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Evaluation of ashes produced from fluidized bed combustion of residues from oranges' plantations and processing

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ABSTRACT

Residues from oranges' plantations and processing may play an important role as biofuels for heat and power production in Mediterranean countries. The management of ashes produced during combustion is a great issue for the energy sector. Ash quality from lab-scale fluidized bed tests of these residues was evaluated in terms of operational parameters, environmental impact and potential uses with respect to legislative restrictions. Bottom and fly ashes were characterized by mineralogical, chemical, particle size distribution and thermal analyses, at different excess air ratios, fuel feed rates and fuel mixing ratios. The results showed that fly ashes were rich in Ca, K, P and Sr minerals. Slagging/fouling potential of pruning was very low, however that of peels and leaves was significant. The effect of excess air ratio or fuel feed rate on the quality of ashes was small. In the case of blends, the composition of the ashes varied between those of the blend components. Fly ashes of orange tree residues could be utilized as soil amendment agents, secondary building materials, or for road construction. Their environmental impact upon land recycling or management strategies is expected to be very low.

1. Introduction

EU directive on renewable energy sets the target for all member states to obtain 20% of its energy needs from renewable sources by 2020 [1]. Market needs for fuel diversification, as a result of high degree of dependence from fossil fuel imports and price fluctuations, as well as for policies aiming at the reduction of greenhouse emissions and financial incentives, such as feed-in tariffs and green certificates, contribute to the increased exploitation of biomass in the heating/electricity sector.

Residues from agricultural production and processing industries are readily available in large quantities, especially in Mediterranean countries, and solid wastes are generated by every social activity, the disposal of which is no longer viable due to the high cost and the environmental regulations. Combustion of these residues either alone, or in mixtures with other fuels, can reduce the volume of wastes, allowing for energy recovery.

Among dedicated combustion technologies applied, fluidized bed has been proven as the most versatile, due to its inherent advantages of simple design and scale-up, fuel flexibility, good mixing and temperature control, high efficiency and low pollutant emissions [2–4]. During combustion, ash-forming species may either leave the process as bottom ash, or become released as fly ash and flue dust. The fate of these species is dependent on their physical characteristics, chemistry, boiler design and combustion conditions [5]. Slagging, fouling and corrosion of surfaces, mainly created by the presence of alkali metals, alkaline earth metals, silicon, chlorine and sulphur, are all problems related to these ash constituents, which can reduce the efficiency and availability of the facilities, thereby increasing the power cost [6–9]. Also, heavy metals contained in the ashes may pose a significant risk to the environment, if irrationally managed and disposed [9–11]. Therefore, the management of ashes is a great issue for the energy generation industry and alternative ways of recycling or utilization of such waste products are becoming increasingly important [4,5,12,13].

There is a lot of information in literature on the characteristics, or the slagging/fouling tendency of ashes from combustion or co-combustion of biomass fuels in fluidized beds. Raw materials used were mainly woody agricultural wastes. Silicate and calcium minerals were predominant in these ashes [13–15] and differing sintering mechanisms were found out [16,17] for the biomass fuels tested, depending on the relative proportions of problematic elements. Also, trace element partitioning in fluidized beds has been the focus of several investigations and the importance of ash matrix, particle size, bed material, combustion system and operating

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conditions has been stressed [3,18–20]. The majority of the studies have concentrated on waste biomass fuels, such as municipal solid wastes, refused derived fuels and sewage sludge.

To the authors' knowledge, fluidized bed combustion of residues from oranges' plantations and processing has not been studied before. The only information comes from a study on chemical characterization of pruning, for use in pulping processes [21]. Therefore, the evaluation of some of the major agricultural residues of Mediterranean countries, which remain unexploited for energy production, becomes an important issue. A previous work by the authors focused on the performance of these residues in fluidized bed, in terms of emissions and efficiency [2]. As a continuation, this study aimed at investigating the thermal behaviour of ashes produced during fluidized bed combustion, the effect of their composition on operational parameters, as well as their environmental impact upon disposal and potential uses with respect to legislative restrictions. Thus, bottom and fly ashes were characterized by mineralogical, chemical, particle size distribution (PSD) and thermal analyses at different operating conditions. The results should be useful for the design of larger units for heat or power production from these wastes and furthermore for the management and recycling of ashes.

2. Experimental section

2.1. Raw materials characterization

Three agricultural residues, characteristic of the Mediterranean countries, which remain unexploited for energy production, were used in this study. Namely, orange tree pruning and dumped leaves, provided by the Institute of Olive Tree and Subtropical Plants of Chania (National Agricultural Research Foundation) and orange peels supplied by a local fruit juice factory BIOXYM A.E, of the city of Chania. After air drying, biomass samples were ground to a particle size of −2000 + 1000 μm and dried in the oven overnight. Characterization of representative samples was performed according to the European standards drawn up by the Technical Committee CEN/TC335. Proximate analysis was conducted using programmable laboratory furnaces, ultimate analysis using a Thermoscientific type analyzer CHNS Flash 2000 and calorific value using a Leco type calorimeter AC-350.

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 (−600 + 425 μm), as this has been found to diminish bed agglomeration problems, when firing biomass fuels [2].

2.2. Combustion tests

Combustion of fuels was carried out in an atmospheric lab-scale fluidized bed reactor ~2 m height, for periods of about 4 h, described in a previous work [2]. The minimum fluidization velocity determined from a Δp-versus-v_o diagram was 0.25 m/s and air flow rates varied between 4.53 and 5.94 m^3/h, for excess ratios of 1.3 − 1.7 during the experiments. No secondary air was supplied. Biomass feed rate was either 0.72 kg/h or 0.84 kg/h. Depending on fuel and feeding rate, bed temperatures ranged between 805 and 988 °C, during all test runs. Freeboard temperatures above the bed were high for all fuels, 810–838 °C, due to volatiles combustion along this region.

The data included fuel feeding, excess air ratios (λ coefficient), bed and freeboard temperature profiles, efficiency and typical flue gas emissions (CO_2, CO, SO_2, NO_x), all presented in the previous investigation. The aim of this research was to evaluate the behaviour of biomass ashes during combustion and determine their chemical composition.

At the end of each experiment, all bed material was drained, weighed, inspected for agglomerates and analysed for unburned carbon in the oven. Fly ash collected in the tangential flow type cyclone (cut size 10 μm, operating velocity ~4 m/s), was also captured, weighed and analysed for unburned carbon. Total output of ash was found to be about 90% of the fuel feed amount. Bed ash comprised 6 ± 3% of this amount, while fly ash was 82 ± 2% of the total mass of the ash fed with each fuel.

2.3. Ash analyses

Chemical analysis of major elements in ashes was conducted using an atomic absorption spectrometer (AAS), model Analyst-100 of Perkin Elmer (detection limits 0.01–0.5% depending on element) with a graphite furnace assembly (model HGA 800) and a deuterium arc lamp background correction system. Phosphorous and chlorine measurements were performed by a spectrophotometer type UV–VIS Hach 4000V (detection limit 200 ppm). Prior to analysis, the samples were dissolved by digestion with HCl or HF or HNO_3 acids, depending on the element under determination, in Teflon beakers heated in a water bath at 80 °C. The loss on ignition percentages were obtained via a thermogravimetric analyzer model TGA-6 of Perkin Elmer at 950 °C. Although the loss on ignition (LOI) is commonly used as a measure of unburned carbon content of ashes, it may also represent mass losses from some minerals in ashes, such as calcite, dolomite and portlandite [15].

Trace element analysis was performed by an inductive 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.

Fly and bottom ashes were subjected to mineralogical analysis, by using 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.

Thermogravimetric analysis experiments were carried out using Pyris TG/DTG analyzer of Perkin Elmer. The samples were heated in air up to 950 °C, with a heating rate of 10 °C/min and a flow rate of 45 ml/min.

The particle size distribution (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.

Ash behaviour and deposition tendencies were predicted through the use of empirical indices, which despite their shortcomings due to the complex conditions that arise in boilers and their associated heat transfer equipment, are widely used and probably remain the most secure basis for decision making, if used in conjunction with pilot plant testing.

The base-to-acid ratio is a useful index, since typically a high percentage of basic oxides lowers the melting temperature, while acidic oxides increase it. This takes the form [22]:

$$R_{b/a} = \frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)} \quad (1)$$

where the label for each compound makes reference to its weight concentration in the ash. When $R_{b/a} < 0.5$ deposition tendency is