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

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.

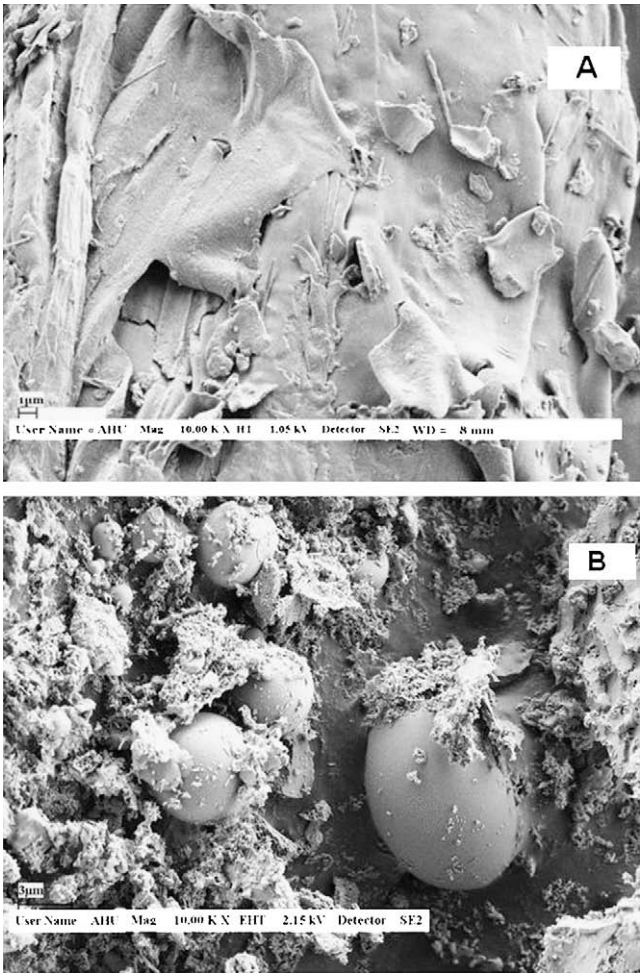

Fig. 1. Scanning electron micrographs of (A) wheat straw and (B) wheat straw ashes.

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

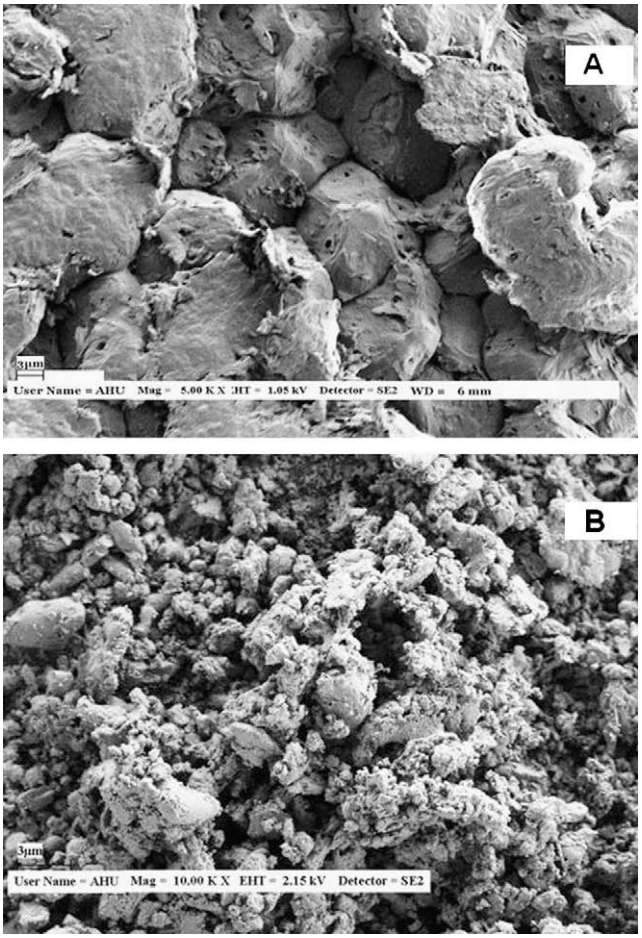

Fig. 2. Scanning electron micrographs of (A) hazelnut shells and (B) hazelnut ashes.