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Study of biomass combustion wastes

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HIGHLIGHTS

- SEM images generally showed homogeneous finely divided structures after 550 °C burning.
- Wood pellets sample presented more than 35% of fly ashes (under 200 μm).
- None sample presented PM10 over 3%. PM2.5 were all negligible meaning low health risk.
- Some samples presented high deposition and corrosion risks. Alkali and Cl presence.

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ABSTRACT

A number of widely referenced environmental and logistic advantages suggest biomass as an interesting feedstock to obtain energy in large quantities. One of the most important problems when using biomass is the amount of solid wastes produced, which causes deposition and corrosion phenomena (slagging and fouling) entailing energy efficiency decrement and maintenance problems.

This work focuses on the study of ashes from eighteen different biomass samples, including energy crops, agricultural, industrial and forestry wastes and commercial fuels.

Morphology (SEM) and grain size (PSD-LD) studies showed a homogeneous structure with low quantities of health risky fine particles for most samples after 550 °C burning.

Compositional studies (EDXA, XRF) suggested that some of the studied samples, such as almond shell or rice husk, may respectively present high deposition and corrosion risks.

1. Introduction

Constant growth in mankind's energy requirements over the last century in addition to the high dependence on fossil fuels has outlined important environmental challenges. In this scenario, renewable energy sources appear to be a sustainable tool to complement and gradually substitute fossil fuels in energy production. Among them, biomass, regarded as a feedstock for thermal conversion, presents some advantages such as its neutrality concerning CO_2 emissions during its life cycle [1] or its low N and S content that entails low NO_x and SO_2 emissions [2]. Besides this, biomass is considered as an autonomous resource which partially avoids foreign energy dependence [3]. Because of the advantages when using biomass for energy production, it has experienced a huge development in recent years. Nevertheless, it also presents some disadvantages, being one of the most important the generation of solid wastes [4]. Ash presence is highly negative for the combustion process as it involves energy efficiency losses and higher maintenance expenses due to *unburnts* and depositions (*slagging* and *fouling*) that cause thermal resistances in heat exchangers, corrosion phenomena and the increase of fumes and aerosol emissions [5,6].

Ashes generated during the biomass combustion may present a variable composition with a wide range of mineral and inorganic components included in its structure. These can proceed from the vegetal biomass itself or from other contaminants added during pre-treatment or transport phases. Because of this, any quality control criterion suggests the exhaustive knowledge of ash characteristics, both morphological and compositional.

To that aim, there are several analytical techniques available, commonly used by several authors that supply complete information about biomass samples. In that way Scanning Electron Microscopy (SEM) coupled to an Energy Dispersive X-ray Analyzer (EDXA) allows simultaneous morphological and semi-quantitative compositional information of the studied sample. Biagini [7] and Umamaheswaran [8] use these techniques to study the structural variations of some biomass fuel after combustion processes. Xiao [9] evaluates the structural evolution of biomass ashes after different ashing temperatures. Nortey Yeboah [10] characterizes coal

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ashes with high carbon content that will be later co-fired with biomass. Carrasco [11] uses SEM to characterize bottom ash from biomass to use in concrete formulation and Abraham [12] studies several ash samples trying to find reuse for them in fertilizer, cement or pollutant adsorbent industries. Wang [13] employs EDXA to obtain the elemental composition of biomass fly ash.

Sample's morphology and grain size information can be obtained by developing particle size distribution (PSD). Bridgeman [14] and Mediavilla [15] sieved and weighted fractions of biomass fuels to study the effect of raw materials size on combustion properties and kinetic parameters, respectively. Becidan [16] determined fly ash grain distribution, by previously dividing the min size cuts using an Electrical Low Pressure Impactor. Roy [17] studied particle size distributions of biomass samples by direct measure on SEM images and Wang [18] did the same to fly ashes by laser diffraction (LD).

To obtain chemical composition data other techniques besides EDXA can be used. One of the most common is X-ray Fluorescence (XRF). Reviews from Vassilev [19,20] provide plenty of information about the elementary composition of several biomass samples. Some other authors also use this technique to study the biomass-ash deposition tendency of different ashes by using predictive coefficients [21,22] or ternary diagrams [23,24].

Thermo Gravimetrical Analysis (TGA) is used by several authors to thermally analyze different biomass samples and determine characteristic points in their burning profiles such as their ignition point, peak temperature, burn out temperature [25,26] or kinetic parameters [27]. Our research group has recently proposed a mechanism to obtain proximate analysis data by using this analytical tool [28].

This work focuses on obtaining ash behavior data of several different biomass samples and comparing them in order to determine which ones would be most suitable for use in further combustion processes.

2. Materials and methods

2.1. Samples

In this work, eighteen different biomass samples were tested after air dried and grinded to assure homogeneity. They were chosen as represent all the classification groups, e.g. as these suggested by Ávila [29]. Energy crops (sorghum – S and thistle – THI), agricultural feedstocks (beetroot pellets – BP, straw pellets – SP and rice husk – RH), industrial sources (almond shell – AS, coffee husk – CH, olive stone – OS, pine kernel shell – PKS and vine orujillo – VO) and forestry wastes (olive tree pruning – OTP, pine apple leaf – PL, and vine shoot chips – VSC). In addition to this some of the most common commercial fuels currently available at the Spanish market were studied (briquette – BRI, charcoal – CC, pine and pine apple leaf pellets – PPLP, wood chips – WC and wood pellets – WP).

General combustion-data for these samples is provided in Table 1. Their ashes obtained at 550 °C were also studied. This temperature was chosen as it is considered by several authors [30–32] to be the optimum one to determine their properties. Proximate and ultimate analysis data and higher heating values (HHV) are summarized from previous works by this research group [33].

2.2. Experimental equipment

SEM images were obtained, in this work, using a MEB JEOL-6100 equipment coupled to an INCA Energy 200 EDX analyser, to simultaneously obtain 3D images and semi-quantitative elemental analyses. To this aim samples were previously air dried and grinded under 500 μm and covered with a thin gold layer, as they must be conductant.

Particle size distribution was developed with a laser diffractometer Malvern Intrument's Mastersizer S2000. Samples were originally burned at 550 °C and the residue grinded to avoid coalescence, and measure real particle size XRF data was obtained using Phillips PW2404 equipment joined to a PW2540 automatic sample loader. Samples ashes were obtained at 550 °C and later burnt at 900 °C in order to obtain the mineral matter. Nine elements data (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti and P) were obtained, considered as oxides in its highest oxidation level.

TGA experiments were developed in a Perkin Elmer STA 6000 thermobalance, using 10 mg of sample and a slow heating rate (5 °C/min) from room temperature up to 900 °C in an oxidant air-atmosphere with an air flow of 40 ml/min.

3. Theory and calculation

Slagging and fouling are two phenomena, directly related to deposition and corrosion, commonly observed when operating a biomass-powered combustion system. The first of them is produced at high temperature zones, mainly on grills or chamber walls, whilst the second is typical of low temperature zones, like the heat exchanger surfaces. They depend on the fuel's chemical composition, conversion technology used and operating conditions [19].

XRF data is a useful tool to calculate some deposition-predictive indexes, some of which are included in Table 2, as this phenomenon is usually increased by high concentrations of low melting point elements, like Na, K, S, Cl (alkali sulfates or chlorides) and decreased by high melting point ones such as Ca, Mg or S (calcium or magnesium silicates).

4. Results and discussion

4.1. Morphology and size

Due to space requirements, only the SEM images that show the most relevant facts are included in this work. In this way a yellow[1] marked fibrous structure can be observed in the wood chips sample (Fig. 1). This is due to the high lignin levels of woody fuels which make them harder and more difficult to grind homogenously. Structural holes (blue) that confer this fuel a high specific surface but low density, are also detected. On the other hand, harder samples such as pine kernel shell (Fig. 2a) present, before burning, isolated particles of high size and quite regular sphere-shape. Those two effects coexist in the pine and pine apple leaf pellets sample (Fig. 2b and c) which is a mix between a woody fuel and a harder one. Images observed after 550 °C treatment changes due to thermal effect are easily seen. At this point structural chemical bonding has been broken so hemicellulose, cellulose and lignin of most biomass samples have turned into gaseous CO_2 and CH_4 having lost up to 70% of their initial weight, giving a finely divided structure. Some particles are outlined (orange) in this structure are unburnts, formed by alkali sulfates with high melting points not vaporized at low temperatures that gain relative weight at high temperatures. Low melting point elements may also agglomerate forming particle clusters and high melting temperature compounds.

Concerning particle size distribution, ash particles can be classified in *thin* or *thick* if they, respectively, cross or do not cross a 400 μm mesh sieve [11]. Fly ash is usually considered to have a diameter between 0.2 and 200 μm and bottom ash as between

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.