CHEMICAL ENGINEERING TRANSACTIONS

VOL. 29, 2012

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Hon Loong Lam, Jiří Jaromír Klemeš

ISBN 978-88-95608-20-4; **ISSN** 1974-9791 DOI: 10.3303/CET1229115

Combustion Behaviour and Products of Dried Sewage Sludge – Prediction by Thermogravimetric Analysis and Monitoring the Co-incineration Process in a Cement Factory

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On WWTP Ljubljana the main by-product of municipal wastewater treatment is the sewage sludge. It contains a high share of organic matter and can therefore be, after drying, utilized as an alternative solid fuel in large combustion plants. In the range of preformed physico-chemical tests of pellets, information was obtained about the elemental composition of biomass (macro and micro), its calorific value, volatile matter and ash content as well as behaviour at the repeated oxidative and reductive conditions at combustion (thermogravimetry supported by QMS). By measuring with TGA during programmed combustion of the pellets in an inert (argon) and oxydative (argon-oxygen) atmosphere, the mass balance of the sample was monitored, precisely the amount of the gas phase. QMS analysis was performed to determine which gaseous components had been formed. DTA measurements gave us an information on the heat balance at each stage of thermal decomposition of sewage sludge. An evaluation of environmental impact is complemented by a practical experience of the thermal utilization of this kind of waste - by co-incineration process in a cement factory.

1. Indroduction

With the treatment capacity of 360,000 PE Ljubljana's Central Waste Water Treatment Plant (further on WWTPL) produces sewage sludge as the largest share of its wastes. Pre-treatment of aerobic biomass is followed by an anaerobical stabilization at mesophilic conditions, mechanical dehydration of the digestate on the centrifuge with the addition of cationic polymer to 20-23 % dryness and drying with hot air up to 90 % dry matter content. A non-hazardous waste in the form of pellets with a diameter of 2 mm to 4 mm is obtained as a final product of the biomass treatment. According to EWL the classification number 19 08 05 has been assigned to this waste (further on pellets).

2. Experimental part

On WWTPL, an extensive analysis of the pellets has been carried out in order to obtain the necessary information for their statistically based specification. Periodical physical and chemical testing of the pellets provides an information about the principle process characteristics as moisture, ash and volatile's content, calorific value and the elemental composition of pelletized biomass (macro and

Please cite this article as: Mislej V., Novosel B., Vuk T., Grilc V. and Mlakar E., (2012), Combustion behaviour and products of dried sewage sludge – prediction by thermogravimetric analysis and monitoring the co-incineration process in a cement factory, Chemical Engineering Transactions, 29, 685-690

micro). With the thermogravimetric analysis (TGA) it was determined the behaviour of pellets when exposed to thermal treatment. The measurements were performed in inert and oxidative atmospheres. The apparatus for coupled TGA analysis consists of a part for thermal analysis, which is coupled to the quadrupolar mass spectrometer (Pfeiffer catalogue, 2005) for the gas phase. The apparatus for simultaneous thermal analysis enables the acquirement of results from TG, DTG and DTA measurements; it also enables the maintenance of a controlled temperature programme.

2.1 Physico-chemical and thermal analysis of representative annual sample of pellets

On WWTPL, in accordance with *the Regulation on the processing of non-hazardous waste into solid fuel* (Ordinance 2008), a regular quality control of pellets takes place, based on the preparation and analysis of representative samples from each consignment shipment to the final pellets processor. From partial daily samples, monthly composite samples are made and tested. Similarly, representative annual composite samples were prepared from the refrigerated monthly samples. The composite annual samples were then ground to < 1 mm by a hammer mill Retsch SK1 and – when necessary - < 0.2 mm on a mill Retsch ZM 200. In this way the annual pellets samples of the years 2009-2011 were prepared, the results of the analyses of the yearly sample 2010 are presented in the Tables 1 (Grilc, 2011).

Table 1: General parameters of the annual sample 2010 (Grilc, 2011)

parameter	Given as	Temperature interval	Unit (as received)	method	results
Dry matter	-	105 °C	%	CEN/TS 15414	91.3
Moisture	-	105 °C	%	CEN/TS 15415	8.7
Ash content	-	550 °C	%	EN 15169	34.1
Loss on ignition	-	550 °C	%	EN 15169	57.2
Ash content	-	900 °C	%	CEN/TS 15403	30.3
Volatile matter	-	900 °C	%	CEN/TS 15403	61.0
Upper calorific value	-		MJ/kg	CEN/TS 15400	13.089
Net calorific value	-		MJ/kg	CEN/TS 15400	11.783
TOC	C		%	ISO 609:1998 and 10693:1996	26.5
Nitrogen	N		%	ISO 11261-mod.	4.47
Hydrogen	H		%	CEN/TS 15407	4.17
Chlorine	Cl		%	ISO 9298	0.010
Sulphur	S		%	ISO 351	0.76

2.2 Simultaneous thermal analysis of pellets and mass spectroscopy of the gases

The conditions used for EGA measurements:

- Initial mass of sample: 100,00 mg to 100,40 mg, heating rate: 10 K/min, temperature range 25 °C to 1200 °C (inert atmosphere, Argon 99.999 vol %); 25 °C to 1000 °C (oxidative atmosphere, Ar-O2 99.999 vol %, 80.0 vol % - 20.0 vol %); both from Messer, Slovenia,
- Gas flow through the micro reactor was 50 mL/min. Gas line from apparatus Netzsch STA409 to Pfeiffer PrismaPlus QMS 220 Quadrupole Mass spectrometer,
- Heated quartz capillary (outer diameter 0.35 mm, inner diameter 0.25 mm, length 1 m), temperature 130 °C, inlet pressure 1 mbar, working pressure 1.25x10-6 mbar ± 5x10-9 mbar, Faraday cup detector, scanning rate 100 ms/AMU,
- Al_2O_3 crucibles, 300 µL,
- Reference material Al_2O_3.

2.2.1 Combustion behaviour in the Ar-atmosphere

- In an inert atmosphere, the decomposition of the pellets takes place in at least three stages. Thermal decomposition was not completely finished, the degradation of the sample was not conclusive, weight loss was 60.4 %. TG and DTG analysis (Figure 1):
- In the first stage, within 25 °C to 185 °C, there is a loss of moisture (H_2O). In the second stage, from 185 °C to 405 °C, there was more likely that more parallel or simultaneous

reactions were occurring, or overlapping signals of thermal degradation within the temperature range from 160 °C to 560 °C were followed, which is shown in DTG curve. The third stage, from 405 °C to 835 °C, proceeds intensely between 600 °C and 830 °C, but from the TG and DTG curves, we see that the decomposition at 1200 °C is not yet complete, because TG curve still shows a weight change as a function of time and temperature of thermal decomposition (TG ≠ const., DTG ≠ 0, Figure 1). Simultaneously the DTA curve was scanning too, which has two distinct diffraction, the first peak at 134.6 ^{o}C.

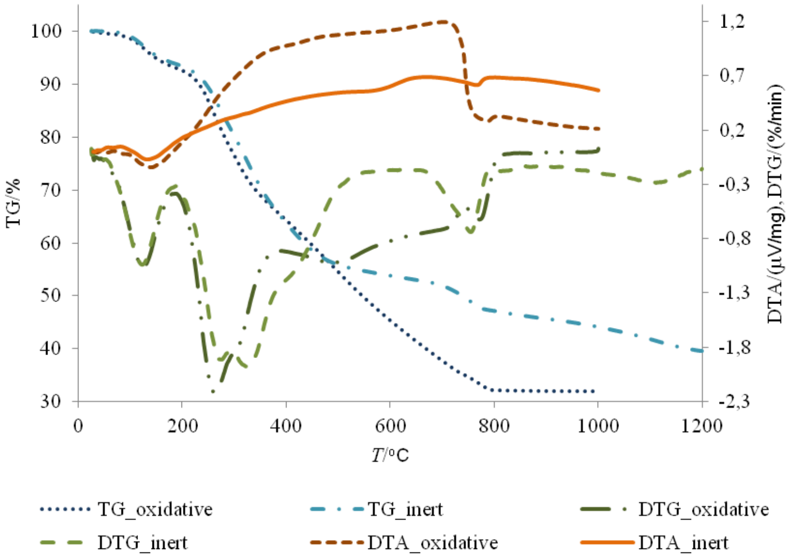

Figure 1: Thermogram of the process of the thermal treatment of pellets in an inert and oxidative

An endothermic change was observed, indicating a probable dehydration process, because there is a concurrent loss of weight and an endothermic reaction. At 745 °C there is again an endothermic peak. Between these temperatures, in other words endothermic changes, there is a subdued exothermic change. Evaluation of the signals of the mass spectrum (Table 2, Figure 2) shows that in the first stage, from 25 °C to 185 °C, the weight is reduced, releasing the water (signal for the mass number 18 m/e) with endothermic DTA signal with a peak at 134.6 °C (evaporation of moisture, H_2O). In the second stage, from 185 °C to 405 °C, the weight is decreasing again, releasing the water (H_2O, crystalohydrate dehydration) and simultaneously released gas with a mass number 44, which may be CO_2 or $C_3H_8^+$ or a C-H compound, hydrocarbon, which is a product of pyrolysis of organic components, which - according to the temperature range - makes more sense. In the third stage, 405 °C to 835 °C, within this temperature range, hydrogen is released, H_2, very intensely up to 835 °C, we detected two signals or two-stages of the releasing of hydrogen, H_2. In between gas product of the mass number of 15 m/e is also released, which could be attributed to CH_3^+ (pyrolysis of C-H compounds) or NH^+. Ammonium compounds are relatively thermally unstable, so the signal can be attributed to the presence of NH_4Cl in the sample or the signal for NH^+. The analysis of the released gas products (Figure 2) indicates the traces of some volatile compounds as well (Table 2).

On the TG (mass loss of the sample) and DTA curves (endothermic reaction) in the temperature range from 600 °C to 835 °C (Figure 1, Figure 2) we see a distinguished change and a signal for the release of the gas of mass number of 44 m/e, which is most likely CO_2 (Figure 2), since the decomposition is endothermic and in a suitable temperature range for the decomposition of carbonates, namely $MgCO_3$ and $CaCO_3$.

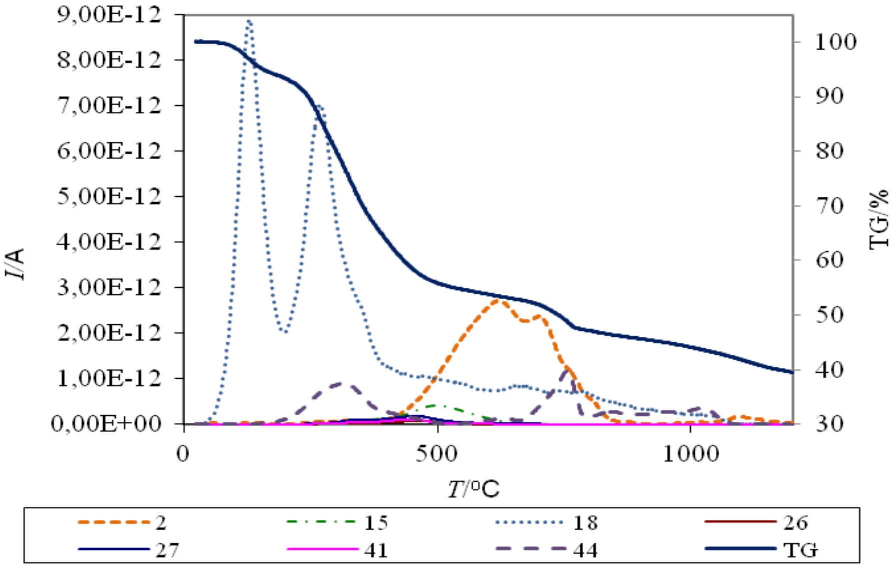

Figure 2: Gas products resulting from thermal treatment of pellets in an inert atmosphere

Gas product with mass number 44 m/e in a temperature regime between 185 °C and 560 °C is not the same as the gas that is released into the T-regime between 600 °C and 835 °C . Gas product of the T - range of 185 °C to 560 °C is probably due to decomposition of volatile fatty acids. In the second stage the key fragment of 44 m/e is almost certainly CO_2 from the decomposition of $MgCO_3$ and $CaCO_3$. This stage is also repeated in the thermal decomposition of the sample in an oxidative atmosphere - incineration in an atmosphere of: Ar :O_2/80: 20 (Figure 3).

2.2.2 Combustion behaviour in an Ar-O_2 atmosphere, incineration

In an oxidative atmosphere, the decomposition took place in at least two stages. Thermal decomposition occurred completely, the decrease of the final mass loss was 68 % (Figure 1). First stage takes place in the T-range from 40 °C to 170 °C with the evaporation of moisture (H_2O). This stage is relatively undistinguished and in it we noticed an endothermic DTA signal which has a peak at 125 °C. Second stage takes place in the T-region from 170 °C to 800 °C. Here begins a specific decomposition of the sample, which certainly takes place in a wider range of T – range and up to 800 °C. This decomposition is an exothermic reaction, except at T = 770 °C, where a smaller signal was noted for an endothermic reaction. This endothermic peak is less distinguished but significant. The decomposition of the sample in an oxidative atmosphere ends at 800 °C with a mass loss of 68 % (Figure 1).

Evaluation of the mass spectrum or in other words the signal analysis of the released gas products (Figure 3) shows that in the first stage, between 40 °C to 180 °C, the key fragment 18 m/e is detected. The course of decomposition is consistent with the previous statements, which means that water is released from the sample in a form of humidity and probably as well as capillary bound water. During thermal treatment of the sample, whether it's in an inert or an oxydative atmosphere, the water behaves the same way. In the second stage, between 180 °C to 800 °C an exothermic reaction takes place, key fragment of 18 m/e is detected, at the combustion of C-H compounds, CO_2 and H_2O are emitted, there is a large amount of water, in the beginning there is more water and less CO_2. Water that is released in the process of thermal treatment is not only the result of C-H combustion, but also of releasing crystalline bounded water. H_2O and CO_2 are released in the T-range up to 740 °C. In the last part of the thermal decomposition of the sample, in the range from 740 °C to 800 °C, only CO_2 is produced. At this time, at the DTA curve, an endothermic reaction is detected. This signal is a consequence of the decomposition of $MgCO_3$ and $CaCO_3$ with a peak at 731 °C. Carbonates are a consequence of the intake of municipal waste water, which has the hardness of 14 °N to 18 °N.

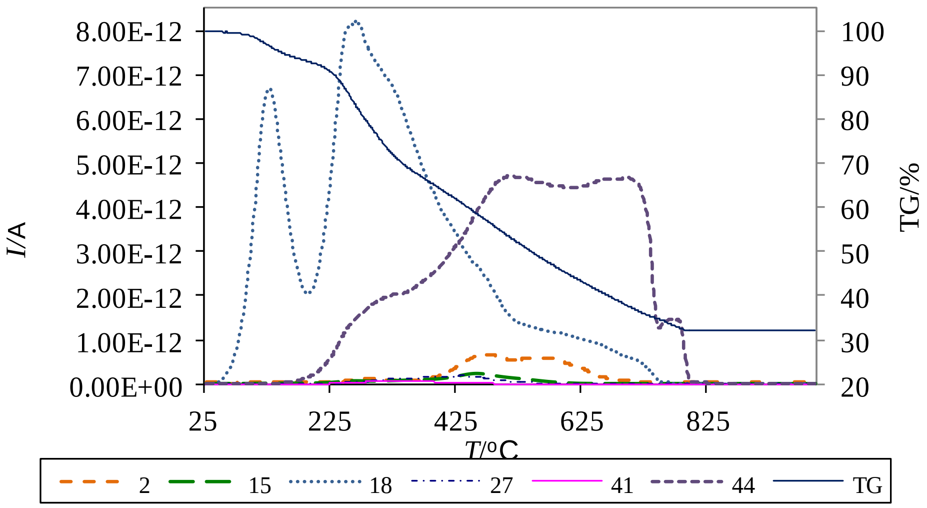

Figure 3: Gas products resulting from thermal treatment of pellets in an oxidative atmosphere

3. Discussion

Evolved gas (Pfeiffer catalog, 2005) analysis was used for the purpose of determining combustion behaviour and gas products during thermal treatment of dried sewage sludge (Table 2) . We observed (Figure 1) pellets mass changes in different combustion atmospheres is considerably different and heat changes in the time of thermal loading.

Table 2: Analysis of combustion behaviour of pellets during pyrolysis and incineration

Atmosphere	Temperature range	Key fragment	Mass loss	Mass loss
	°C	AMU	%	%
Ar	25 - 185	18	- 6.09	- 60.43
(pyrolysis)	185 - 405	the main signals: 18, 44; traces: 27,15, 39, 29,41, 26, 2	-30.86	
	405 - 835	the main signals: 18, 2, 44, 15; traces: 27, 41, 26, 29, 39,	-16.50	
	835 - 1200	the main signals: 18, 44; trace: 2	-6.98	
Ar-O_2	40 - 170	18	-6.07	- 67.96
(incineration)	170 - 800	the main signals: 18, 44, 2; traces 15, 27, 29, 41, 26, 39	-61.68	
	800 - 1000	-	-0,21	

Carbon can be, in the thermal oxidative process, released from the sample in the form of CO_2 and C-H. In the sample MgO and CaO remained. Carbon can be, in an inert thermal process, released from the sample in the form of CO_2 and C-H. The residue contains C, C-H, MgO, CaO and SiO_2. Inorganic fraction of CO_2 can be seen in both atmospheres of the thermal treatment.

For water we have two sources in the sample. As water originally present as moisture, capillary and crystal bounded water. The second source is combustion of different forms of hydrocarbons, C-H compounds.

Hydrogen, H_2, can be in the thermal oxidative process released from the sample in the form of H_2O as a source component, such as water, originally present in the sample in the form of moisture or as capillary or crystally bound water. The second form is H_2O, as a result of combustion of hydrocarbons. Hydrogen can be, in an inert thermal process, released from the sample in the form of H_2O as a source component, such as water, present in the sample in the form of moisture or as capillary or crystal bound water. Other forms, released in the thermal process under inert atmosphere are:

- various organic gaseous products in the form of C-H compounds such as hydrocarbons,
- NH^+, as a result of thermal decomposition of various ammonium salts,
- molecular hydrogen, H_2, the signal is more distinguished than in an oxidative atmosphere.

4. Co-incineration of dry sewage sludge in a cement kiln

The final utilization of pellets from WWTP Ljubljana is performed in a cement kiln. In recent years this kind of final utilization of dried sewage sludge has become conventional in this industry. In most cases, the sludge represents a minor part of the kiln energy supply. In the cement factory Salonit Anhovo, the system for pellets utilization consists of a storage silo of 140 m^3, where helical transporters are placed at the bottom, providing continuous emptying of the silo. From the silo, material is led over a scale by means of pneumatic transport, that feeds the material into the main burner. In this way, the material is inserted into the core of the flame, where it burns. The flame temperature is estimated to range between 1800 °C - 2000 °C. The sewage sludge contains a high percentage of ash (32-40 %), which is then incorporated into the cement clinker - a product of the cement kiln. Therefore no waste is generated with the sludge usage.

The nominal system capacity of the pellet supply is 3 t/h, which would represent 5-7 % of the heat input to the furnace. In practice, such high dosage is impossible due to the relatively low calorific value of sludge (~10 MJ/kg, Grilc, 2011), which does not provide sufficiently high temperatures in the process. Therefore, about 1 t/h is used in practice. At this level, there are no major problems with the usage, technologically speaking. In addition to the sludge from the WWTPL, a few similar materials from other sources are used.

Prior to the regular use of sludge, the cement factory conducted a prolonged trial test. During this time, technological and environmental acceptability was estimated. In this period, it was found that in the tested extent of usage, there were no notable impacts on the emissions from the cement factory (Mlakar and Vuk, 2009). Cement factory regularly monitors the emission values of its surrounding as well. Even at these levels there were no notable negative effects.

To ensure a safe and economical usage of sewage sludge, a permanent control of input materials is required. In the case of sludge usage, experience has shown that the following is very important - material moisture, ash composition and calorific value. All these characteristics have a significant impact on the utilization and the final product quality. Therefore, all these parameters are monitored and according to the values obtained, technological parameters and methods of usage are adapted.

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