Valorization of a bio-solid for the production of a H_2-rich gas through CO_2 capture by a waste material and for soil amelioration

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Introduction

The amounts of bio-solids generated from human wastewater treatments plants are very high and increase continuously, as a result of the growing global population and urbanization. Over 45 dry million tons of sewage sludge (Huang et al., 2020) are produced annually worldwide. The corresponding quantities produced from small countries, such as Greece, are about 30 kg/per capita (Directive EC, 2009).

Sewage sludge contains several contaminants such as parasites, bacteria, organic micro-pollutants and heavy metals, which renders it a potentially hazardous material for human health and the whole ecosystem. Conventional management methods, such as landfilling or biological treatment, can cause not only environmental pollution and health problems, but they are also less cost-effective (Kang et al., 2024). Furthermore, composting, if mismanaged, can cause contamination of soil and ground waters.

The high calorific value of dried bio-solids, up to about 20 MJ/kg, is challenging, making them promising renewable energy sources (Alper et al., 2025). Thus, Waste-to-Energy technologies have emerged as a viable alternative to traditional management methods, by reducing the volume of wastes and their adverse environmental impacts, while simultaneously producing energy and fuels. The gasification process offers the advantages of reduced pollutant emissions, higher efficiency and generation of a range of useful products, in comparison to incineration.

Research on the steam gasification of human-derived bio-solids, in combination with CO_2 capture for yielding higher H_2 concentrations and reducing greenhouse gas emissions, is very insufficient and limited to the use of lime as a sorbent (Chen et al., 2020; Cheng et al., 2024; Lin et al., 2024). Current study aimed to integrate the thermochemical conversion of a bio-solid via steam gasification for the production of a hydrogen-rich syngas, with reduction of carbon dioxide greenhouse emissions through the use of a building waste material, supporting in this way renewable energy initiatives, circular economy and environmental management of wastes. This novel concept was extended to the investigation of the potential of this waste material to be used for amelioration of soils, filling the gap (De Figueiredo et al., 2019; Rehman et al., 2018; Yuan et al., 2016) of its current co-application with composts or biomass.

Material and methods

The waste material was a bio-solid, from the biological wastewater treatment unit in the area of West Crete. The sludge was undigested and was received after the thickening and de-watering processes of the plant. Raw material was air-dried, followed by grinding in a jaw crusher and a ball mill and sieving, to achieve a particle size less than 500 μm. A quartzitic soil, consisting of 55 % sand, 45 % silt and 6 % clays, was sampled according to the rectangular grid technique, from the area of Chania in West Crete, to be used for the leaching experiments of the material. The soil was sieved to a particle size below 2 mm. For the adsorption of CO_2 produced during the gasification tests, a fine powder of particle size less than 90 μm, generated as a waste from concrete mortar production, was furnished by the private corporation Finomix AE. The material was calcined at 950 °C in air, so that its high calcite content to be converted to lime and subsequently it was kept under a water-saturated environment within a sealed quartz vessel for about 10 days, to transform lime into the active form of CO_2 sorbent, $Ca(OH)_2$.

The gasification experiments were conducted in a fixed-bed reactor system coupled with a thermogravimetric/differential thermogravimetric-mass spectrometer system, whereas the soil application experiments were carried out by column leaching, simulating field conditions of Mediterranean countries. Outcomes included the composition of the resultant gas, its heating value and the yield of hydrogen, as a function of temperature and amount of carbon dioxide sorbent used from the gasification tests, as well as the leachability of several nutrients and heavy metals through the soil from the leaching tests.

Results and conclusions

When the gasification process temperature increased, the composition of the gas was greatly affected. The volume fractions of H_2 and CO_2 progressively increased with temperature. This trend is attributed to the endothermic nature of reactions (1) and (2) shown below, as well as the water-gas shift reaction (5), which becomes thermodynamically beneficial at high temperatures. Conversely, the concentration of CO in the gas mixture decreased to a high extent as the temperature rose. This drop in CO content reveals that, although the Boudouard reaction (3) was promoted at the higher temperatures, CO was consumed by reaction (5) and reverse reaction (6).

The small increase in CH_4 gas confirms its production through reverse reaction (6), as reaction (4) needs elevated pressures to be favored. The concentrations of CxHy were very low, between 0.02-0.1 mol%.

$$C + H_2O \rightarrow CO + H_2 \quad (1)$$
$$C + 2H_2O \rightarrow CO_2 + 2H_2 \quad (2)$$
$$C + CO_2 \rightarrow 2CO \quad (3)$$
$$C + 2H_2 \rightarrow CH_4 \quad (4)$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (5)$$
$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (6)$$

When the sorbent was added to the reactor to capture the CO_2 produced, the final temperature was maintained at 750 °C to inhibit the breakdown of $CaCO_3$, which would enrich the output gas in CO_2. The active CO_2 sorbent was $Ca(OH)_2$:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (7)$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (8)$$

The concentrations of COD, NO_3^-, PO_4^{3-} and phenols as a function of leaching time, along with the pH and EC values, were measured in the liquid extracts from the column leaching experiments. The pH of the sample increased from 7 to 7.9 with time after a period of 90 days, due to the high amount of carbonates in the char, which could have been partly dissolved in the water during the experiments. The electrical conductivity was low, thus favoring the availability of nutrients through the soil. The COD value measured from the sewage sludge char was negligible. The release of nitrates in the leachates decreased with time, implying some retention of these ions on the surface of the char, which could be beneficial for soils and plants. The release of phosphate ions in the extracts was negligible. The amount of phenols leached was very low. Alkali cations presented higher mobility, whereas the leachability of heavy metals was extremely low.

Conclusions

By addition of waste concrete fines sorbent, 88% of carbon dioxide from the steam gasification of the bio-solid studied was captured, the molar fraction of hydrogen in the generated gas increased from 33.2% up to 68%, the hydrogen-to-carbon monoxide molar ratio was 2.4 and the yield of hydrogen 1.7 m^3/kg char. During leaching some nitrates were retained on biochar's surface, while the release of phosphorus was negligible. Alkali cations presented higher mobility, whereas the leachability of heavy metals was extremely low.

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Keywords: bio-solid, hydrogen, CO_2 capture, soil