Available online at www.sciencedirect.com
ScienceDirect

Thermochimica Acta 454 (2007) 135–143

thermochimica acta

www.elsevier.com/locate/tca

Evaluation of the aerobic composting process of winery and distillery residues by thermal methods

F.C. Marhuenda-Egea [a,*], E. Martínez-Sabater [a], J. Jordá [a], A. Sánchez-Sánchez [a], R. Moral [b], M.A. Bustamante [b], C. Paredes [b], M.D. Pérez-Murcia [b]

[a] *Department of Agrochemistry and Biochemistry, University of Alicante, Ctra San Vicente S/N, E-03080 Alicante, Spain*
[b] *Department of Agrochemistry and Environment, Miguel Hernandez University, EPS-Orihuela, Ctra Beniel Km 3.2, 03312-Orihuela (Alicante), Spain*

Received 10 May 2006; received in revised form 11 January 2007; accepted 12 January 2007
Available online 19 January 2007

Abstract

The possibility of using thermal analysis for a quick characterization of chemical changes was tested in the organic matter from composting materials. Differential thermal analysis (DTA), thermogravimetry (TG) and the first derivative of the TG (DTG) were calculated in oxidizing conditions on compost samples obtained from three composting piles. The composting piles were made by mixing winery and distillery residues with sewage sludge (pile 1), with cow manure (pile 2) and hen droppings (pile 3). The temperature values in the pile 1 showed a different evolution during the thermophilic stage of the composting process in relation to the piles 2 and 3. The thermophilic stage for pile 1 was 17 days, meanwhile for the piles 2 and 3 were around 80 and 110 days, respectively, and probably pile 1 was not well composted. The curves of ion current of CO_2 have been recorded in order to shed light on changes occurring in organic matter during composting. Particularly DTG curves allowed us to distinguish between well (piles 2 and 3) and poor (pile 1) stabilized organic matter. The energy released was calculated for each sample by integrating the DTA curves and these results are agreed with the previous hypothesis. Information deriving from weight losses, registered by the TG and DTG curves, enables to follow the evolution state of the organic matter and therefore changes in its stability. These data could determine the final point of the composting process of winery and distillery residues and then reduce the time for compost harvest.

Keywords: Winery residues; Compost; Aerobic digestion; Differential thermogravimetry; Differential thermal analysis

1. Introduction

Composting of agricultural and urban residues such as winery and distillery residues (WDR) is an useful method for producing a stable material, which can be used as a source of nutrients and as a soil conditioner in the field [1]. Part of the organic matter is mineralized into carbon dioxide, ammonia and water during composting, and part is transformed into refractory humic substances. In the agriculture field a process for rapid conversion of fresh organic matter into humus is available for commercial purposes [2]. The composting technique is an accelerated version of the processes involved in the natural transformation of organic debris in soil, and can be obtained through the provision of the most favorable conditions for microbial activity [3]. This process needs controlled conditions, particularly moisture and aeration, to reach favorable temperatures for thermophilic microorganisms, to decompose the organic substrate and to transform it into stabilized organic matter. It is a complex microbial process that comprises self-heating, multistage temperature conditions and different microorganisms [4]. The understanding of organic matter transformation throughout the composting process and the proper evaluation of compost stability and maturity are essential for a successful utilization of compost [5]. Compost quality is defined by its stability and maturity. Stability is related to the level of biological activity of the compost and depends on the degree of degradation achieved during the composting process and maturity is related to the lack of phytotoxicity on vegetation growing in the soil treated with compost [6,7].

New analytical methods and well established methods with new applications get insight into the compost samples, such as thermal methods, contributing to a better understanding of the

* Corresponding author. Tel.: +34 965903525; fax: +34 965903880.
E-mail address: frutos@ua.es (F.C. Marhuenda-Egea).

0040-6031/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2007.01.015

decomposition and stabilization processes that take place. Thermal degradation techniques, such as thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA), have been applied for many years to elucidate structural features of decayed natural heterogeneous organic matter [8,9], providing important information about the chemical characteristics of the sample [10].

The objective of the present study is to verify the previously assessed applicability of thermal analyses in order to determine the stability and maturity of compost elaborated with WDR from real agricultural activities in industry. Thermogravimetry (TG/DTG) and differential thermal analysis (DTA) are combined with the information from the mass spectrum of evolved gases.

2. Materials and methods

2.1. Composting procedure

Three different piles were prepared by the Rutgers static pile composting system, using in all of them wastes from the winery and distillery industry. Pile 1 was initially prepared with mixtures of grape stalk (GS), grape marc (GM) and exhausted grape marc (EGM) and after 17 days sewage sludge (SS) was added as source of microorganisms and nitrogen (about a 29% of fresh weight of the pile). Pile 2 and pile 3 were elaborated using exhausted grape marc (EGM) and cow manure (CM) and poultry manure (PM), respectively (Table 1). SS came from a treatment plant of urban wastewater placed in Torrevieja (Alicante, Spain). CM was collected from a cattle farm placed in Santomera (Murcia, Spain) with a productivity of 35,000 heads per year. PM was collected from a poultry farm with 30,000–40,000 laying hens located in Orihuela (Alicante, Spain). GS and GM were collected from a winery placed in Jumilla (Murcia, Spain) and EGM from an alcohol distillery placed in Villarrobledo (Albacete, Spain).

The mixtures (about 1800 kg weight each) were composted in a pilot plant, in trapezoidal piles (1.5 m high with a 2 m × 3 m base); thereafter, a forced aeration conducted through three basal PVC tubes (3 m length and 12 cm diameter) was applied. Aeration system was imposed for 30 s every 30 min, at 55 °C as ceiling temperature for continuous ventilation. Turning treatments for improving both homogeneity and fermentation processes were applied when necessary (Table 1). After 17 days, the pile 1 was amended with 735 kg of sewage sludge (SS) (228 kg of dry matter).

Table 1
Characteristics of the composting heaps

Waste[a]	Composition[b]		
	Pile 1[c]	Pile 2	Pile 3
GS	63 (56)	–	–
EGM	25 (28)	70 (80)	70 (79)
GM	12 (16)		–
CM	–	30 (20)	–
PM	–	–	30 (21)
Turning (days)	18–53–86	92	144

[a] GS: grape stalk; EGM: exhausted grape marc; GM: grape marc; CM: cow manure; PM: poultry manure; SS: sewage sludge.
[b] Data expressed as percentage on a fresh weight basis (dry weight basis in parentheses).
[c] Initial proportions, after 17 days sewage sludge was added (about a 29% of fresh weight of the pile).

The bio-oxidative phase of composting was considered finished when the temperature of the pile was stable and near to that of the surrounding atmosphere. Then, the piles were allowed to mature for 2 months. The moisture of the piles was controlled weekly by adding the necessary amount of water to maintain a moisture content around 40%. Excess of water leached from the piles was collected and added again to the piles. Samples were obtained by mixing subsamples from seven different zones of the piles. The sampling was made at the beginning of the process (I), during the thermophilic phase (T), at the end of the bio-oxidative phase (E) and during the maturing phase (M) in order to analyze physical and chemical parameters.

2.2. Chemical methods

Total organic carbon (C_{org}) was determined by automatic microanalysis [11], as were the 0.1 M NaOH-extractable organic carbon (C_{EX}) and fulvic acid-like carbon (C_{FA}), the latter after precipitation of the humic acid-like carbon (C_{HA}) at pH 2.0, [12]. The C_{HA} was calculated by subtracting the C_{FA} from the C_{EX}. The humification ratio (HR), the humification index (HI) and the percentage of humic acid-like carbon (P_{HA}) were calculated as $(C_{EX}/C_{org}) \times 100$; $(C_{HA}/C_{org}) \times 100$ and $(C_{HA}/C_{EX}) \times 100$, respectively. The cation exchange capacity (CEC) was determined with $BaCl_2$-triethanolamine [13]. All parameters were determined in triplicate and significant differences among the values of each humification index studied during composting were calculated by the LSD (least significant difference) test at $P < 0.05$.

2.3. Sample preparation and thermal analysis

Samples were air-dried, ground in an agate mill, then sieved through a 0.125 mm mesh, and milled again with an agate mortar. Thermal analyses were performed with a METTLER TOLEDO (TGA/SDTA851e/LF/1600) and PFEIFFER VACUUM (THERMOSTAR GSD301T) mass spectrometer that enables the recording of thermograms and mass spectra of combustion gases simultaneously. All samples were combusted with a mixing stream of oxygen/He (20/80%), a gas flow 100 ml min^{-1} within a temperature range from 25 to 1000 °C, a heating rate 10 °C min^{-1}, a sample weight about 5 mg, Al_2O_3 pan, and self-controlled calibration. All the assays were carried out in triplicate. The enthalpy of combustion, ΔH, of the samples was calculated from the DTA curves, as the area between the baseline and the exothermic combustion peak, using a calibration curve plotting with the fusion enthalpy of different metals: In (3.28 kJ mol^{-1}), Pb (4.80 kJ mol^{-1}), Al (10.67 kJ mol^{-1}) and Au (12.55 kJ mol^{-1}).