Trace elements in Turkish biomass fuels: Ashes of wheat straw, olive bagasse and hazelnut shell

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ABSTRACT

Ash contents of wheat straw, olive bagasse and hazelnut shells were 7.9%, 3.9%, 1.2%, respectively, which seemed to be within the average values of ash of biomass. The microstructure of ashes included smooth, polygonal, granular and molten drop structures. A large percentage of particles present in ashes are commonly ~1–20 μm in size. SEM/EDS analyses performed on the major ash forming elements in different ashes indicated that Si, Ca, K and Mg and P were generally the most abundant species. Trace element levels in ash samples of various biomass types such as hazelnut shell, wheat straw, olive bagasse were analysed using ICP spectroscopy. The elements determined were some of those considered being of great environmental concern such as, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb. In all of the ashes studied Fe had the highest concentration among other trace elements, Mn was the second element that exhibited higher concentrations. The order of concentration of elements in the ashes from the highest to the lowest values was as follows: Fe > Mn > Zn > Cu > Ni > Cr > Pb > Co.

1. Introduction

Compared to other renewable energy sources, the thermal use of biomass or bio-waste fuels, corresponds to an economically and technically feasible alternative to contribute to the reduction of the global CO_2 emissions, a main goal of the Kyoto protocol. Therefore, the target of the European Union defined in the White Paper is to increase the percentage of biomass on the primary energy consumption from 3.1% in 1995 up to 8.5% in 2010 [1]. The solution of these technical problems is necessary for a technically and economically feasible and environmentally advantageous co-utilization of fossil and renewable fuels and will promote a wide-spread utilization of existing biomass resources.

The inherent inorganic material, exists as part of the organic structure of the fuel, and is most commonly associated with the oxygen, sulphur and nitrogen-containing functional groups [2]. The extraneous inorganic material, could be added to the biomass fuel during harvesting, handling and processing of the fuel [3]. Biomass fuels are commonly contaminated with soil and other materials, which have become mixed with the fuel during collection, handling and storage.

During combustion of the biomass fuels, some of inorganic content is volatilized, calcined, oxidized and sulphated. Consequently, the contents of elements and compounds change according to the dry ashing temperature. At incineration temperatures above 600 °C, the liberation of CO_2 will take place at the same time as the liberation of other volatile inorganic compounds such as sodium and potassium compounds. The use of biomass fuels for power production leads to atmospheric emissions and produces solid wastes that concentrate metals and other elements from the original feedstock.

However, little information exists on trace metal mobility and concentrations in the combustion by-products from biomass fueled power plants. Such information is essential to the utilization of ash waste products as well as to environmental monitoring and protection. The need for this information is expected to grow. If biomass fuel utilization increases as forecasted, the total volume of by-products and waste will also drastically increase, resulting in even stronger pressures on the power industry to discover alternative uses and/or secure storage facilities for the by-products of biomass combustion. Additionally, the adoption of advanced conversion technologies for biomass under different reaction conditions other than used in direct combustion systems requires previous knowledge of the content of trace elements in biomass as well as information of their fate during conversion. Trace elements, especially heavy metals, are considered to be one of the main sources of pollution in the environment since they have a considerable consequence on ecological quality. Heavy metals in the environment may also have harmful effects on animal and human health [4,5].

Trace elements have received increasing attention in recent years, because of the rising scientific and public consciousness of environmental issues, and because of the development of the analytical techniques to measure their concentrations accurately. Determination of trace metals in ashes generally include some type

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of mineral acid extraction (wet oxidation) followed by atomic absorption (AAS) or inductively coupled plasma (ICP) spectroscopical analyses. Wet oxidation is normally carried out by digestion of the sample in a mixture of strong acids such as sulphuric, hydrochloric, hydrofluoric, nitric and perchloric acids. The use of microwave ovens, with both open and closed pressurized systems, shorten the total time of analyses as well as the risk of sample contamination [6–8]. Closed digestion systems are used for total determination of volatile elements to prevent losses of more volatile metals (e.g. As, Se, Hg, Cr), whereas open systems allow analysis of high amount of samples and helps the acid evaporation to dryness.

In this paper, we report the analysis of trace elements in ashes produced from some biofuels obtained from various areas of Turkey such as hazelnut shell, wheat straw and olive bagasse in oxidizing atmospheres and using a microwave-assisted total digestion with various types of acid mixtures. The elements ana-

lysed were some of those considered being of great environmental concern such as, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb.

2. Materials and methods

2.1. Biomass fuels and chemicals

In the present report, hazelnut shell, wheat straw and olive bagasse taken from various areas of Turkey were used, Table 1. Hazelnut shells were the residues of hazelnut crushing plants. Olive bagasse was the residue of olive oil production process. Wheat straw consisted of stems and leaves of the wheat plant.

De-ionized water was used throughout the work. Hydrochloric acid (37%), nitric acid (65%) and hydrogen peroxide (30%) were spectroscopic grades (Merck, Darmstadt, Germany).

2.2. Ashing of biomass materials

The optimal temperature and the best process for dry ashing of lignocellulosic biomass are currently matters of debate and investigation. Generally, the lignocellulosic biomass dry ashing is carried out in the laboratory at temperatures of up to 600 °C, as is shown in the norm for determining the ash content in wood [9], where 580–600 °C is the temperature range selected. For many biomass materials, however, a significant portion of the inorganic material is volatile at the conventional ashing temperatures for coal, and an ashing temperature of 550 °C has been adopted as standard for ash content determination, to avoid underestimation of the ash content of the fuel, due to loss of the volatile inorganic

Table 1
Proximate analysis of the materials used.

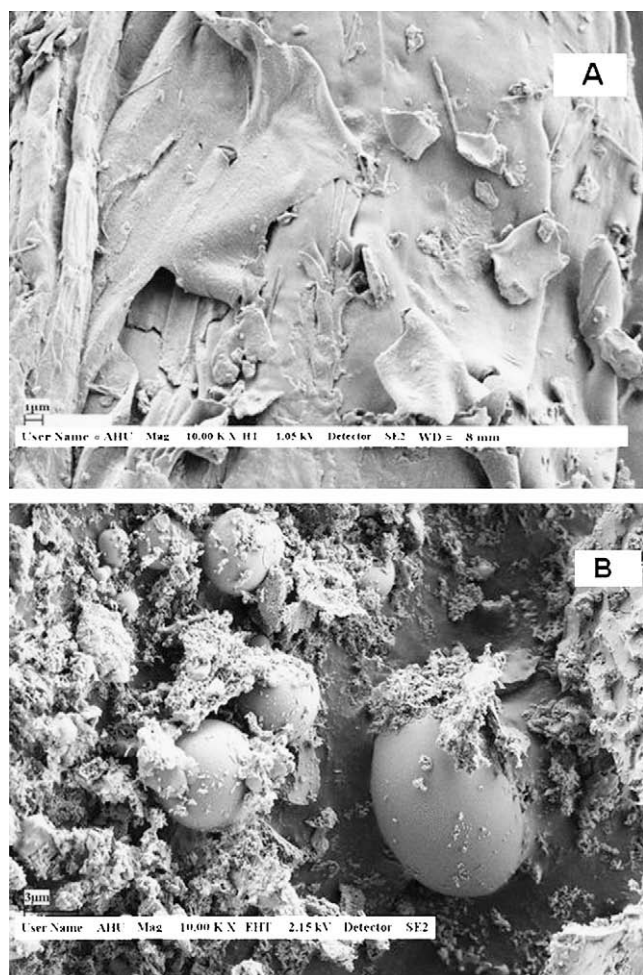| Material	Volatile matter[a], %	Fixed carbon[a], %	Ash[a], %	Moisture[b], %
Wheat straw	83.7	8.4	7.9	7.1
Hazelnut shells	86.2	12.6	1.2	7.8
Olive bagasse	86.8	9.3	3.9	7.5

[a] Dry basis.
[b] As received.

Fig. 1. Scanning electron micrographs of (A) wheat straw and (B) wheat straw ashes.
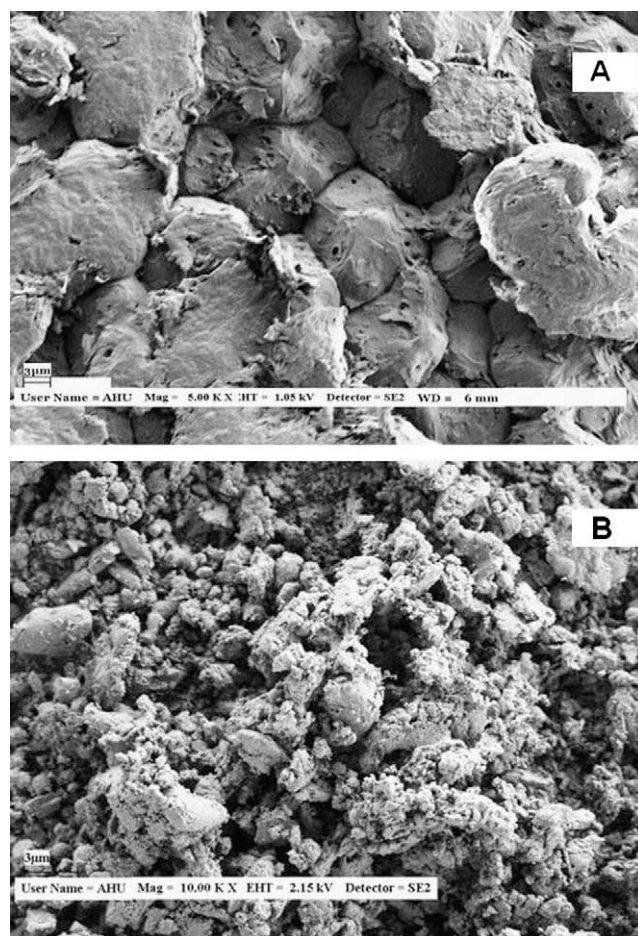

Fig. 2. Scanning electron micrographs of (A) hazelnut shells and (B) hazelnut ashes.
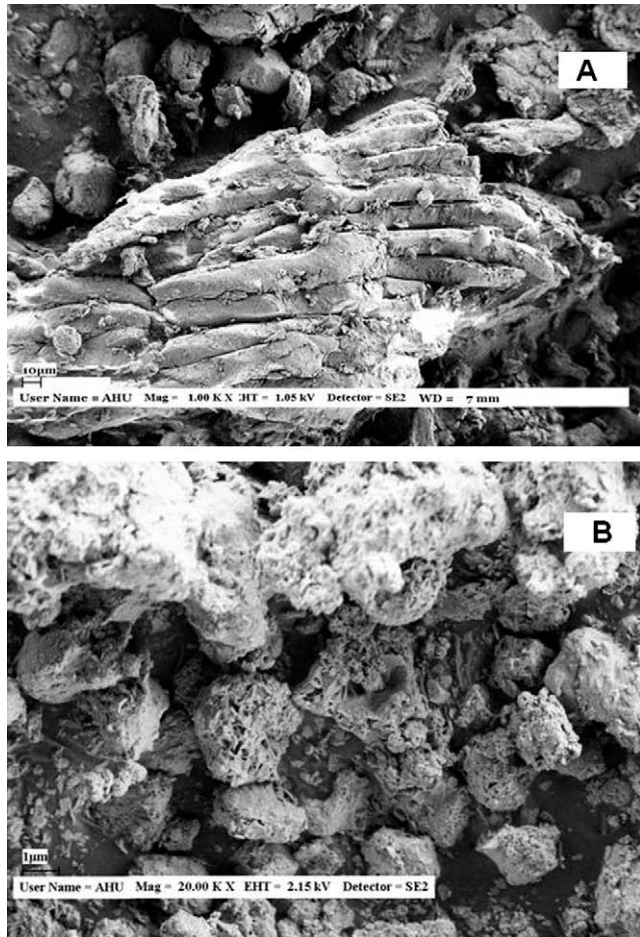
Fig. 3. Scanning electron micrographs of (A) olive bagasse and (B) olive bagasse ashes.

The proximate analyses of the biomass were carried out in the laboratory according to the standard procedure. The biomass samples were burned to determine their ash content using the standard test method for ash in biomass [11]. This test method was utilized to the determine the amount of ash, expressed as the mass percent of residue remaining after dry oxidation (oxidation at $575 \pm 25\,°C$), of biomass. Ashes obtained after constant weight were analysed for their trace element contents.

2.3. Digestion of the samples

For elemental analysis of biomass materials, wet chemical digestion of the raw biomass rather than of the laboratory-prepared ash is preferred, prior to elemental analysis using inductively coupled plasma techniques, again principally because of concerns about the potential for the loss of volatile inorganic components during the ashing process. Biomass samples were digested in a Mars Express, CEM Corp., Matthews, NC, USA microwave digestion system. 0.2 g of samples and 8 mL of four different acid mixtures were added to the tubes of the oven. The tubes were sealed and heated at three different temperatures of 105, 150 and 200 °C for 30 min. Leaching mixtures prepared with concentrated acids and hydrogen peroxide were as follow:

A: 3:1 by wt of HCl: HNO_3.
B: 1:3 by wt of HCl: HNO_3.
C: 1:1 by wt of HCl: HNO_3.
D: 2:1 by wt of HNO_3: H_2O_2.

After the reaction the tubes were allowed to cool to room temperature and they were centrifuged to obtain clear extraction solutions. The solutions obtained were separated by decantation and were analysed by inductively coupled plasma technique.
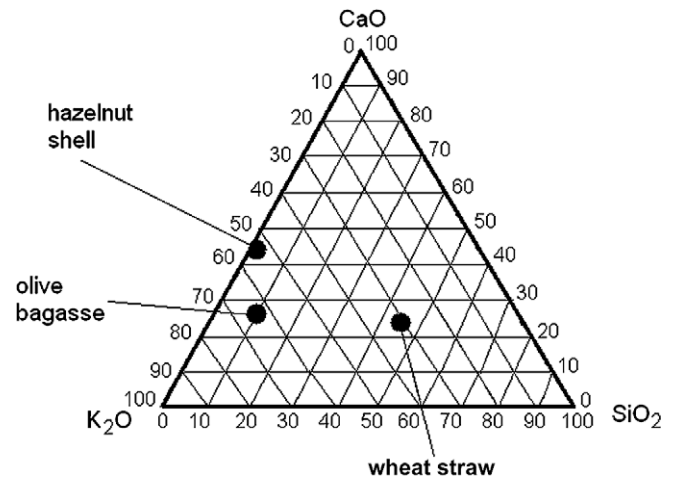
Table 2
EDS elemental analysis of the ashes (carbon and oxygen free basis).

Element	%, By weight		
	Wheat straw	Hazelnut shells	Olive bagasse
K	33.7	48.8	60.2
Ca	22.6	30.0	23.4
Si	27.0	0.9	4.6
Mg	4.2	6.8	1.9
Al	–	0.5	1.4
P	4.5	3.2	4.6
S	4.5	9.8	2.5
Cl	3.5	–	1.4

components. The International Energy Agency (IEA) has recommended an incineration temperature of 550 °C for straw [10].

Fig. 4. Ternary diagram of the K_2O–CaO–SiO_2 system showing the measured composition of different biomass samples, obtained by SEM/EDS analyses.

Table 3
Composition of ash forming oxides.

Oxide	%, By weight			K_2O–CaO–SiO_2 system %, by weight		
	Wheat straw	Hazelnut shells	Olive bagasse	Wheat straw	Hazelnut shells	Olive bagasse
K_2O	24.6	38.7	51.6	47.6	72.9	77.3
CaO	19.1	27.6	23.3	18.5	26.0	17.6
SiO_2	35.6	1.3	7.1	33.9	1.1	5.1
MgO	5.2	7.4	2.3			
Al_2O_3	–	0.7	1.9			
P_2O_5	6.4	4.8	7.5			
Others	9.1	19.5	6.3			

2.4. Analytical technique

Concentrations of the following trace elements of Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb in the ashes as a function of different leaching solutions and leaching temperatures were determined with a Vista-Pro Axial; Varian Pty Ltd., Mulgrave, Australia, inductively coupled plasma optical emission spectrometer (ICP-OES).

2.5. Scanning electron microscopy (SEM)

The morphology of various kinds of biomass used and their ashes was examined by scanning electron microscopy. Leo Supra 35VP Field emission scanning electron microscope (SEM), Leo 32 and energy dispersive X-ray spectrometer (EDS) were used for images and analyses of the major ash forming elements in different ashes. Ash samples were mounted on stubs and gold-coated prior

to analysis, to make them electrically conductive. Imaging was generally done at 2–5 keV accelerating voltage, using the secondary electron imaging technique.

3. Results and discussion

3.1. Proximate analysis

Proximate analyses of the biomass used in the present report are given in Table 1. All the biomass contained different percentages of volatile matter, fixed carbon and ash. This is because of the variety of relationships between soil, climate and genetics, so that samples taken of the same kind of biomass may have appreciably different chemical analysis, heat content and ash content from one of a different species grown a some distance away. Volatile matter refers to the part of the biomass that is released when
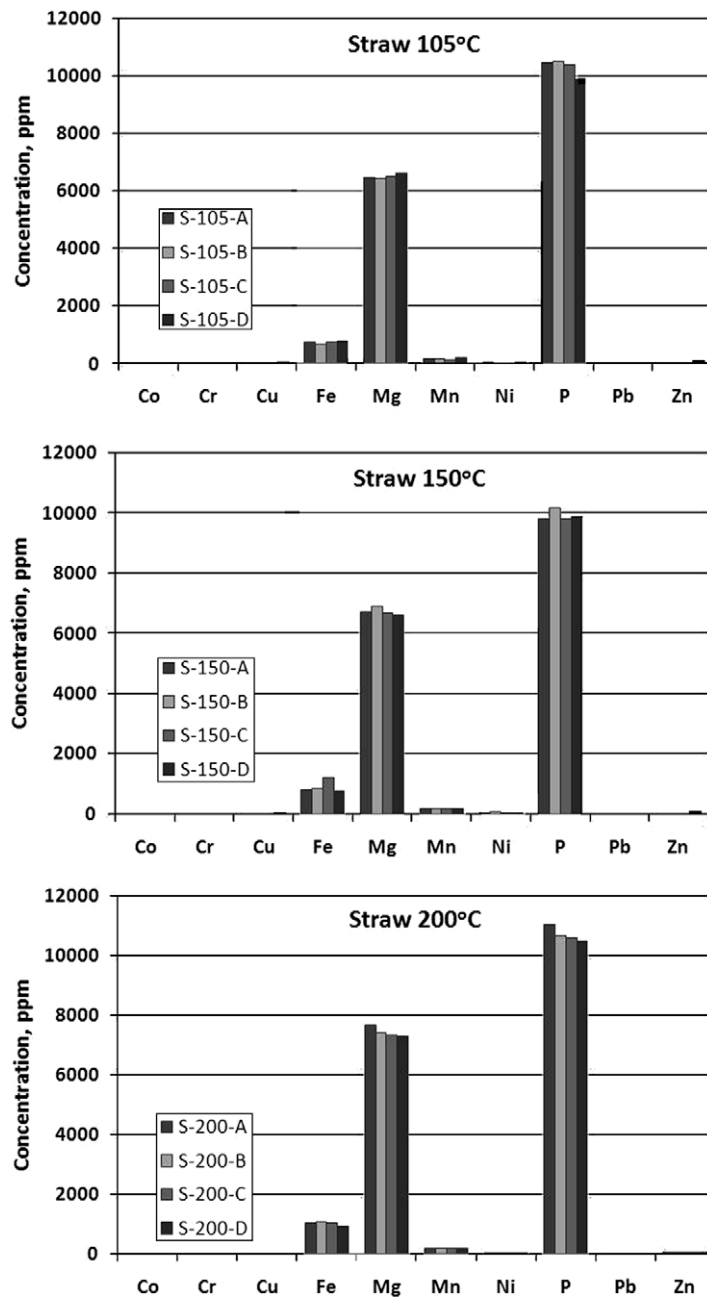

Fig. 5. Some ash forming elements and trace elements determined in wheat straw ash using different experimental conditions.

the biomass is heated up to 400–500 °C [12]. During this heating process the biomass decomposes into volatile gases and solid char. Biomass typically has a high volatile matter content up to 80–90% [13]. Wheat straw, hazelnut shells and olive bagasse contained volatile matter within the range specific for biomass. Higher volatile matter content of the biomass causes an improved combustion, resulting in a better burn out and lower unburned carbon in the ash.

Ash content in diverse agricultural crop materials typically changes between 0.5% and 10% but in rice husks and milfoil the ash content is extraordinarily high up to 30–40% [12]. Ash contents of hazelnut shells, olive bagasse and wheat straw were 1.2%, 3.9%, 7.9%, respectively, which seemed to be within the average values of ash for biomass [13].

3.2. SEM/EDS analysis

Morphology of the biomasses and their ashes was investigated by SEM, Figs. 1–3. Physical appearances of all the biomass used and their ashes were quite different. The SEM photographs indicated that these contained material with diverse morphology. While micro structure of the wheat straw contained amorphous flakes, hazelnut shells had lumpy granular structures and olive bagasse consisted of polygonal lamellar porous structure. Ashes of the biomass were also entirely unlike; wheat straw produced ashes containing powders and micron-scale microspheres of 10–20 μm size, hazelnut converted into ashes containing very tiny lumps of 1–10 μm size and olive bagasse formed ash particles that looked like 2–3 μm small sponges. The microstructure of ashes included
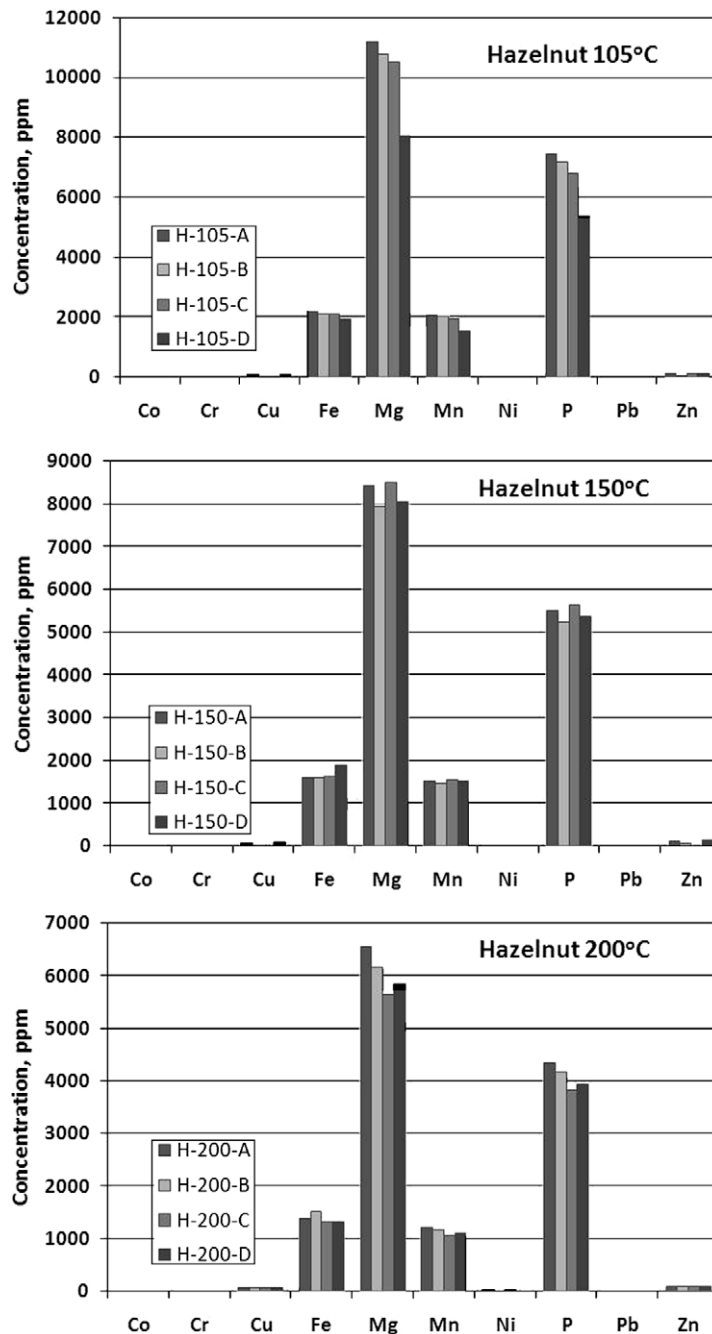

Fig. 6. Some ash forming elements and trace elements determined in hazelnut shells ash using different experimental conditions.

smooth, polygonal, granular and molten drop characteristics. A large percentage of structures present in ashes are commonly ~1–20 μm in size.

The EDS analyses carried out on the samples have been organized and compared with each other, on the basis of the appearance of the spot in the SEM micrograph where the analysis was performed. Table 2 presents the results of the EDS analyses performed on the major ash forming elements in different ashes. It must be recalled here that EDS is a semi-quantitative analysis, so that comparison with ash compositions should be carried out with care. Differences among samples from the three types of biomass mostly reflect the differences in the composition of the ashes.

Straws of cereals have relatively high potassium and chlorine contents [14]. The wheat straw used in the present study also con-

tained high potassium and chlorine contents, 33.7% and 3.5%, respectively. Straws of cereals have about 5–10% ash [14], the ash content of the wheat straw in the present work was found to be 7.9%, Table 1. The biomass ashes tend to be rich in a fairly similar suite of inorganic species, i.e. the compounds of calcium, potassium, silicon, phosphorus and magnesium. Although variations are large, SiO_2 is the main ash component [11], as was the case for the wheat straw, 35.6%, Table 3. The other main ash components are K_2O: 5–30%, CaO: 4–14% [14]. K_2O and CaO percentages of the wheat straw were observed to be 24.6% and 19.1%, respectively. The effect of large amounts of alkalines of biomass on combustion is positive because they accelerate fouling and slagging formation. In addition, oxidation potentials of alkali metals are considerable lower than those of heavy metals.
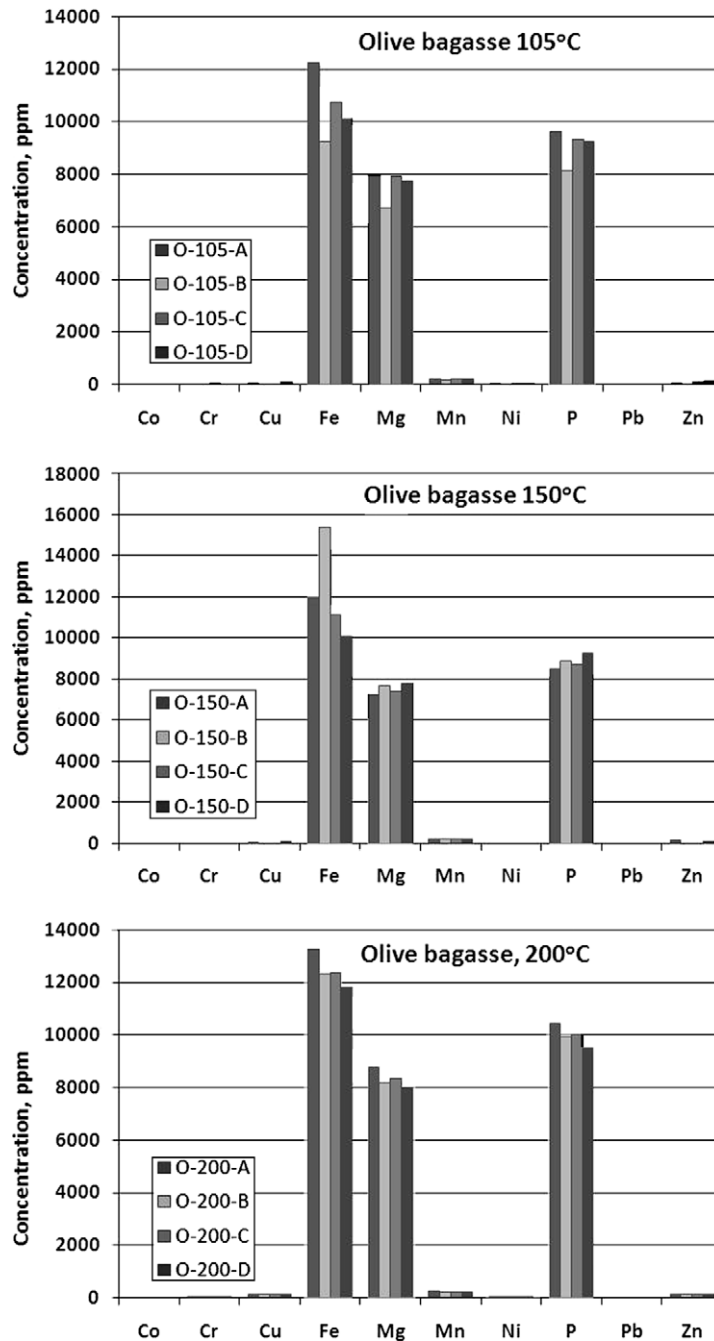

Fig. 7. Some ash forming elements and trace elements determined in olive bagasse ash using different experimental conditions.

Occasionally, also P_2O_5 content is quite high, up to 8%; P_2O_5 content of the wheat straw used was 6.4%. Percentages obtained for characteristic elements and oxides for the ash of wheat straw seemed to be within the average ranges. Phosphorus is one of the most important indices for evaluating the agricultural value of ashes; phosphorous content of all of the ashes used in the present study was in the range of 3.2–4.6%, which could classify these biomass ashes as useful plant nutrients [15].

In analyzing the composition of the different samples it appears that Si, Ca and K were generally the three most abundant species therefore the three ashes were examined in the light of the ternary system K_2O–CaO–SiO_2 [16], Fig. 4. Wheat straw seemed to contain the highest SiO_2 percentage of 44.9, while hazelnut shells and olive bagasse contained very low amounts of SiO_2, 1.9% and 8.7%, respectively. On the other hand, while hazelnut shells and olive bagasse contained high amounts of K_2O, 57.2% and 62.9%, respectively,

wheat straw contained relatively much less amount of K_2O, 31.0%. CaO content of wheat straw and olive bagasse were found to be comparable, 24.1% and 28.4%, respectively, but the hazelnut shells contained relatively higher amounts of CaO, 40.8%. These results placed the three biomasses on different spots in the ternary diagram of K_2O–CaO–SiO_2 system; it seemed that hazelnut shell and olive bagasse showed similar properties; high K_2O contents of these probably give these materials low melting properties [16]. The wheat straw due to its high SiO_2 content could be considered suitable for ceramic products [17].

Chlorine contents of the wheat straw and olive bagasse were determined as, 3.5% and 1.4%, respectively. Presence of chlorine may increase corrosion risk due to increased HCl formation during combustion which is the case in co-combustion of biomass fuels especially of cereal types. Hazelnut shell did not contain any amounts of Cl. Straw with a high content of chlorine and potassium
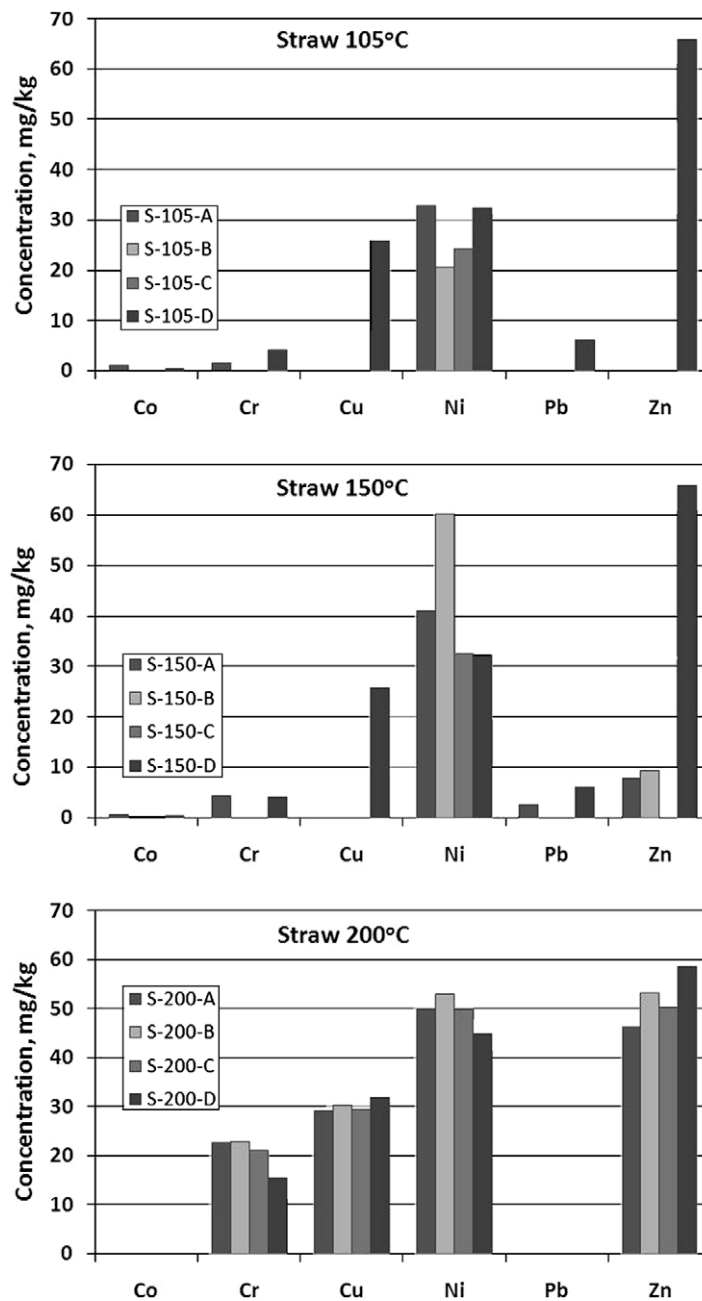

Fig. 8. Low concentration trace elements determined in wheat straw ash using different experimental conditions.

are very undesirable in power plant fuels. Levels of K_2O and Cl are found as 20.0% and 3.6%, respectively, in wheat straw in a previous published work [13].

High contents of sulphur in the biomasses of the present work, (wheat straw: 4.5%, hazelnut shell: 9.8% and olive bagasse: 2.5%) may also be considered as an increased risk of corrosion also.

3.3. ICP spectroscopy

Concentrations of ash forming elements Mg and P and trace elements such as Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb in the ashes of wheat straw, hazelnut shell and olive bagasse as a function of different leaching solutions and leaching temperatures of 105, 150 and 200 °C, as determined by ICP spectroscopy are presented in Figs. 5–7, respectively. The effect of leaching temperatures on the

extraction of inorganic elements was different in all the biomass. It seemed that while leaching experiments done at 200 °C for straw (Fig. 5) and olive bagasse (Fig. 7) produced higher concentrations of inorganic elements the optimum temperature for hazelnut (Fig. 6) was 105 °C. The reason for this phenomenon might be the different morphology and structure of the biomass which permitted leaching of the inorganics into acidic media at different temperatures.

Analyses of ashes of wheat straw revealed these contained mainly P (10,000–11,000 mg/kg) and Mg (6500–7500 mg/kg) of the ash forming elements and Fe and Mn of the trace elements. All of the other trace metals were in minority relative to Fe and Mn. Fe and Mn concentrations in the ashes changed in the ranges of 700–1100 mg/kg and 150–200 mg/kg, respectively, depending on the temperature of digestion and type of digestion acid mixture. The highest amounts of metals were leached at 200 °C and all of
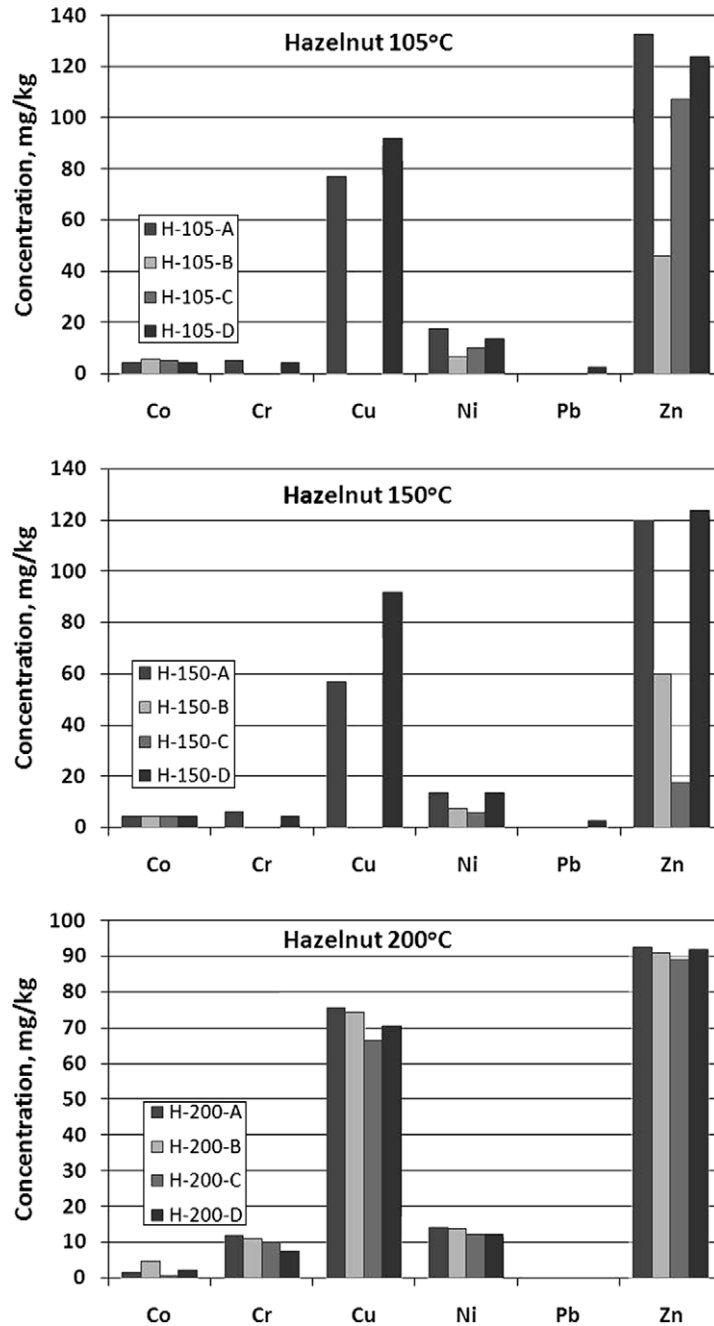

Fig. 9. Low concentration trace elements determined in hazelnut shell ash using different experimental conditions.

the types of acid mixtures were equally effective in leaching in the case of wheat straw ashes, Fig. 5.

Ashes of hazelnut shells contained more Mg (6000–11,000 mg/kg) than P (4000–7000 mg/kg) and also contained Fe and Mn as the highest concentration trace metals. The concentrations of these metals in the ashes of hazelnut shells were found to be comparable. The concentrations of Fe and Mn changed in the range of 1400–2200 mg/kg and 1200–2000 mg/kg, respectively, depending on the temperature of digestion and type of digestion acid mixture. The temperature of highest concentrations of leaching was found to be 105 °C and while the acid mixtures A, B and C were all equally efficient, the acid mixture D was found to be the least effective in the case of ashes of hazelnut shells, Fig. 6.

Analyses of ashes of olive bagasse indicated that only Fe was the most concentrated metal. Concentration of iron in olive bagasse

ashes was very high; it changed between 10,000 and 15,000 mg/kg, depending on the method of leaching and temperature of digestion. The highest concentrations of Fe were determined with acid mixture B at 150 °C, Fig. 7. Olive bagasse ashes contained P (8000–10,000 mg/kg) and Mg (7500–8000 mg/kg) as ash forming elements and minor quantities of the other trace elements.

In order to present the low concentrations trace elements, the results of analyses were again plotted in the absence of metals of high concentration (generally Fe and Mn) in Figs. 8–10. In the ashes of wheat straw the observed elements and their concentrations using different leaching acid mixtures and leaching temperatures were as follow: Co (0.5–1 mg/kg), Cr (1–23 mg/kg), Cu (26–32 mg/kg), Ni (20–55 mg/kg), Pb (4–8 mg/kg) and Zn (8–65 mg/kg), Fig. 8. Ashes of hazelnut shells contained Co (1–6 mg/kg), Cr (5–12 mg/kg), Cu (57–92 mg/kg), Ni (6–18 mg/kg),
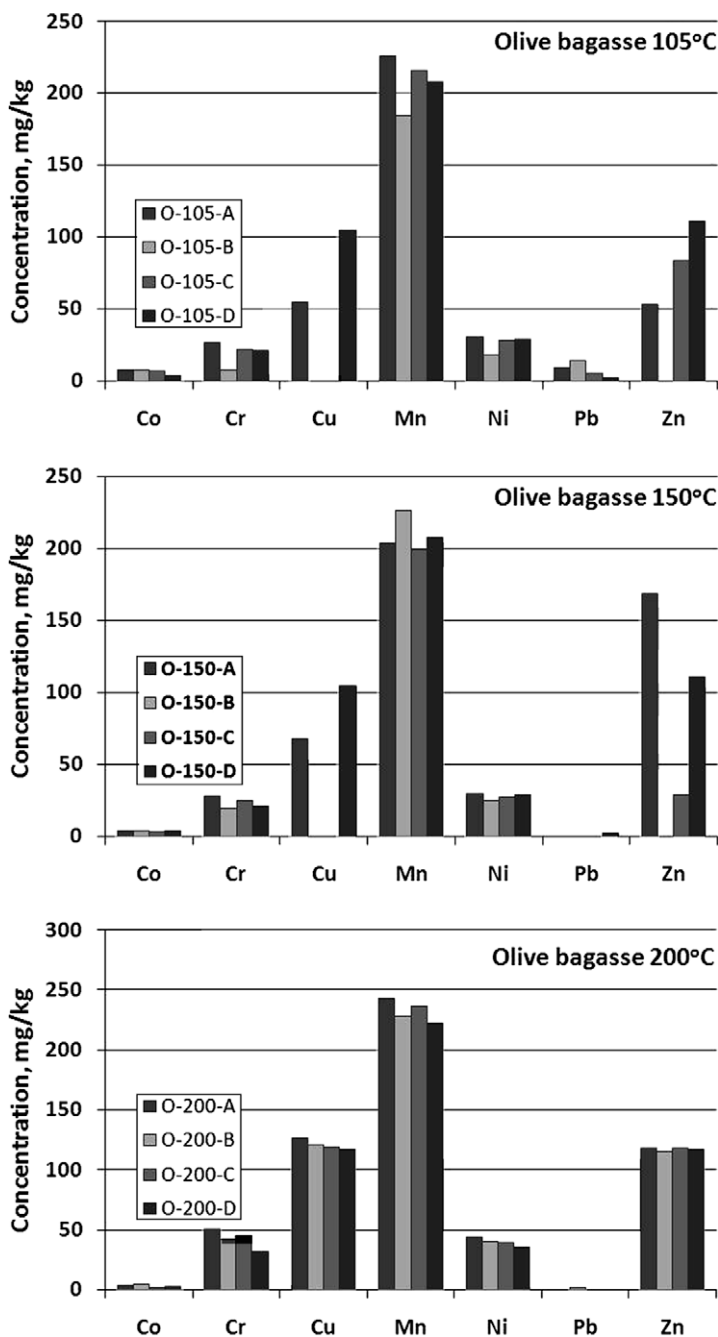

Fig. 10. Low concentration trace elements determined in olive bagasse ash using different experimental conditions.

Pb (0–3 mg/kg) and Zn (18–133 mg/kg), Fig. 9. Low concentration elements determined in ashes of olive bagasse were Co (2–8 mg/kg), Cr (8–50 mg/kg), Cu (55–127 mg/kg), Mn (184–243 mg/kg), Ni (18–44 mg/kg), Pb (2–9 mg/kg) and Zn (53–168 mg/kg), Fig. 10. In a recent study on olive kernel ash [18], trace element concentrations were found as follow: Co (20–65 mg/kg), Cr (83–2000 mg/kg), Cu (35–664 mg/kg), Mn (50–1800 mg/kg), Ni (30–1084 mg/kg), Pb (0.05–9 mg/kg) and Zn (22–127 mg/kg). Reason for the appreciable differences between our results and findings of Vamvuka [18] in chemical analyses for the same kind of biomass is probably due to varieties of soil, climate and genetics that changed the characteristics of the samples.

In all of the ashes among the low concentration trace elements only zinc seemed to be of relatively higher concentration when compared to the other low concentration elements. Cobalt and lead contents of the ashes were very low; less than 10 mg/kg. In all of the ashes studied Fe had the highest concentration among the other trace elements, Mn was the second element that exhibited higher concentrations. The order of concentration of trace elements in the ashes from the highest to the lowest values was as follows: Fe > Mn > Zn > Cu > Ni > Cr > Pb > Co. Miller et al. [19] found that the levels of arsenic, cadmium and copper in the straw and wood-bark samples were too low to allow clear cut comparisons and wood-bark sinter ash was enriched in Cu, Zn and Mn. The concentration of beryllium, lead, molybdenum, vanadium and zinc varied, depending on the biomass. Information on trace metal mobility and concentrations in the combustion of biomass is essential for the utilization of biomass as well as to environmental monitoring and protection.

4. Conclusions

Ash contents of hazelnut shells, olive bagasse and wheat straw were 1.2%, 3.9%, 7.9%, respectively, which seemed to be within the average values of ash for biomass. The microstructure of ashes included smooth, polygonal, granular and molten drop characteristics. A large percentage of structures present in ashes are commonly $\sim$1–20 μm in size.

SEM/EDS analyses indicated that while wheat straw seemed to be of high SiO_2 content 44.9%, hazelnut shells and olive bagasse contained very low amounts of SiO_2, 1.9% and 8.7%, respectively. On the other hand, while hazelnut shells and olive bagasse contained high amounts of K_2O, 57.2% and 62.9%, respectively, wheat straw contained relatively much less amount of K_2O, 31.0%. CaO content of wheat straw and olive bagasse were found to be comparable, 24.1% and 28.4%, respectively, but hazelnut shells contained relatively higher amounts of CaO, 40.8%.

Analyses performed with ICP revealed that ashes of wheat straw contained mainly Fe and Mn. All of the other metals were in minority relative to Fe and Mn. In all of the ashes studied Fe had the highest concentration among the other trace elements, Mn was the second element that exhibited higher concentrations. The order of concentration of elements in the ashes from the highest to the lowest values was as follows: Fe > Mn > Zn > Cu > Ni > Cr > Pb > Co. Biomass fuels are composed of very heterogeneous constituents. Very wide ranges are found within the same biomass group and between biomass groups for elemental composition content. Comparison shows that the ranges of elemental compositions presented in this paper are consistent with other studied in most elements. The concentration of trace elements varied, depending on the biomass. For wider utilization of biomass as predicted, further work is needed to measure the concentration and distribution of trace elements in different types of biomass.

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