

Valorization of a bio-solid for the production of a H₂-rich gas through CO₂ capture by a waste material and for soil amelioration

D. Vamvuka, I. Papakyriakopoulos, K. Kyriakidis, S. Sfakiotakis, D. Pentari¹

¹School of Mineral Resources Engineering, Technical University of Crete, Chania, 73100, Greece
Presenting author email: papakyriakopoulos@gmail.com, ipapakyriakopoul@tuc.gr

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 CO₂ capture for yielding higher H₂ 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

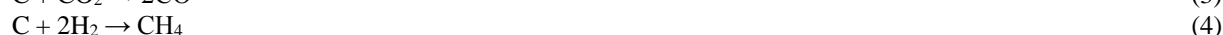
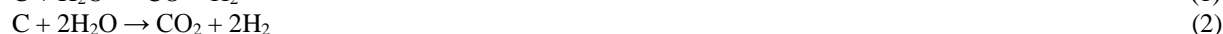
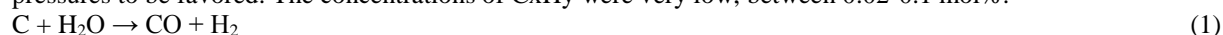
The waste material was a bio-solid, from the biological wastewater treatment unit in the area of West Crete. The sludge was undigested and was received after the thickening and de-watering processes of the plant. Raw material was air-dried, followed by grinding in a jaw crusher and a ball mill and sieving, 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 CO₂ 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 CO₂ 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 H₂ and CO₂ 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 CH₄ gas confirms its production through reverse reaction (6), as reaction (4) needs elevated pressures to be favored. The concentrations of C_xH_y were very low, between 0.02-0.1 mol%.



When the sorbent was added to the reactor to capture the CO₂ produced, the final temperature was maintained at 750 °C to inhibit the breakdown of CaCO₃, which would enrich the output gas in CO₂. The active CO₂ sorbent was Ca(OH)₂:



The concentrations of COD, NO₃⁻, PO₄³⁻ 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 m³/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.

References

- D. Alper, E. Babayigit, G. Zengin, H. Okutan and A. Sarioglan, The catalytic influence of low-cost natural minerals on sewage sludge gasification for hydrogen production, *Int. J. Hydr. Energy*, vol. 142, pp. 966-980, 2025.
- S. Chen, Z. Zhao, A. soomro, S. Ma, M. Wu, Z. Sun and W. Xiang, Hydrogen-rich syngas production via sorption-enhanced steam gasification of sewage sludge, *Biomass Bioenergy*, vol. 138, pp. 105607, 2020.
- Y. Cheng, Z. Guo, R. Hong, N. Chen and R. Han, Enhanced production of hydrogen-rich gas from municipal sewage sludge gasification using a CaO-RM composite catalyst, *Int. J. Hydr. Energy*, vol. 77, pp. 824-833, 2024.
- C. de Figueiredo, J. Chagas, J. da Silva and J. Paz-Ferreiro, Short-term effects of a sewage sludge biochar amendment on total and available heavy metal content of a tropical soil, *Geoderma*, vol. 344, pp. 31-39, 2019.
- Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009, Promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, *Off J. L 140 (05/06/2009) 0016-62*, 2009.
- Y. Huang, M. Chen and Q. Li, Decentralized drying-gasification scheme of sewage sludge with torrefied biomass as auxiliary feedstock, *Int. J. Hydr. Energy*, vol. 45, pp. 24263-24274, 2020.
- B. Kang, A. Farooq, B. Valizadeh, D. Lee, M. Seo, S. Jung et al., Valorization of sewage sludge via air/steam gasification using activated carbon and biochar as catalysts, *Int. J. Hydr. Energy*, vol. 54, pp. 284-293, 2024.
- D. Lin, W. Kai, X. Xie, A. Kozlov, M. Penzik and B. Li, Steam gasification of lime dried sewage sludge: Effects of temperature and addition of lime, *Fuel*, vol. 371, pp. 131932, 2024.
- R. Rehman, M. Rizwan, M. Qayyum, S. Ali, M. Zia-ur-Rehman, M. Zafar-ul-Hye et al., Efficiency of various sewage sludges and their biochars in improving selected soil properties and growth of wheat (*Triticum aestivum*), *J. Environ. Manag.*, vol. 223, pp. 607-613, 2018.
- H. Yuan, T. Lu, Y. Wang, Y. Chen and T. Lei, Sewage sludge biochar: Nutrient composition and its effect on the leaching of soil nutrients, *Geoderma*, vol. 267, pp. 17-23, 2016.

Keywords: bio-solid, hydrogen, CO₂ capture, soil