A Thermogravimetric Study on Tannery Sewage Sludges

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Abstract: Two different tannery sewage sludges (sludge 1 and sludge 2) have been characterized by thermal analysis coupled with mass spectrometry of evolved gases (TG-DSC-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), Gas chromatography - mass spectrometry (GC-MS), Purge and trap GC-MS. Four main temperature ranges of weight loss are individuated in air flow TG-DSC-MS experiments on sludge 1. The first, below 200°C, coupled to an endothermic signal, is related to water release. Between 200 and 350°C, an exothermic signal accompanies the loss of sulphate as evolved SO_2, and organic substances, aromatics and saturated cyclic compounds. In the latter range, development of CO_2 was also observed, that becomes prevalent in the range 350-600°C. From 600 to 700°C carbon dioxide coming from carbonate decomposition was observed. On sludge 2 three main temperature ranges of weight loss are present, below 150°C, between 150 and 350°C and from 350 to 600°C, attributed, respectively, to water, sulphate, CO_2 plus aromatic and carbonylic compounds releases. A larger amount of Cr and Al was found by ICP-AES on sludge 2. The differences between the samples evidence the influence of the different composition of the parent wastewater and of the depuration process. The influence of additives on combustion profiles has been also evaluated. Catalyst addition to the sludge results to reduce the emission of cyclic and aromatic substances, to lower temperature and to increase the oxidation rate of the organic fraction combustion.

Key words: tannery sewage sludges; thermal behavior; TG-DSC-MS; ICP-AES; GC-MS; Purge and trap GC-MS.

1 Introduction

The sewage sludge constitutes the major byproduct of wastewater treatment plants [1]. Sewage sludge typically consists of a heterogeneous mixture of organic and inorganic materials [2-4].

The composition and characteristics of sewage sludge depend mainly from the origin of the wastewater. In Italy, the wastewaters produced during the tanning process are usually collected to central industrial wastewater treatment plants. The most common treatment foresees of coagulation-flocculation and activated sludge biological oxidation steps. Even using the same wastewater treatment process, some parameters as the flocculation agent or the stabilization temperature of the sewage sludge may imply differences in the sewage sludge composition. The excess sludge produced during the treatment process contains the pollutants removed from water and it is still a waste to treat and dispose off [5]. Typical disposal processes for sewage sludge from tannery wastewater are landfilling and thermal conversion (combustion, incineration, and pyrolysis). Due to land limitations and risks of groundwater contamination, stringent regulations result in costs increasing for landfilling. With respect to the latter, thermal conversion presents many advantages, such as reduction of mass and volume of solid waste and energy recovery from the organic sludge fraction, determining lower disposal costs. Anyway, careful evaluation has to be performed

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in waste-to-energy plants, due to successive necessity of ashes disposal and potential relevant emissions of atmospheric pollutants [6]. In this perspective, the aim of this work was to characterize two different tannery sewage sludges by chemical and thermal analysis coupled with mass spectrometry of evolved gases (TG-DSC-MS), to evaluate the potential environmental impact of combustion/incineration process by, identifying the substances released during the thermal treatment. The influence of additives on combustion profiles was also studied.

2 Experimental

2.1 Materials

Tannery sewage sludges (sludge 1 and sludge 2) were obtained by two different italian tannery wastewaters central plants. A catalyst additive (UNISASSIP [7]) with a specific surface area of 80 m^2/g was used to improve the combustion of the tannery sewage sludges.

2.2 Sludges Characterization

2.2.1 Moisture, Inorganic and Organic Matter Analysis

Moisture content was evaluated by gravimetric analysis of samples before and after an isothermal treatment at 100°C ± 2°C up to achieving constant weight.

Total ashes percentage was obtained by weighing the inorganic residue after isothermal treatment at 550°C for 8 hours. Finally, the organic matter was calculated by difference with the moisture and inorganic matter content in the samples.

2.2.1 ICP-AES Analysis

The mineral content was analyzed by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) Liberty Series II Varian with axial torch. The samples were analyzed after acidic digestion.

2.2.2 GC-MS Analysis

The organic fraction of sludge was analyzed by GC-MS after solvent extraction (hexane). By cool-on-column injector the sample was introduced into GC column (Restek Rtx-5ms, 5% diphenyl and 95% dimethyl polysiloxane, 0.25 mm ID, 30 meter), then the separated compounds were analyzed by a Quadrupole Mass Selective Detector (HP 5973).

For the analysis of volatile compounds a Purge and Trap (P&T) device has been used to introduce samples into the GC-MS. The target analytes were extracted and introduced into an airtight chamber. The volatile compounds are drawn along a pressure gradient (caused by the introduction of the purge gas) out of the chamber and are collected by the trap, that is then heated and the sample compounds are introduced to the GC column (Restek Rtx-624, 6% cyanopropylphenyl and 94% polysiloxane, 0.25 mm ID, 60meter) via split/splitless inlet system.

2.2.3 TG-DSC-MS Analysis

The thermal behavior of samples as a function of temperature was determined by an air flow simultaneous TG/DSC thermal analyser (SDTQ600, TA Instruments), coupled to a mass detector of the gas evolved from the thermal analyzer in the range m/z = 15-103 (Pfeiffer Vacuum Benchtop Thermostar). Measurements were carried out on about 30 mg of sample in 100 (stp) cc/min air flow (chromatographic grade) at 10 °C/min heating rate in the temperature range of 20-1000 °C.

TG-MS analysis was also carried out on a mixture of sludge and catalyst additive UNISASSIP (sludge-catalyst mass ratio of 6.7) prepared by careful grinding in an agate mortar to obtain an intimate contact.

3 Results and discussion

3.1 Sludges Composition

The analytical results obtained for sludge 1 and 2 are shown in Tab.1. The two samples are mainly constituted by water (which represents the portion loss at 102°C) and organic matter, while the inorganic matter (residue at 550°C) is present in a smaller, but not negligible, percentage. The pH values are around the neutrality (between 6 and 8 pH units). Water content in the sludges results quite different because of the different drying process by which they are obtained. With regard the organic matter, the sludges are predominantly constituted of fatty substances and non aromatic hydrocarbons (C>12) according to the materials used during the tanning process. The comparison of the two sludges evidenced slight higher organic substance content for sludge 2 (Tab.1, dry basis).

Tab. 1 Results of analytical tests on sludge 1 and sludge 2

Characteristic	Unit	Sludge 1 Wet basis	Sludge 2 Wet basis	Sludge 1 Dry basis	Sludge 2 Dry basis
Moisture and volatile matter at 102°C	wt%	8.5	46.5	-	-
Inorganic substances residue at 550 °C	wt%	30	14	32	27
Organic substances	wt%	62	39	68	73
pH	pH	6.8	7.7	6.8	7.7
Al	mg/Kg	15685	12459	17143	23288
Cr	mg/Kg	18962	22202	20723	41499
Fe	mg/Kg	6550	2456	7159	4591
Cr VI	mg/Kg	< 0.02	< 0.02	< 0.02	< 0.02
Cu	mg/Kg	69	17	75	32
Zn	mg/Kg	1559	377	1703	705
Mn	mg/Kg	72	11	79	21
Total oils and fats	mg/Kg	160940	77531	175891	144918
Alcohols and fatty acids	mg/Kg	5.110	4.780	5.554	8.935
Polycyclic aromatic hydrocarbons (PAHs)	mg/Kg	2.6	17.6	3.0	33.0
Aromatic solvents	mg/Kg	1.8	0.3	2.0	1.0
Chlorinated solvents	mg/Kg	1.3	0.0	1.0	0.0
Carbonylic compounds	mg/Kg	3150	46	3443	87
Phenols	mg/Kg	812	41	887	76
Benzoalkanes	mg/Kg	952	356	1040	665
Chlorinated alkanes with long chain	mg/Kg	-	61	-	114
Organic nitrogen compounds	mg/Kg	521	3.7	569	7.0
Non-aromatic light hydrocarbons (C<12)	mg/Kg	12	31	14	57
Non aromatic heavy hydrocarbons (C>12)	mg/Kg	7940	4928	8678	9211

Aromatic solvents are present in very small quantities, while the not-negligible amount of other kinds of aromatic compounds, such as benzoalkanes, can be correlated to their use as surfactants for fatliquoring mixtures, waxes and other finishing compounds in the leather processing. Non-aromatic hydrocarbons (C<12) are detected in low amounts, with values ranging between 12.5 and 30.6 mg/Kg. For both sludges the most representative components of the inorganic fraction are trivalent chromium (Cr^{3+}), aluminum (Al) and iron (Fe). The abundance of chromium in the sludge depends of the initial composition of wastewater, as they are collected and equalized, i.e. from the prevalent tanning process in the relative industrial district. A higher amount of Cr was found in sludge 2 (see Table 1, dry basis values).

The presence of aluminum and iron in the sludges strongly suggests that iron and aluminum salts, such as $FeSO_4$ and $Al_2 (SO_4)$ have been used as coagulants agents during primary treatments to allow the precipitation of suspended substances, although they can derive, in small quantities, also from the tanning industry.

3.2 Sludges Thermal Behavior

TG-MS analyses in air were carried out with the aim to characterize the combustion behaviour of sludges. Four main temperature ranges of weight loss can be individuated for sludge 1 (Fig. 1a).

The first, below 200°C, coupled to an endothermic signal, is due to water release (m/z = 18). From 200 to 350°C, an exothermic signal accompanies the loss of sulphate (evolved as $SO_{2,}$ m/z = 48, 64) and CO_2 (m/z = 44).

Despite the presence of air in the reaction medium, besides the release of CO_2 (m/z = 44) the combustion of sludge 1 is accompanied by organic substances release, together with aromatic and cyclic hydrocarbons (m /z = 78, 100, 101) and carbonylic compounds relevant to signal m/z = 43 and m/z = 58. In the range 350-600°C, the development of CO_2 becomes prevalent. In the last range, between 600 and 700°C, CO_2, coming from the endothermic inorganic carbonates decomposition, is observed.

For sludge 2, three main temperature ranges of weight loss are present (Fig. 1b). The first below 150°C is attributed to water release, the second, from 150 to 350°C, to the presence of sulphate identified by 48 and 64 m/z fragments. The last, exothermic loss, between 350 and 600°C, is due to organic substances release (m/z = 43, 58), aromatic hydrocarbon (m/z = 78) and carbon dioxide (m/z = 44).

The combustion profiles differences between the samples arise from the different composition of the parent wastewater and of the depuration processes.

With the aim of improving the efficiency and selectivity of the sludge combustion, the possibility of using additives to improve combustion behaviour was investigated (Fig. 2).The addition of UNISASSIP to the sludge 1 caused a dramatic improvement of the combustion performance: the peak temperature of the organic fraction combustion decreased from 292°C for sludge 1 alone (Fig. 2) to about 264°C in the presence of UNISASSIP (Fig. 2). Similar results were obtained on sludge 2 (the peak temperature of combustion decreased from 358°C for uncatalysed to about 320°C for catalysed combustion. Moreover, the peak combustion rate (maximum value of derivative weight peak) strongly increased for the catalysed combustion of sludge: from 6%/min in the absence of catalyst to about 24 %/min for sludge 1, and from 2%/min to 14%/min for sludge 2. It is worthwhile to note that in the catalytic combustion of sludge we found an evident decrease of the amount of released cyclic compounds and aromatics (m/z = 78,100) in the evolved combustion gases, since they are selectively oxidized to CO_2. Therefore, a significant reduction of emissions of those substances to the atmosphere is also obtained.

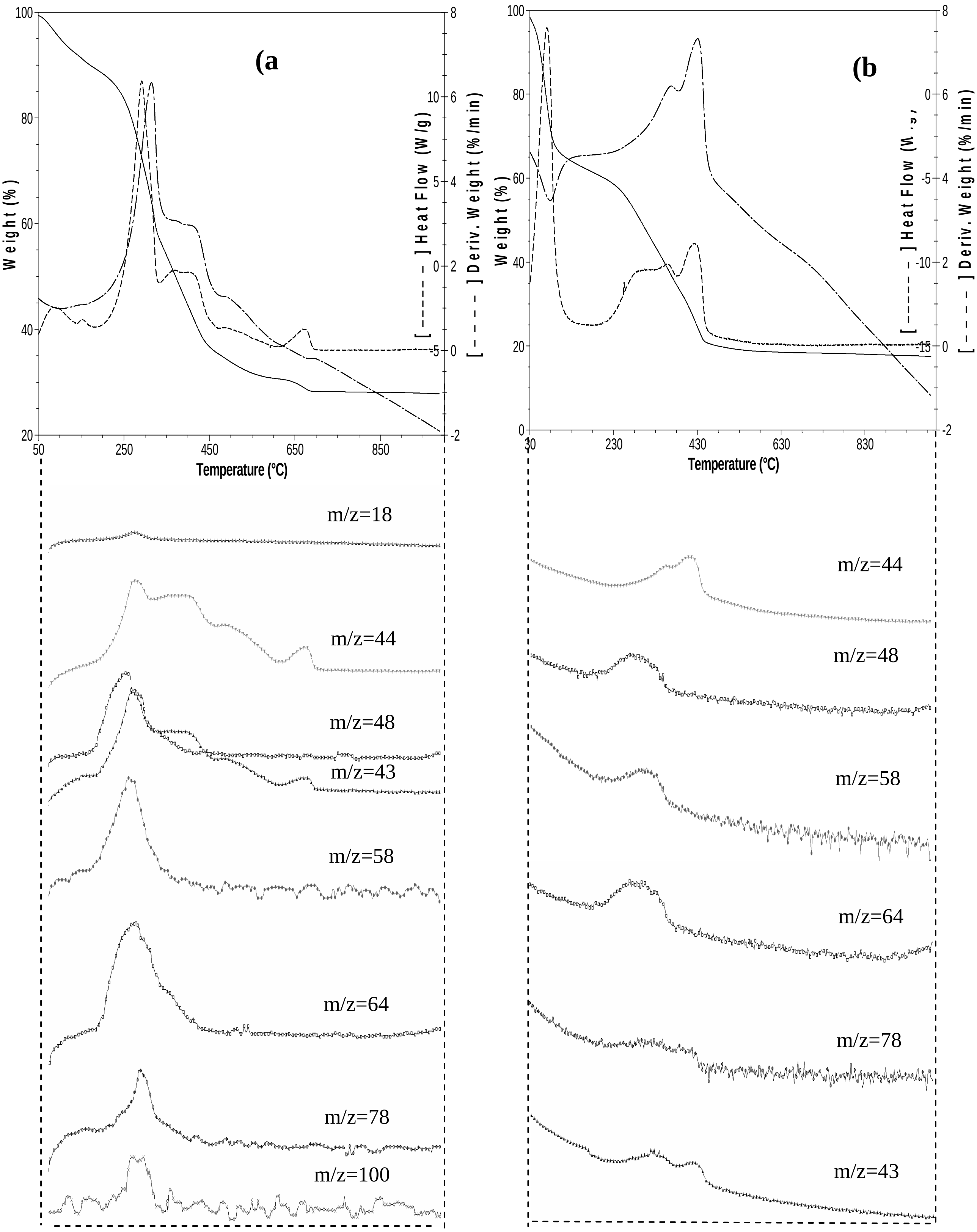

Fig. 1 TG-MS results on sludge 1 (a) and sludge 2 (b)

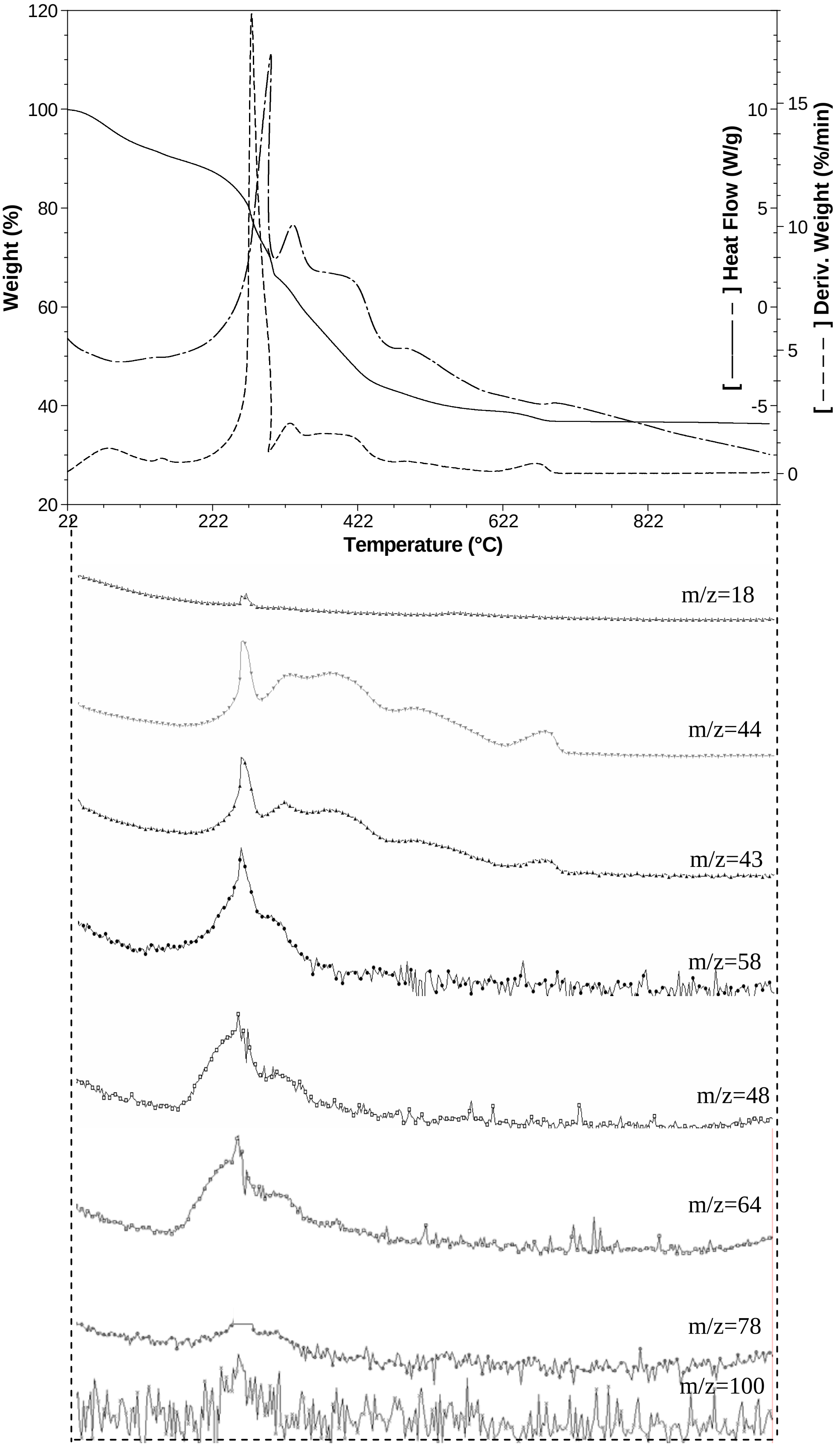

Fig. 2 TG-MS results on sludge 1 mixed with additive UNISASSIP

4 Conclusions

Two different tannery sewage sludges have been characterized by thermal analysis in air flow coupled with mass spectrometry analysis of evolved gases (TG-DTG-MS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), gas chromatography-mass spectrometry (GC-MS) and purge and trap GC-MS. Experimental results have shown the presence in both samples of organic substances and the release of aromatic and cyclic hydrocarbons during their combustion. The oxidation behavior was influenced by the different composition of the parent wastewaters and of the depuration processes. Successful attempt to improve the thermal behavior of the organic fraction, increasing the selectivity to CO_2 and thereby avoiding the emission of pollutants, was performed by adding a catalyst as oxidation promoter. Catalyst addition to the sludge caused positive effects for both samples, either with regard to the selectivity of the process by reducing the emission of cyclic and aromatic substances, either with respect to the operating conditions, resulting in lower temperature for the combustion process and higher the oxidation rate of the sludge organic fraction.

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[7] UNISASSIP, material under patent procedure.