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Analysis of the combustion and pyrolysis of dried sewage sludge by TGA and MS

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ABSTRACT

In this study, the combustion and pyrolysis processes of three sewage sludge were investigated. The sewage sludge came from three wastewater treatment plants.

Proximate and ultimate analyses were performed. The thermal behaviour of studied sewage sludge was investigated by thermogravimetric analysis with mass spectrometry (TGA-MS). The samples were heated from ambient temperature to 800 °C at a constant rate 10 °C/min in air (combustion process) and argon flows (pyrolysis process). The thermal profiles presented in form of TG/DTG curves were comparable for studied sludges. All TG/DTG curves were divided into three stages. The main decomposition of sewage sludge during the combustion process took place in the range 180–580 °C with c.a. 70% mass loss. The pyrolysis process occurred in lower temperature but with less mass loss. The evolved gaseous products (H_2, CH_4, CO_2, H_2O) from the decomposition of sewage sludge were identified on-line.

Contents

1. Introduction

Sewage sludge is the residual matter from the treatment processes of household and industrial wastewaters. It contains micro-organisms and harmful substances, such as heavy metals, poorly biodegradable organic compounds, bacteria, viruses, pharmaceuticals, hormones and dioxins, which make their disposal difficult (Seggiani et al., 2012).The quantity of sludge in Europe (Kelessidis and Stasinakis, 2012; Cao and Pawłowski, 2012; Werle, 2012a,b) varies widely in different countries (16–94 g dry basis/(person·day). During the last 20 years, there has been a major change in the way in which sludge is disposed from the traditional methods, including landfill and agricultural use. In Europe the Landfill Directive 1999/31/EC restricts landfilling biodegradable municipal wastes, and in some countries it is even banned. EU Directive 86/278/EEC prohibits the use of untreated sludge on agricultural land, unless it is injected or incorporated into the soil. This directive also sets limit values for heavy metals and organic compounds to avoid bioaccumulation in plants and animals. Such disposal is declining all over Europe.

In its dry form, sewage sludge could be considered a special type of renewable fuel, due to the high quantity of organics of sufficiently high calorific value, similar to that of brown coal (Werther

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and Ogada, 1999; Spliethoff, 2010; Garcia et al., 2013). There is therefore increased interest in utilisation of sewage sludge, resulting also from limited reserves of fossil fuels (and limited global security of energy supplies) and environmental and climatic regulations on CO_2 emissions. There are several thermal technologies for utilising municipal sewage sludge to obtain useful forms of energy, such as pyrolysis, gasification, combustion, and co-combustion processes (Manara and Zabaniotou, 2012; Calvo et al., 2013; Chun et al., 2011; Judex et al., 2012; Rushidi et al., 2013). The advantages of thermal processes are the large reduction in volume, the thermal destruction of toxic organics and the recovery of the energy of organic sources in the sludge. One of the most promising options is combustion.

Combustion characteristics of sewage sludge have been widely studied using thermo-analytical techniques. The influence of temperature and atmosphere has been investigated by thermal analytical techniques (Viana et al., 2011; Varol et al., 2010; Magdziarz and Wilk, 2013; Otero et al., 2007; Wu et al., 2012). Thermogravimetric analysis of the kinetics of combustion processes has been performed by Scott et al., 2006; Lee and Bae, 2009; Magdziarz and Wilk, 2013. Its advantages include a rapid assessment of the fuel value, the temperatures at which combustion starts and ends, the maximum reactivity temperature, the amount of ash and total combustion time. Because thermo-chemical conversion requires the control of outflow gas emission, chemical composition of exhaust gases should be determined before any industrial application. The combination of MS and TGA offers several advantages, such as a real-time analysis and qualitative and quantitative analyses. Results for combustion, co-combustion and pyrolysis of urban plant sewage sludge have been published, e.g. by Ischia et al. (2007) and Calvo et al. (2004).

Currently only 1% of sewage produced in Poland is thermally decomposed, but legislation requires an increase to 60% by the year 2018. Accordingly an appraisal of the combustion and pyrolysis of sewage sludge from Polish wastewater treatment plants is timely. In the work now reported TGA (burning profiles) and MS (gaseous products) data were used to determine the combustion and pyrolysis characteristics of three types of sludge, using coal as a reference fuel.

2. Materials and methods

2.1. Fuel feedstocks and their characterisation

The three sewage sludge (SS1, SS2, and SS3) samples were taken from Polish wastewater treatment plants and coal, used in thermal power plants, from a Polish mine. The sewage sludge was submitted to stabilisation treatment by anaerobic digestion, dehydration and thermal drying. The feedstocks were milled before thermal analysis (diameter equal to 1 mm) and analysed regarding properties that affect thermal conversion. Procedures were according to European Standards: DIN 51718A/CEN/TS 1514–1/-2 – moisture content, DIN 15403 – ash content, DIN 51900 + CEN/TS-15400 + 15170 – heating value and chemical composition: DIN 15407 – carbon, DIN 51732 – hydrogen, DIN EN 15407 – nitrogen, EN 14582/EN ISO 11885/CEN/TS 15289 – sulphur. The Elemental Analyser Truespec CHN Leco was used to determine carbon, hydrogen and nitrogen contents and for sulphur ICP-OES Vista Varian apparatus was employed. Proximate and ultimate analyses were performed, and the calorific values of the samples determined.

3. Experimental procedure

The thermogravimetric analyses were conducted using a Mettler Toledo TGA/SDTA 851 apparatus. The instrument was calibrated using indium, zinc and aluminium. Its accuracy was 10^{-6} g. For the thermal analyses (TG/DTG/DTA), the samples were placed in alumina crucibles. Approximately 15 mg of sample was heated from ambient temperature to 800 °C at a constant rate of 10 °C/min in a 40 ml/min flow of air and argon. Each sample had to be measured under exactly the same conditions, including temperature range, atmosphere, and heating rate, to determine the correct conditions. The TG and DTA curves for each of the samples were obtained as the outputs for combustion and pyrolysis. DTA detects thermal effects that are accompanied by physical or chemical changes by recording the temperature difference between the test substance and the reference substance. The ordinate on the TG curves was the percentage ratio of the instantaneous weight of the sample to the initial weight. DTG curves are the result of mathematical transformation ($dm/dt = f(t)$, where m – mass of sample, t – time).

The evolved gaseous products from decompositions were identified on-line using a ThermoStar GSD300T Balzers quadruple mass spectrometer (QMS). It was operated in the electron impact mode (EI) using a channeltron as a detector. Screening analyses were performed in the selected-ion monitoring (SIM) mode. The following ions, which are characteristic of the molecules of interest, were monitored: 2, 15, 17, 18, 30, 44, and 64 for H_2, CH_4, $OH(NH_3)$, H_2O, $NO(C_2H_6)$, CO_2 and SO_2, respectively. The QMS spectrum of mass 17 can represent not only NH_3, but also OH^- fragment of H_2O fragmentation, and that of mass 30 can represent both NO and C_2H_6. All these gaseous molecules are important from the point of view of air pollution and energy value.

4. Results and discussion

4.1. Characterisation of materials

The results of elementary and proximate analyses for coal and the three sewage sludges are shown in Table 1. The coal has a high carbon content and a very high value of HHV (high heating value). Its ash yield is much lower (7.8 wt.%) than that of the sewage sludges (32–36 wt.%). Their samples have variable characteristics depending on the type of process used at the wastewater treatment plant. Typical raw sewage sludge has a moisture content of approximately 95%, but these samples were analysed after thermal drying. The dry sludge, on average, consists of 65% organic and combustible components and 35% ash. The samples had a low carbon content (approximately 30%), with SS3 the lowest, and a high oxygen content. The H, N and S contents are different from those of coal, with relatively high values for nitrogen and sulphur. SS3 sludge had the highest sulphur content (1.1 wt.%), whilst the SS1 sludge has the highest contents of hydrogen and nitrogen. The sewage sludge is characterised by a much lower HHV than coal, because of the former's higher inorganic content and also because of the high oxygen content. The calorific value of sewage sludge is determined by its moisture, ash and oxygen contents, with the drying process having a direct impact on the calorific value. SS1 sample has the highest value (13.12 MJ/kg) of HHV for 32% ash. Otero et al. (2007), Garcia et al. (2013), and Soria-Verdugo et al. (2013) have shown comparable values of chemical composition and HHV for sewage sludge.

4.2. Thermal analysis results

Figs. 1–4 present the TG and DTG data for coal and sewage sludge samples in oxidising (synthetic air: 20% oxygen and 80% nitrogen) and inert (argon) atmospheres. The coal DTG curves, Fig. 1, shows typical coal combustion profiles with the only peak between 330 °C and 660 °C, resulting from decomposition of all