially for S and Cl. At the opposite, Ca, Mg, Si, P, Al, Fe and Mn elements are concentrated in the bottom ash.

The decrease of K, Na, Cl and S is in agreement with the results found in literature on the analysis of the fly ash composition during biomass combustion. In particular, Garcia-Maraver et al have identified, in addition to unburned carbon, a significant amount of K, Cl and S during the analysis of PM chemical composition in various particle sizes during olive pellets combustion [14]. Authors have also noted the presence of Ca and P for PM10.

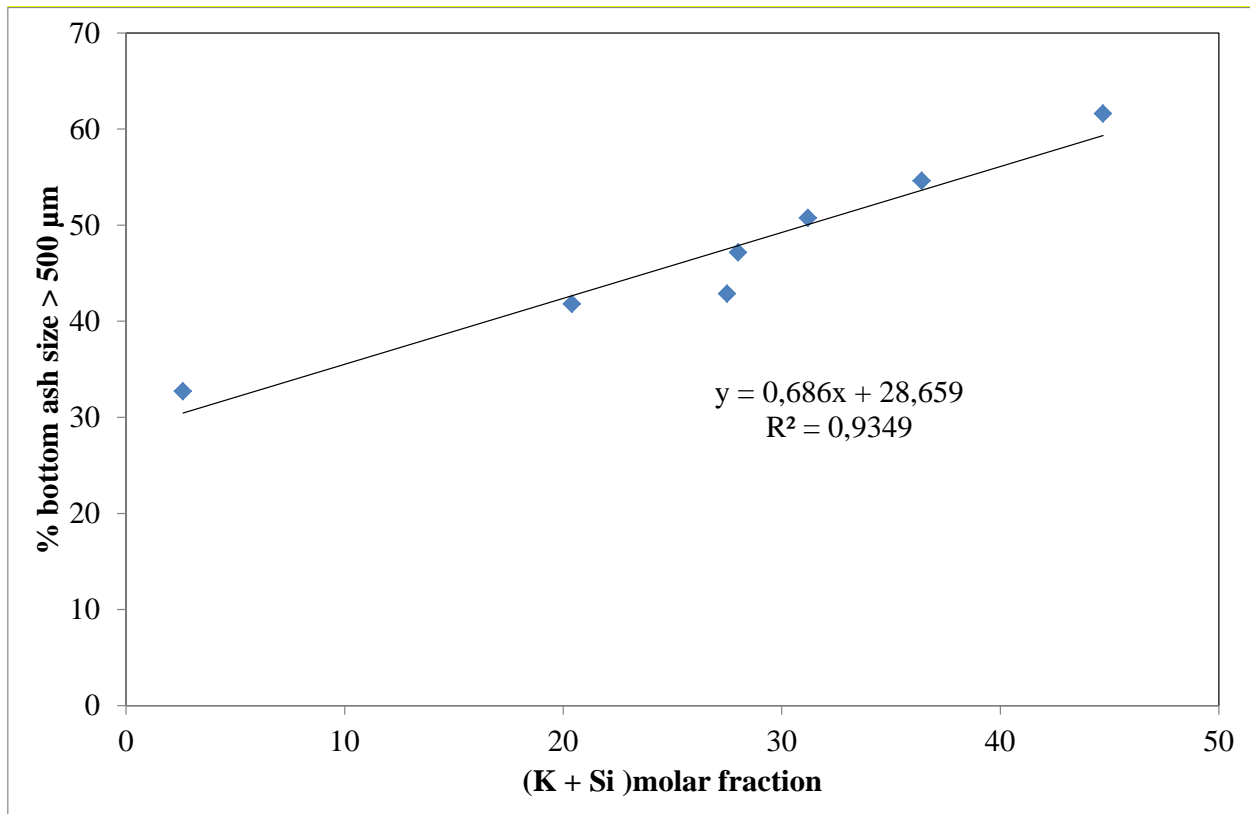
In order to identify the correlation between the mineral contents and the PM emissions, analysis (PCA) was performed. In fact, PCA techniques may be useful for the treatment of these data sets due to their complexity. The obtained calculation shows three principal components which could explain the majority of the variance (89 %) of data. Factor 1 describes 51.30%, Factor 2 describes 19.87% and Factor 3 describes 16.41 % of the total variance. The loading plot in Figure 8 indicates that a correlation may be observed between the potassium concentration (K), the K/Si ratio and total PM emissions as well as PM1, PM2.5 and PM10. A correlation was observed between P and Mg concentration and PM emissions in Figure 8. However, this correlation disappears when using Factor 3 (not shown). Such observation may indicate that this correlation is not significantly effective. Furthermore, PCA results indicate that Al, Si and Ca concentrations have no significant effect on the PM emissions. These elements are retained in the bottom ash. In addition, it is seen that PM0.1 is not significantly affected by the mineral contents. This size fraction may be composed essentially by unburned carbon. In fact, Garcia-Maraver shows that PM0.1 included 70% organic fraction. Concerning the impact of Na, although its impact on PM emissions was mentioned in literature, no strong correlation was identified in this study.

The correlation between K, K/Si and PM emissions observed in this current study is in agreement with the investigation of Ramirez-Diaz et al [20]. Authors found that the release of K during energy crops combustion was strongly influenced by the molar ratios Cl/K and K/Si in fuels. In our case, PCA technique could not identify clearly the effect of Cl/K. Such results confirmed the complexity of the mechanism of minerals release during the combustion of biomass pellets.



**Figure 8.** The loading plot from the principal components analysis of the molar mineral contents and PM emissions

The effect of minerals on the bottom ash distribution was also examined. PCA analysis (not shown) indicates a strong correlation between the (Si + K) molar fraction and bottom ash particle with diameter higher than 500µm. Hence, Figure 9 shows this correlation for the seven tested agropellets.



**Figure 9.** (K+ Si) molar fraction and percentage of large particles in bottom ash

The correlation between K, Si and large particles is in agreement with the results given by Fagerström et al during their investigation of the alkali behaviour during the combustion of wheat straw pellets [25]. Authors noted that for agriculture residues K was captured by almost fully molten ash of glassy silicates. Such results may explain the largest particles obtained in the bottom ash for GM-PS pellets.

## Conclusion

Seven agropellets with high mineral contents were combusted in a domestic boiler in order to identify their impact on PM emissions and bottom ash characteristics. During combustion tests, PM emissions were dominated by particles with sizes below 1µm. These emissions were affected the amount of K, Na and Cl and correlated by the K/Si molar ratio. In particular, the PM emissions increase significantly for higher K/Si ratio. In contrast, for lower K/Si ratio, K is retained by Si in the bottom ash.

The minerals concentrations have also a significant effect on bottom ash. In fact, the low ash content and the presence of Ca lead to a homogenous bottom ash with lower particle size. In contrast, the high ash content and the presence of K and Si lead to an agglomerated bottom ash with a significant percentage of large particles.

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