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Study of the Thermal Behavior of Sewage Sludge from a WWTP in Cantabria (Spain) by TG-DSC-MS

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According to European Directive and national regulations in Spain, techniques based on thermal decomposition are proposed for the sewage sludge disposal. In this work, the sludge from the wastewater treatment plant (WWTP) of Casar de Periedo, in Cantabria (Spain) is studied by Thermogravimetry – Differential Scanning Calorimetry – Mass Spectrometry (TG –DSC – MS). A sample of this sludge was submitted, after drying, to different atmospheres: 100 % He, N_2 /air or He/air 80/20 and 100 % air, from 20 to 900 ºC, to study primary decomposition reactions in pyrolysis, gasification and combustion respectively. The purpose was to determine the weight loss at different temperatures, the heat flow at each atmosphere and the presence of some gas products like H_2, CO, CO_2, CH_4, or HCl, SO_2, SO_3, NO and NO_2 released, these last five gases to know the contaminants emitted. Combustion conditions (air) rend the greatest mass loss and energy production. Reactions take place at lower temperatures, being mainly CO_2 and H_2O the products detected in MS, with little amounts of CH_4, as it is expected for mainly total oxidation reactions. In gasification conditions, essayed with two atmospheres (N_2-air and He-air), quantitative results found are similar, but the highest thermal conductivity of He produces exothermic reactions at lower temperatures, observed in the mass loss and heat flow profiles. From reactions of decomposition, partial oxidation and total oxidation, CO_2, H_2, H_2O and CH_4, were identified by MS. Pyrolysis conditions (He) produce the lowest mass loss and slightly endothermic reactions, mainly because of decomposition reactions. Higher H2 amounts were obtained at higher temperatures than in gasification conditions. No gas contaminant (HCl, SO_2, SO_3, NO and NO2) has been detected by MS, considering this sewage sludge as a “clean sludge”. Comparing the thermal behaviour of the sewage sludge of this plant to that obtained in the WWTP of Santander, the sludge from Casar de Periedo is more appropriated to thermal valorization.

1. Introduction

The amount of sewage sludge generated from wastewater treatment has increased in the last few years due to the growth of urban wastewater treatment plants, causing disposal problems in many industrialized countries (Lundin et al., 2004). The implementation of the Urban Waste Water Treatment Directive (European Commission, 91/271/EEC) requires the installation of treatment systems in every urban zone exceeding 2000 inhabitants from 2005. This has caused a major increase in sewage sludge production, being a 50 % the increase by year 2005, 10 Mt/y in the European Union (European Commission, 91/271/EEC). In Europe, dry weight per capita production of sewage sludge is in average 50 - 90 g per person per day according to different studies (Fytili and Zabaniotou, 2008; Rulkens, 2008).

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The priorities for the sludge management, as in the rest of residues, are (a) prevention of waste (minimization), (b) waste recovery through reuse, recycling and energy recovery (valorization) and (c) improved treatment conditions before disposal. The European Union target is to reduce final waste disposal by 50 % compared with 2000 by 2050 (Lundin et al., 2004).

Sewage sludge uses in Spain are regulated by the II Wastewater Sewage Sludge National Plan that establishes quantitative alternatives that must be given in recovery in agriculture and energy recovery, minimizing the landfill. According to this plan, techniques based on thermal treatment, like pyrolysis, gasification and combustion, which are also stabilization processes, are proposed for the sewage sludge management. Pyrolysis is a thermal degradation process (cracking) of biomass using heat in the absence of oxygen, which results in the production of char (solid), bio-oil and tar (liquid) and fuel gas products. In gasification, there is a partial oxidation at high temperature to obtain a combustible gas. In combustion the aim is to get a total oxidation to reduce the sludge volume and to obtain energy.

The wastewater treatment plant located in Casar de Periedo was designed to 20,000 equivalent inhabitants. The plant operates according to a pre-treatment followed by a biological treatment, being the sludge reduced by thickening and centrifugation.

The use of a Mass Spectrometer (MS) linked to the Thermogravimetric Analyzer (TG) and Differential Scanning Calorimeter (DSC), (TG-DSC-MS), allows knowing the nature and quantity of volatile products released on heating and provides information about possible chemical reactions occurring during thermal decomposition. It is particularly useful in supplying direct chemical information to complement the physical data obtained from TG or DSC. Additional advantages that have emerged include specificity -a single decomposition can be followed against a background of concurrent processes- and sensitivity, which can be far greater than with TG alone. Evolved gas analysis is of great value in the interpretation of complex TG and DSC curves (Alcolea et al., 2009).

In this work, a sample of the sludge from the WWTP of Casar de Periedo, Cantabria (Spain) previously dried is studied by TG –DSC – MS at different atmospheres: 100 % N_2 to simulate pyrolysis conditions, nitrogen /air or He/air at 80/20 ratio for partial oxidation conditions and 100 % air for combustion conditions, always from 20 to 900 ºC. The purpose was to determine the weight loss at different temperatures, the heat flow at each atmosphere and the presence of some gas products like H_2, CO, CO_2, CH_4, or HCl, SO_2, SO_3, NO and NO_2 released, in order to increase the knowledge of the primary reactions of these thermal processes and also to know the contaminants emitted in these processes.

2. Material and Methods

The composition of the sewage sludge of this plant was previously studied (Fernández and Renedo, 2011).

The simultaneous TG-DSC-MS curves were obtained on a SETARAM thermal analyzer, model SETSYS-1700. The samples of approximately 10 mg (particle size < 0.25 mm) were heated in platinum crucibles in different atmospheres (100 % nitrogen, nitrogen / air and helio / air in a ratio of 80/20, and 100 % air), at a total flow rate of 50 ml min^{-1}, with a heating rate of 10 ºC min^{-1} and a final temperature of 900 ºC. All the TG measurements were blank curve corrected. Each experiment was repeated to check for consistency. The TG instrument was coupled to a Balzers Thermostar/OmniStar mass spectrometer (Pfeiffer vacuum) for evolved gas analysis. Quadrupole mass spectrometer model was QMS 200. The number of m/z signals selected was 2 (H_2^+, corresponding to Hydrogen), 15 (CH_3^+, corresponding to methane and other hydrocarbons), 18 (H_2O^+, to water), 28 (CO^+, $C_2H_4^+$) and 44 (CO_2^+, to carbon dioxide). The m/z signals corresponding to HCl (36), SO_2 (64), SO_3 (80), NO (30) and NO_2 (46) were also analyzed. A qualitative analysis was only performed in this work.

3. Results and Discussion

The experimental variations of the mass loss, heat flow and intensities of different m/z values versus temperature in the dynamic runs, were carried out in the different atmospheres. The masses evolved in temperature intervals were also obtained in different mass intervals in the atmospheres tested, in order to evaluate the presence or not of some compounds emitted.

Figure 1 shows, as a summary, the mass loss obtained at the different atmospheres tested. It can be observed that the same mass loss is obtained with air (combustion conditions) or N_2/air, He /air 80/20 (gasification conditions), but combustion produces this loss at lower temperature, as corresponds to the best oxidation conditions. These are the expected results for mainly total oxidation reactions.
Gasification conditions were essayed with two atmospheres (N_2-air and He-air). Quantitative results found between them are similar, but the mass loss observed in He/air takes place at lower temperature. This fact can be explained by the highest thermal conductivity of He, that produces the reactions at lower temperatures.
As it is expected, pyrolysis conditions (He) produce the lowest mass loss, because decomposition reactions eliminate a lower mass.

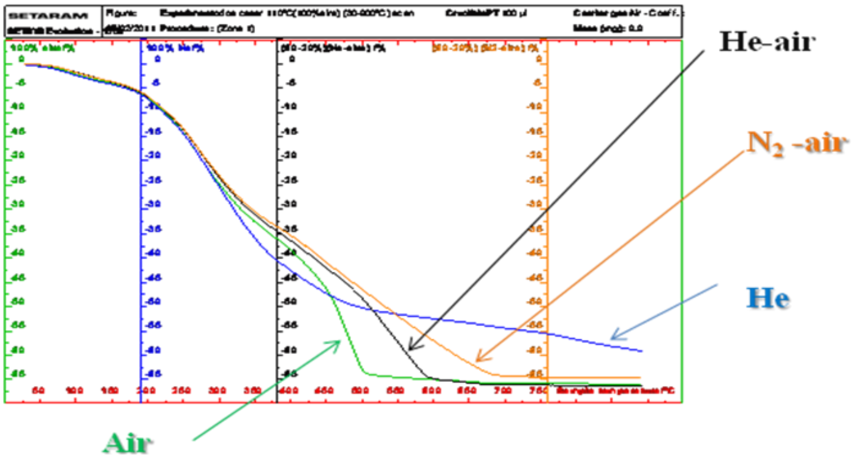

Figure 1. Mass loss profiles for dry sewage sludge of Casar de Periedo in different atmospheres.

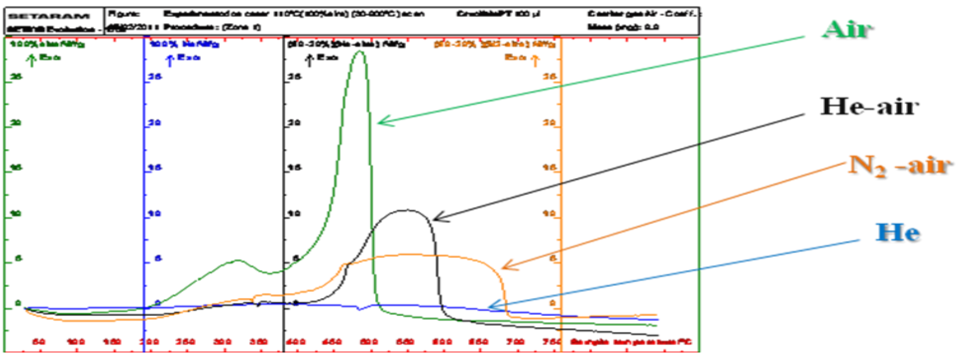

Figure 2. Heat flow profiles for dry sewage sludge from Casar de Periedo

Figure 2 shows the profile of heat flow obtained at the conditions tested. A little endothermic peak corresponding to water vaporization is observed for all the conditions essayed at temperatures lower than 200 ºC. An exothermic zone for the combustion (100 % air) and gasification conditions (80/20 N_2/air or He/air ratio) was obtained in Figure 3, being slightly endothermic for pyrolysis conditions (100 % He). As it was expected, the heat released increases as the amount of air increases in the flow gas. The temperature range for heat release is wider for gasification conditions, and takes place at similar interval of temperatures than the mass losses previously described, showing that oxidation reactions are prolonged at higher temperatures in a deficient oxygen atmosphere. As it has been also discussed, the higher thermal conductivity in He produces mass losses and heat flow at lower temperatures than N_2/air conditions.

For combustion conditions, two differentiated mass loss can be observed between 200 and 500ºC, that correspond with the two exothermic peaks clearly found from DSC results in Figure 2. According to the suggestions by Shao et al. (2008) and Font et al. (2005), the first mass loss will correspond to the oxidation of biodegradable matter and the second one will be mainly due to the oxidation of organic polymers from the sludge or from dead bacteria. From 500 to 600 ºC approximately, the mass loss is negligible, indicating that nonbiodegradable matter, that burns only at temperatures higher than 550 ºC, is not present in the Casar de Periedo sludge.

The continuous mass loss observed for partial oxidation conditions up to temperatures near 600 ºC (He/air 80/20) or 700 ºC (N2/air 80/20), indicate a lower and delayed oxidation, as was observed with the exothermic peaks in Figure 2, as a consequence of a deficient oxygen atmosphere.

The quantification of the heat interchanged in the different atmospheres was also carried out, with these results: -3252 cal/g (100 % air), -1846 cal/g (He/air 80/20), -2137 cal/g (N2/air 80/20) and 60 cal/g (100 % He). The different values obtained in gasification conditions can also be attributed to the experimental error in the measure of the peak area, but it can be observed that combustion conditions produce the highest heat interchanged (this was the calorific value of the sludge), being lower the value for gasification conditions and slightly endothermic the peak for pyrolysis conditions.

Figure 3 shows, as an example, the profiles obtained by mass spectrometry for the interval from m/z 12 to 16, in the experiment carried out with 100 % air. The cycles showed in the z axis correspond to temperature, having into account that each cycle is equivalent to 100 s (the equipment was programmed to detect one mass per second, and masses from m/z 1 to 100 were detected). According to the programme in the TG experiment, each cycle corresponds to an increase of 16.6 ºC. After cycle 56, the mass detected corresponds to volatile compounds emitted during the cooling of the TG equipment. The presence of nitrogen (with peaks in the mass spectrum at m/z 14 and 28) and oxygen (m/z 16 and 32) from the carrier gas is responsible of the continuous peaks at m/z 14 and 16. Other peaks that would appear at the same mass (as CO+, m/z 28) will not be able to be identified. It can be observed that peak at m/z 15, corresponding to methane and other hydrocarbons, is evolved during the thermal treatment, and also a peak at m/z 12.

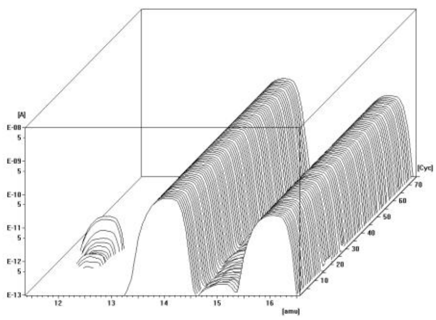

Figure 3. Peaks in the interval of m/z 12 to 16 for sludge in 100 % air.

The evolution of the peak obtained at m/z 15 with the temperature, for the sludge heated in 100 % air, can be obtained from this figure and also the intervals of temperature at which this fragment is emitted.

A similar study was carried out for all the peaks in the interval from m/z 1 to 100, analyzing the main peaks obtained in the scan and determining their evolution with the temperature in all the atmospheres tested. Figure 4 presents as an example, a comparison of the peaks at m/z 2. All the peaks that are usual in combustion, pyrolysis and gasification processes were studied in a similar way.

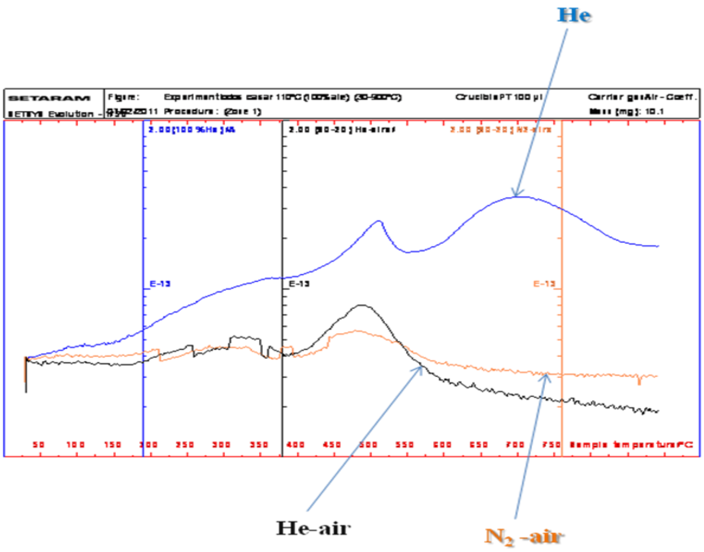

Figure 4. Evolution of the peak at m/z=2 with the temperature emitted by the sludge in the different atmospheres showed .

In Figure 4 it can be observed that H_2 is emitted at higher temperatures and in a wider interval in pyrolysis conditions than in gasification conditions, being similar the data found for the two gasification conditions tested. No hydrogen production was found for the combustion experiment (100 % air). The emission of this gas can be associated to dehydrogenation and aromatization reactions.
The production of CH_3^+ fragments in the atmospheres tested (figure omitted) can be associated to methane production and also is a fragment obtained in hydrocarbons. Very different baseline is obtained for the two gasification conditions tested, but a similar interval of temperature in all the cases is found, also similar to combustion conditions, where this fragment is also emitted as a consequence of an initial step of pyrolysis during combustion. It was not found this peak for pyrolysis conditions.
The H_2O and CO_2 (figures omitted) are also emitted after 500 ºC in gasification conditions, and before this temperature in the combustion experiment. For the pyrolysis, these signals appear at lower temperatures (200 to 400 ºC) as a consequence of decomposition (not oxidation) reactions.
The study of the peaks corresponding to possible contaminants emitted in these processes (HCl^+, m/z 36, SO_2^+, m/z 64, SO_3^+, m/z 80, NO^+, m/z 30 and NO_2^+, m/z 46) was also carried out in the same way, showing the absence of HCl, SO_2, SO_3 and NO_2 in all the conditions tested. A peak in the m/z 30 for combustion and gasification conditions was found, but can also be attributed to ethane. Because no signal was found at m/z 46 in the presence of air, it is not probably that the signal at m/z 30 corresponds to NO. With these results, this sewage sludge can be considered as a “clean sludge”.
Comparing the thermal behaviour of the sewage sludge of this plant to that obtained in the WWTP of Santander, previously studied (Fernández et al. 2008, 2010), a lower mass loss at higher temperatures and a lower heat production were found in the sludge from Santander, according to the anaerobic treatment carried out to the sludge in this plant. Because of that, the sludge from Casar de Periedo is more appropriated to thermal valorization.

4. Conclusions

The calorific value of the sludge, (-3,252 cal/g), corresponds to a sludge with high organic content.
The two exothermic peaks observed for combustion conditions can be associated to the total oxidation of biodegradable material, and to the oxidation of organic polymers and the char formed, with the elimination of water and carbon dioxide in both. Methane formation shows that pyrolysis take place as a first stage in combustion.

In gasification conditions, the oxidation reactions extend to higher temperatures than in combustion conditions, 600 ºC in He/air and near 700 °C in N_2 / air, being lower the temperature according to the higher thermal conductivity of helium gas.

Pyrolysis conditions produced lower mass loss than combustion and gasification conditions and endothermic behaviour. The little water and carbon dioxide release between 250 and 500 ºC, is associated mainly to decarboxylation and dehydration reactions. Hydrogen was detected from 400 ºC, associated to dehydrogenation and aromatization reactions.

No gas contaminant (HCl, SO_2, SO_3, NO and NO_2) has been detected in the conditions tested and because of that this sewage sludge can be considered as a "clean sludge".

The sludge from Casar de Periedo is appropriated to thermal valorization.

Analysis of sewage sludge by TG-DSC-MS can supply powerful information about the complex reactions that take place in the thermal treatment.

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