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Full Length Article

Evaluation of gaseous and solid products from the pyrolysis of waste biomass blends for energetic and environmental applications

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ABSTRACT

An industrial swine sludge and its blends with agricultural wastes from the oil industry were pyrolyzed in fixed bed and TG-MS units. Gaseous species were quantitatively analysed and the energy potential was evaluated. The biochars produced at different temperatures were characterized by physical and chemical analyses. Leaching experiments of biochar mixtures through soil predicted their suitability for soil amendment, as well as their environmental impact. The Higher Heating Value of the gases was found to be satisfactory for the energy requirement of pyrolysis units. Alkali metals Na and K and alkaline earth metal Mg were leached in high amounts through the soil, increasing the pH of the extracts and decreasing the leachability of heavy metals, which were below legislation limits. Biochars examined could be used as liming agents or for soil amendment providing plant nutrients. The waste materials examined could be valorized for energy and agronomic processes.

1. Introduction

Residues from agricultural production and processing industries or from the livestock sector are readily available in large quantities in most European countries. Given the European Union directives 1991/31/EC and 1991/676/EC [1] for reduction in the amount of biodegradable wastes going to landfill, their thermal treatment seems a highly promising solution, allowing for energy recovery and increasing returns to rural communities. In Greece, where animal breeding activity is intense, about 41 Mm^3 of animal wastes are annually produced and stocked in rural areas or outside processing industries, creating environmental pollution. On the other hand, about 3.8 M dry tons of agricultural wastes remain annually unexploited [2]. Consequently, local enterprises are highly interested in using own by-products together with agricultural wastes for obtaining heat or power for their needs, or even valuable products.

Pyrolysis is an attractive thermal approach that can be used to decompose organic pollutants and destroy pathogens from such waste materials [3], converting them simultaneously into energy and added-value products for agriculture. Bio-oil and gas generated from pyrolysis can substitute fossil fuels for providing heat, electricity and/or chemicals. Biochar, the carbon rich product of pyrolysis, recently is gaining increased attention, due to its potential to improve some of the physical, chemical and biological properties of soils [4]. Biochar can improve soil productivity and fertility due to its nutrient content, remediate contaminated soils by adsorbing pollutants due to its porous structure, contribute to carbon storage and sequestration by remaining in the soil for centuries and alternatively it can be used as a fuel [5–8]. The properties of biochar depend on the type of biomass used and the pyrolysis conditions, especially temperature [3,8–11]. For agricultural uses low pyrolysis temperatures are recommended, to keep high nitrogen content in biochars.

There is a lot of information in literature about the properties of biochars derived from agricultural and forestry residues, such as surface area, porosity, pH, cation exchange capacity, electrical conductivity and heavy metal content [3,5,6,8,9,11–14]. Some studies deal with sewage sludge biochars (from municipal waste water treatment plants) [3,6,10,15] and very few with animal manure biochars [5,16]. The carbonizing kinetics, the oxidation behaviour and the chemical characterization of swine manure biochar have been examined by thermogravimetric analysis and NMR spectroscopy [12,13]. The effect of biochar's nutrient retention or release properties on various soils and its impact on soil quality has been investigated for woody residues [4,14,17,18], sugarcane straw [18] and sewage sludge [6]. The variation in dissolved organic carbon, nitrogen, phosphorous and potassium leaching/retention [14,17] and the mobility [18] of heavy metals have been reported, with significant discrepancies in the results obtained, due to the different solid materials involved, experimental equipment and conditions used. Recently, several studies have analyzed the physical and chemical properties of bio-oil produced from fast pyrolysis of

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agricultural wastes and sewage sludge [19–22]. However, due to the high water and oxygen content, the low heating value, solids content, high viscosity, incomplete volatility, chemical instability and corrosiveness, bio-oil is not suitable for direct application as a fuel and upgrading processes, such as catalytic cracking, hydrodeoxygenation, steam reforming etc. are required [7,19,20,23,24]. Since upgrading is a highly complex and expensive process, an economic solution for small enterprises which are interested in valorizing their byproducts through thermal treatment, would be to recycle gases produced from the conventional pyrolysis units for their energy needs. To the author's knowledge there is lack of literature data on the quantitative analysis and energy content of the gaseous products from the pyrolysis of similar materials as those adopted in present work and even more of industrial animal and agricultural waste mixtures. Qualitative analysis of pyrolysis gases via Thermogravimetry-Mass spectrometry (TGA-MS), Thermogravimetry-Fourier transform infrared spectrometry (TGA-FTIR) and Pyrolysis-Gas chromatography/Mass spectrometry (Py-GC/MS) techniques has been reported for lignocellulosic wastes, sewage sludge [25,26] or municipal solid wastes [27].

Past research [28], reporting the great differences in the pyrolysis products according to the origin of the waste materials, strengthens the argument that there is need for their separate study. In this context and based on the above discussion, present work aimed at investigating the valorization of an industrial swine sludge and its blends with agricultural wastes from the oil industry, for which there is lack of information, whereas important for most countries in promoting recycling of wastes for energy recovery or added-value products. Pyrolysis of materials was carried out in a fixed bed unit. A TG system coupled with an MS allowed the real-time and sensitive detection of evolved gaseous species which were quantitatively analyzed, an important and often difficult task in thermal applications, for evaluating their energy potential. The biochars produced at different temperatures were characterized by physical and chemical analyses and their environmental impact was assessed by leaching tests to a phyllitic and quarzitic soil. The leachability behaviour of the biochars was examined and their suitability for soil amendment was determined.

2. Experimental

2.1. Raw materials and characterization

The raw materials studied in this work were a sludge from the primary sector of a biological animal waste (swine) treatment unit of Creta Farm industry in the island of Crete (SWS), as well as olive kernel (OLK) and olive pruning (OLP) provided by a local olive oil factory and cultivated field, respectively, in the neighbourhood of the industry. Mixtures of SWS with each of the agricultural wastes were prepared with blending ratios 50% of SWS by weight in the mixture.

The materials were air-dried and ground, SWS in a jaw crusher and ball mill and agricultural wastes in a cutting mill, to a final size of < 500 μm. For the thermogravimetric tests, raw materials were ground to a size of < 200 μm. After homogenization and riffling, representative samples were characterized by proximate analysis, ultimate analysis and calorific value according to the European standards CEN/TC335.

The soil used for the leaching tests was collected from the area of Chania in Crete. The < 2 mm fraction was analysed by the hydrometer method [29] for the proportions in sand, silt and clay. Total organic carbon (TOC) was measured by a Gasometric Carbon analyzer 572-100, while cation-exchange capacity by applying the ammonium acetate method [30]. Chemical analysis was performed using the same techniques as for the biochars described below (Section 2.3).

2.2. Pyrolysis experiments

Pyrolysis tests for biochar production were carried out in a lab-scale stainless steel fixed bed unit heated by a furnace (Fig. 1). The temperature, which varied between 450 and 650 °C during the tests (for maximizing char yields [7,10,11,14,16,23]) was measured by a Ni-Cr-Ni thermocouple inside the reactor. The flow rate of nitrogen was 100 mL/min, the heating rate 10 °C/min, while the retention time at the final temperature was 30 min. Bio-oil was collected during the experiment in *iso*-propanol cooled by salt-ice baths. In a typical experiment, about 15 g of biomass sample was placed onto a net stainless steel holder and then inserted in the tubular reactor. After assembling the apparatus and introducing it in the furnace, it was purged with nitrogen at room temperature for 30 min. The furnace was then set to the desired pyrolysis temperature at a constant heating rate. Following pyrolysis and retention time, the reactor was cooled under nitrogen and the resulting biochar weighed and stored for further analysis. The yield of bio-oil was determined by difference from final liquid product and *iso*-propanol weight. The yield of gas was obtained by difference between initial sample mass fed and the sum of liquid and biochar yields.

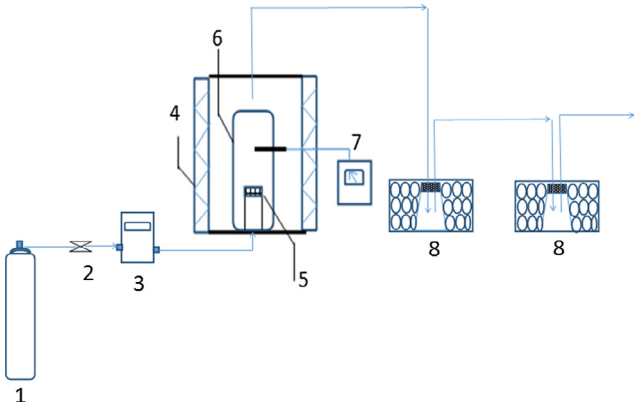

Fig. 1. Schematic diagram of the equipment: (1) N_2 cylinder, (2) flow control valve, (3) flow meter, (4) programmable furnace, (5) sample, (6) reactor, (7) thermocouple with indicator, (8) salt-ice bath.

Pyrolysis gases were analysed by a differential thermogravimetric analyser TGA-6/DTG of Perkin Elmer, connected online with a quadrupole mass spectrometer (Balzers QME-200). The tests were conducted under pure argon atmosphere with a flow rate of 35 mL/min and a heating rate of 10 °C/min up to 900 °C. Prior to the experiments the apparatus was purged with argon for 1 h. Gases were pumped into the MS through a transfer line heated to 200 °C to prevent condensation. The capillary was from fused silicon with i.d. 0.32 mm and was encased with a stainless steel sheath. The ion source was operated at 82 eV electron energy and the mass detection range was 1–400 atomic mass unit (amu). The ions separated according to their mass-to-charge ratio were detected by a Secondary Electron Multiplier (SEM). The collection of the TGA/MS data was performed by Pyris v.3.5 and Quadstar 422 softwares. About 65 mass spectrometric intensities were recorded during the experiments. More details are given in a previous study [31].

For quantitative measurements, the mass-to-charge ratios (m/z) 2, 15, 18, 24–27, 28, 44 accounting for H_2, CH_4, H_2O, C_2-C_3, CO and CO_2 respectively, were continuously monitored. The contribution of fragments from more than one compound to the intensity of a specific m/z ratio was taken into account, by determining all the compound calibration factors for each m/z ratio that this compound contributes. Calibration factors were determined using standard gases (purity 99.999%) of known concentrations of each gas in argon, while the CO_2, CO and H_2O calibration factors were provided by the aforementioned experiments of calcium oxalate monohydrate pyrolysis. For high system performance, prior to calibration, the criteria of high-flow stability through TGA/MS and independence of MS intensity by the temperature increase in TGA furnace and the heating rate applied, were checked to be met. Calibration tests were carried out under the same conditions used in the experiments. All tests were performed in triplicate and their