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Thermal Characterization and Lifetime Estimation of the Humus Lombricospt

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ABSTRACT

Through this study, the humus produced in the breeding place of Universidad Autonoma de Occidente was thermally characterized. The humus was submitted to a heating program controlled by the Differential Scanning Calorimetry (DSC) technique to characterize the type of transition, Thermogravimetry (TGA) to study the equilibrium of phasesand Mass Spectrometry (MS) coupled to TGA to identify detached elements in a temperature range. The temperature range used in this study was 30˚C < T < 600˚C. The energy required for the water desorption in the humus has been found in this study. The humus showed a quick desorption between 30˚C ≤ $T_{Desorption}$ ≤ 110˚C at a heating rate of 10˚C/min and presented decomposition around 250˚C. Moreover, the kinetics of the desorption of the humus was studied to obtain the activation energy three TGA measures for three different heating rates. The average activation energy was about 26 kJ/Mol. This result was carried out to obtain an estimation of the desorption time of water in the range from room temperature to the decomposition temperature around 350˚C.

KEYWORDS

Thermal Analysis; Thermogravimetry (TGA); Differential Scanning Calorimetry (DSC); Mass Spectrometry (MS); Activation Energy; Decomposition Kinetics; Humus

1. Introduction

The red Californian worm compost is made from the skin of *Solanum tuberosum* (potato), cattle excrements (cow dung), plant sludge from waste water treatment WWTP at Universidad Autónoma de Occidente (UAO) and leaves that are cut to maintain symmetry in the garden. These four components are supplied to the Californian worms.

The Differential Scanning Calorimetry (DSC) technique quantifies some physical properties of the materials such as the heat capacity, the melting temperature, the crystallization, the glass transition temperature, the enthalpy of the reactions, among others [1].

The Thermogravimetry (TGA) technique quantifies the weight losses which are associated with the dehydration or decomposition of the material or compound being analyzed. This technique is supplemented with the Mass Spectrometry which identifies the gases that are released as they are subjected to different temperatures. In this way it is possible to obtain a qualitative analysis of the analyzed material or compound. This work seeks to establish alterations in the physical properties of the humus due to variations in temperature through the study of the heating capacity, the activation energy and the estimated lifetime. Moreover, it seeks to analyze phenomena such as dehydration and evaporation of the components of humus.

2. Materials and Methods

The red californian worm compost elaborated at UAO is located in an enclosure of 6.30 × 2.30 m and a height of 0.55 m. For the elaboration of humus the compounds listed in **Table 1** are supplied to the worms [2].

For the thermal analysis the humus was taken directly from the breeding place to be thermally characterized at the Thermal Analysis Laboratory (TAL). The characte-

Table 1. **Compounds supplied to the californian worms for the production of humus.**

	Compound	Days	Quantity
1	Cow dung	15	60 kg
2	Plant sludg	15	45 kg
3	Gardening	15	120 kg
4	Skin	15	40 kg

rization was done through a Differential Scanning Calorimetry DSC Q2000 with a temperature range of 30˚C < T < 600˚C at a heating rate of 10˚C/min and a Thermogravimetry TGA Q500 with a temperature range of 30˚C < T < 600˚C at a heating rate of 10˚C/min. The TGA evaporated elements were passed directly to a mass spectrometry MS Discovery (TA Instruments brand), where the detached elements were analyzed.

The collected humus sample was exposed to the method shown in Table 2 according to the characterization-technique.

3. Results and Discussion

3.1. Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA)

Figure 1 shows the DSC and TGA Thermograms for the humus sample in a nitrogen atmosphere conducted at a heating rate of 10˚C/min. The TGA curve shows two degradations: the first from room temperature to 100˚C atributed to water desorption or moisture loss, shows a weight loss of about 52.8%; the second degradation is observed at temperatures between 200˚C and 400˚C, attributed to proceses of decomposition of organic material showing a weight loss in the humus of about 10.7%.

The DSC thermogram displays an endothermic anomaly around 90˚C which corresponds to the desorption process with an associated enthalpy of 1200 J/g. The second anomaly is shown in the box in Figure 1. It corresponds to an endothermic process around 400˚C and is attributed to the process of decomposition.

Table 3 summarizes the thermal stability of the humus in the two temperature ranges mentioned.

Table 4 summarizes the phase behavior of the humus within the two temperature ranges mentioned, indicating the enthalpies of the process.

3.2. Mass Spectrometry (MS)

Figure 2 shows the TGA thermogram simultaneously with the registered masses by MS.

The masses are generated by the release of gases that occurs during the thermal scanning process to which the humus sample was programmed under an inert atmosphere of nitrogen. The released masses whose m/e ratio belongs to the values 16, 18, 28, 32 and 44, are asso-

Table 2. **Description of the Heating Program.**

	DSC	TGA	MS
Temperature	25˚C to 450˚C	25˚C to 600˚C	-
Heating Rate	10˚C/min	10˚C/min 5˚C/min 2.0˚C/min 1.0˚C/min	-
Athmosphere	Ni_2		-
Sample Quantity	6.9 mg	27.5 mg	-
Mass rang	-	-	70 a.m.u

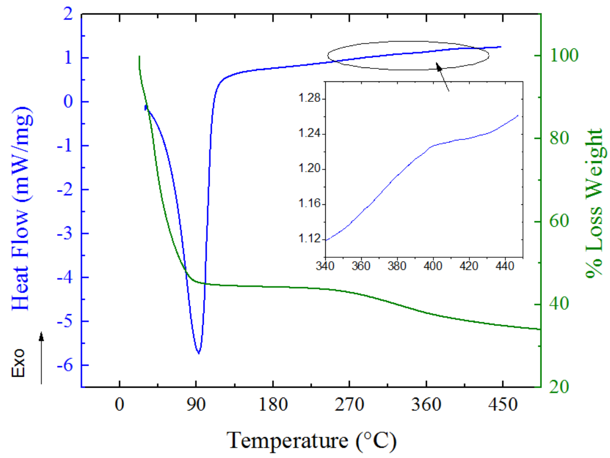

Figure 1. **DSC and TGA Thermograms.**

Table 3. **Degradations present in the humus.**

TGA			
Temperature Range (˚C)	Initial Weight (mg)	Weight loss (mg)	% Weight loss
25 - 150	49.118	26.76	54.49
200 - 600	27.009	2.889	67.07

Table 4. **Anomalies present in the humus.**

DSC		
Anomaly (˚C)	Onset Point (˚C)	Enthalpy (J/g)
25 - 150	56.16	1271
200 - 600	360.28	6.09

ciated with: O, H_2O, CO, O_2 and CO_2.

The data shows that the first anomaly occurs around 100˚C due to the release of H_2O. The second anomaly starts around 200˚C and ends around 400˚C due to the release of CO_2. The results also show that the levels of O, H_2O, CO and O_2 decrease while the level of CO_2 increases. This shows the decomposition that undergoes the humus.

According to the TGA thermogram the humus decomposes in two phases, in the first due to dehydration and in the second due to the release of CO_2.

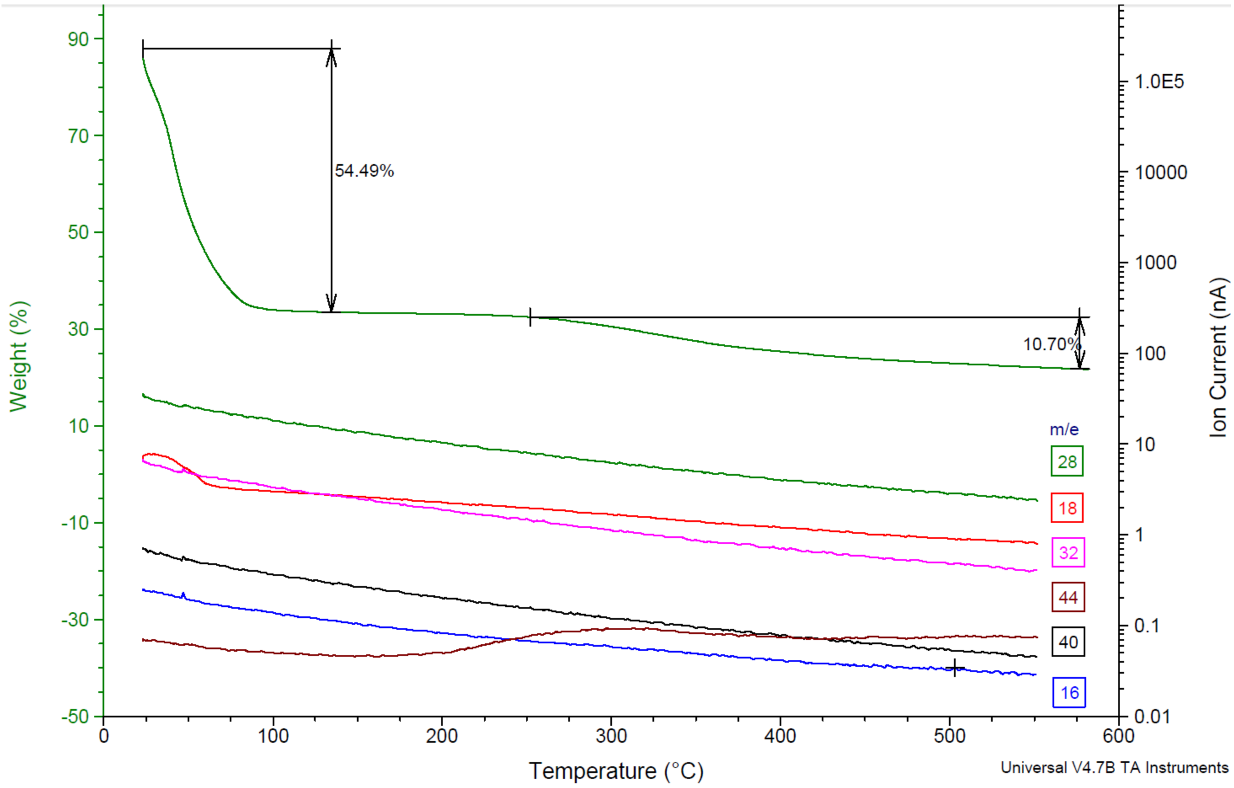

Figure 2. **TGA and MS Thermograms.**

3.3. Kinetic Study of the Humus Based on Thermogravimetic Results

The thermogram in **Figure 3** shows the weight loss of the humus exposed to different heating rates: 2˚C, 5˚C and 10˚C/min.

Figure 3 gives information on the desorption kinetics based on the Flynn and Wall method [3] used in this study which describes a quick and direct way to determine the activation energy of a material from thermogravimetric data and based on the ASTM E1641 norm [4] which suggest the following procedure:

- Subject the material to at least three different heating rates (1˚C/min - 10˚C/min).
- Determine the temperature at which there is loss of mass of the material (typically 10%).
- Graph the heating rate vs. 1/T.
- Perform the linearization of the graph: heating rate versus 1/T.
- Calculate the activation energy (iterative procedure) and the pre-exponential factor of Arrhenius starting from the slope found in the linearization.

Plotting the heating rates versus the inverse of the temperature in degrees kelvin (1/k), as illustrated in **Figure 4**, we obtained three linearizations which correspond to the three measures of the humus. These establish that the derivative expression (dlog (B)/dlog (1/t)) is the slope of the linearization obtained in **Figure 4**.

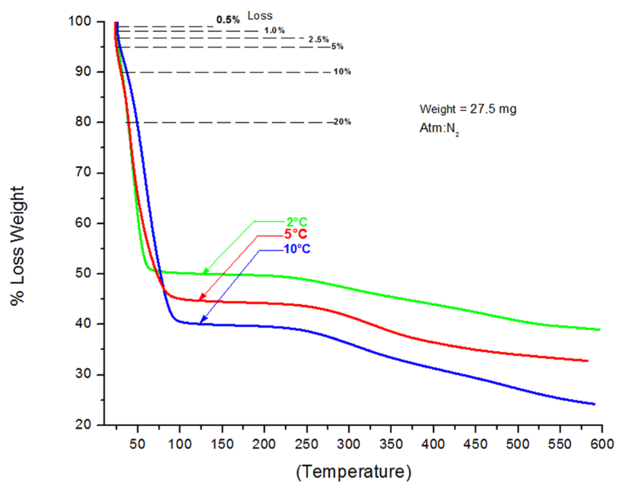

Figure 3. **TGA Thermograms at Different Heating Rates.**

$$E_a = -\frac{R}{b} + \left[\frac{E \log \beta}{d(1/T)}\right] \quad (1)$$

Where:
E_a: Activation Energy
R: Constant (8.314 J/mol)
T: Temperature (k)
β: Heating Rate(˚C/min)
b: Constant (0.457).

Table 5 shows values for the activation energy and the

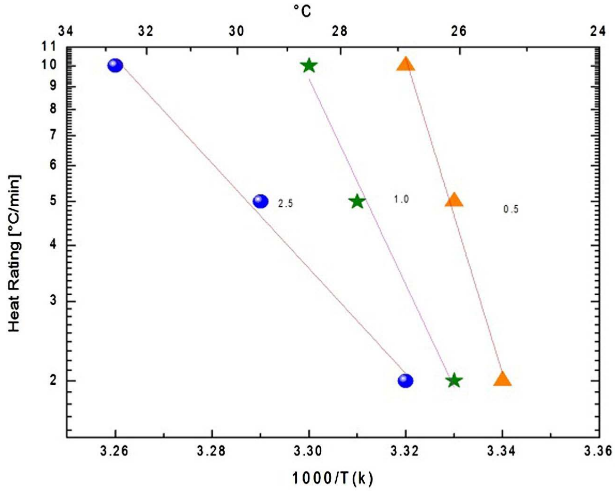

Figure 4. **Relationship between the heating rate and the inverse of the temperature.**

Table 5. **Activation energy for different weight losses humus.**

Conversion %	$\frac{E}{RT}$	Ea [KJ/Mol]
0.5	11.649	33
1.0	22.813	65
2.5	34.948	96

corresponding values for E/(RT) calculated for the three conversion cases shown in **Figure 4**. All the activation energy values calculated on the first iteration yield $E/(RT)$ values within the expected range. Thus, no additional iterations are required.

In his work Toop [5] demonstrates in detail how to obtain a value b within the range 10 ≤ E/(RT) ≤ 40.

Once obtained the activation energy for the different conversions used, the useful lifetime of the humus can be estimated with theToop method [5]:

$$T_F = \frac{E/R}{\ln t_f - \ln\left[\frac{E}{\beta R}\cdot P(X_F)\right]}; \qquad (2)$$

where:

t_f: Estimated Time to Failure (min)

E: Activation Energy (J/mol)

T_f: Failure Temperature (K)

R: Gas Constant (8.134 J/mol·K)

$P(X_F)$: A function whose values depend on E at the failure temperature.

Tc: Temperature for 5% Loss at b (K)

β: Heating Rate (˚C/min)

$$-\log P(x') = -\log\left[\frac{1}{x'e^{x'}} - \int_{x'}^{\infty}\frac{dx}{xe^{x}}\right] \qquad (3)$$

Figure 5 shows the estimated dehydration time of the humus at a particular temperature. This means that if the humus would be in a moisture-free atmosphere without any type of irrigation, it would maintain its hydration properties at a temperature of 30˚C for at least14 hours. Thus, if the humus would be exposed to a temperature of 60˚C its properties would be maintained only for 5 hours.

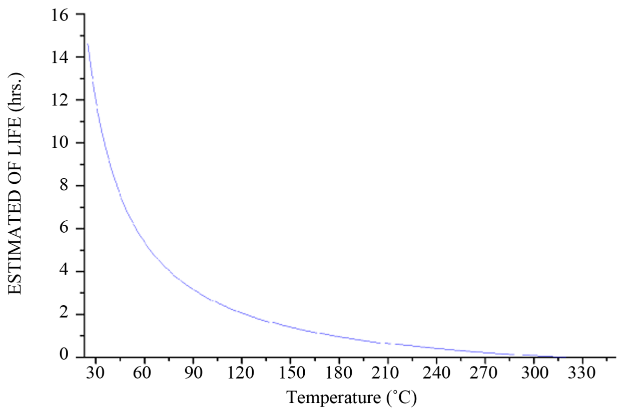

Figure 5. **Desorption time of the Humus in an atmosphere of N_2.**

4. Conclusions

For the first time we study the behavior of dehydration and decomposition of humus by californian earthworms produced through thermal analysis techniques such as thermogravimetric, Differential Scanning Calorimetry and Mass Spectrometry.

The results show a strong connection between the results of the DSC and the TGA techniques. This confirms that humus presents two phases, the first attributed to the dehydration of the humus and the second attributed to its decomposition hereby releasing CO_2. This was expected based on the composition of the humus.

Using the Flynn and Wall method based on thermogravimetric data, we identified the useful lifetime of the humus. This has been done by focusing on the desorption zone to estimate the time in which the properties are conserved depending on the exposure temperature. This estimated value of the desorption time of water shows that the desorption process can take around 14 hours at a temperature between 25˚C and 30˚C.

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