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Characterization and evaluation of fly and bottom ashes from combustion of residues from vineyards and processing industry

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ABSTRACT

In view of the abundance of residues from vineyards and processing industry in Mediterranean countries and their importance for local energy production, fly and bottom ashes from lab-scale fluidized bed experiments were evaluated as a function of operational parameters, in terms of system performance, environmental impact and potential uses. Ashes of raw fuels and their blends were characterized by physical, chemical, mineralogical and thermal analyses. Under the fluidized bed conditions of the tests, no slagging/fouling occurred and fly ashes were rich in Ca, K, P and Sr minerals. Combustion temperature and residence time governed the fate of major ash elements in the system, whereas fuel loading influenced trace element partitioning to a greater extent. Fly or bottom ashes could be used as secondary building materials, or for road construction. Grape husks fly ash could be used as a soil ameliorant. The environmental impact of these ashes upon land recycling or management strategies is expected to be low.

1. Introduction

The abundance and the important environmental attributes of biomass fuels, mainly related to the reduction of greenhouse emissions, will lead to their increasing use in the future for power production, in view of the energy crisis. The target of the EU is to increase the percentage share of biomass fuels in the primary energy consumption [1]. By 2050 up to 33–50% of the world's current consumption could be met by biomass [2].

Agricultural and agro-industrial wastes are readily available in large quantities in South European countries. Their thermal treatment is becoming more attractive as a disposal option, by destroying hazardous constituents, reducing their volume, allowing for energy recovery and increasing economic returns to rural communities. EU legislation requires significant reduction in the amount of biodegradable wastes in the landfills.

However, all power generating plants produce a number of residues (bottom ash, boiler ash, fly ash, etc.) the relative amount of each one depending on the nature of the feed, the technology, the operating conditions and the emission control devices [1,3]. Approximately 480 million tons of ash from biomass combustion could be generated worldwide annually, as 95–97% of the world's bioenergy is produced by direct combustion of biomass [4,5]. The successful operation of combustion systems depends among others on the ability to control the technical and environmental problems associated with these ashes, which can reduce the efficiency and availability of the facilities, thereby increasing the power cost [6]. These problems include slagging, fouling and corrosion of surfaces, as well as pollutants and are mainly created by the presence of alkalis, silicon, chlorine and sulphur [7–10]. Also, heavy metals contained in the ashes may pose a significant risk to the ecosystem, if irrationally managed and disposed [9,11]. Therefore, the management of ashes would remain a great concern of the energy industry and demonstrates the need for their utilization in various applications [12–16].

Fluidized bed combustion technology is regarded as the most promising technology for biomass fuels, combining not only high efficiency and low emissions, but also preventing many of the ash-related problems, which might occur in other units [17,18]. There are a great number of studies in literature dealing with the characterization of fluidized bed ashes from the combustion of biomass materials. Sintering

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mechanisms have been proposed [13,19] and the factors influencing trace element partitioning have been discussed [5,20,21]. A considerable amount of research has also been carried out on the possible use of ashes for soil amelioration or in concrete manufacturing [14–16]. The majority of these studies have concentrated on woody agricultural or forestry wastes.

The heterogeneity and variable composition of biomass fuels implies a thorough knowledge of their behaviour in fluidized bed systems and an assessment of ash properties. When mixtures of fuels are used for increasing supply options, data on the final ash materials can make it possible to avoid fuel combinations with unwanted properties, or even to design an ash material for a certain application.

As a continuation of a previous work [22], this study aimed at evaluating the ashes produced from the fluidized bed combustion of residues from vineyards and wine/spirit processing industry, for which there is lack of information in literature. These residues are abundant in Mediterranean countries. In Crete, the largest Hellenic island, about 190,800 t of vine by-products remain practically unexploited annually, although their energy potential is 3.6 PJ/y. As the annual increase of the energy demand is very high (8.5%), creating big problems in the power supply, embodiment of biomass combustion technologies in the Cretan energy system will play a significant role. An economic solution could be to use these residues for fuelling small-to-medium size units within the processing factories for heat production (if combined with a distillation plant or other, or to pre-dry raw fuels) and possibly electricity production, in which case the impact of ashes is important, due to fouling of heat exchangers. More specifically, fly and bottom ashes of vine shoots, grape husks and their blends, produced under different operating conditions in a fluidized bed unit, were characterized by physical, chemical, mineralogical and thermal analyses. The influence of these ashes on system performance, their environmental impact and their potential uses were discussed.

2. Experimental section

2.1. Raw materials characterization

The raw materials used for the combustion tests of this study were residues from a vineyard in the area of Chania, in the island of Crete and from the local wine/spirit making factory. These were vine shoots collected after pruning and grape husks after extraction of juice. Following air drying, the residues were ground in a cutting mill to a particle size of −2800 + 1000 μm and pre-dried in the oven. For co-combustion tests, blends of shoots with husks were prepared with mixing ratios 10, 20, 30 and 50% of husks by weight in the mixture.

Characterization of representative samples was performed according to the European standards drawn up by the Technical Committee CEN/TC335.

Fluid bed material consisted of a Na-feldspar $NaAlSi_3O_8$ (SiO_2 = 67.7%, Al_2O_3 = 20.3%, Fe_2O_3 = 0.05%, CaO = 0.5%, MgO = 0.05%, TiO_2 = 0.05%, Na_2O = 11.2%, K_2O = 0.15%), with a narrow size range (−500 + 350 μm).

2.2. Combustion tests

Combustion of the residues was carried out in an atmospheric lab-scale bubbling fluidized bed reactor, with an inner diameter (ID) of 70 mm and a total height of ~2 m, as described in detail in a previous work [22]. The minimum fluidization velocity determined from a Δp-versus-v diagram was found to be 0.16 m/s. The experiments were performed at excess air ratios 1.3–1.5 and feed rates 0.6 kg/h and 0.72 kg/h. Depending on fuel and operating conditions, air flow rates varied between 3.5 m^3/h and 5.8 m^3/h, while bed temperatures ranged between 830 °C and 876 °C during the runs.

The results presented in the previous work included temperature profiles along the reactor height, efficiency and flue gas emissions, as a function of fuel loading, excess air and blending ratio of the two fuels. The present study aimed at evaluating fly and bed ashes produced during the combustion experiments through physical, chemical, mineralogical and thermal analyses.

Bed material and fly ash collected from the tangential flow type cyclone from each experiment were drained, weighed and analyzed for particle size distribution (PSD), surface area, unburned carbon (in order to calculate combustion losses in the bottom and fly ashes), major and trace elements, mineral phases, thermal decomposition and fusion temperatures. The results are the average of two replicates.

2.3. Ash analyses

The PSD of fly ashes was determined using a Mastersizer S laser diffractometer by Malvern Instruments. The distribution was derived from a diffraction pattern resulting from a laser irradiated suspension of ash and water.

Specific surface areas of fly ashes were determined according to the BET method from nitrogen adsorption at 77 K, using an automatic volumetric apparatus, type Nova 2200 of Quantachrome. Prior to each adsorption measurement the samples were out-gassed overnight at 110 °C, under vacuum of 10^{-6} torr.

Chemical analysis of major and trace elements in ashes was performed by an inductively coupled plasma mass spectrometer type ICP-MS 7500cx, coupled with an Autosampler Series 3000, both by Agilent Technologies (detection limits 0.4–34 ppb, depending on element). The samples were dissolved by a microwave-assisted digestion with HNO_3 acid. The microwave digestion was carried out by using Anton Paar Multiwave 3000 oven. Phosphorous measurement was conducted using a spectrophotometer type UV-VIS Hach 4000V (detection limit 200 ppm). Prior to analysis, the samples were dissolved by digestion with HCl, HF and HNO_3 acids in Teflon beakers heated in a water bath at 80 °C. For silicon measurement, the samples were digested by fusion with $Li_2B_4O_7$ at 980 °C and then analyzed in an atomic absorption spectrometer (AAS) Analyst-100 of Perkin Elmer, equipped with a graphite furnace assembly (model HGA 800) and a deuterium arc lamp background correction system.

Crystalline compounds in fly and bottom ashes were identified with an X-ray diffractometer (XRD) model D8 Advance of Bruker AXS, with application of Cu Kα radiation and nickel filter (U = 35 kV, I = 35 mA). The XRD scans were performed between 2 and 70 2θ°, with increments of 0.02°/s. A software system DIFFRAC plus Evaluation by Bruker AXS and the JCPDS database were used for data processing and identification of crystalline components.

The weight loss behaviour of the ashes up to 1000 °C was studied by a thermogravimetric analyzer TGA-6/DTG analyzer of Perkin Elmer. The heating rate was 10 °C/min and the flow rate of air 35 ml/min.

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