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COMPOSTING OF URBAN SOLID RESIDUES (USR) BY DIFFERENT DISPOSITIONS
Kinetics of thermal decomposition

M. S. Crespi[*], *A. R. Silva, C. A. Ribeiro, S. C. Oliveira and M. R. Santiago-Silva*

Instituto de Química, Unesp-Araraquara-São Paulo-Brazil

Abstract

The thermal behavior and non-isothermal kinetics of thermal decomposition of three different kinds of composting of the USR like: stack with drilled PVC tubes (ST), revolved stack (SR) and stack with material of structure (SM), from the usine of composing of Araraquara city, São Paulo state, Brazil, within a period of 132 days of composting were studied.

Results from TG, DTG and DSC curves obtained on inert atmosphere indicated that the cellulosic fraction present, despite the slow degradation during the composting process, is thermally less stable than other substances originated from that process. Due to that behavior, the cellulosic fraction decomposition could be kinetically evaluated through non-isothermal methods of analysis.

The values obtained were: average activation energy, E_a=248, 257 and 259 kJ mol^{-1} and pre-exponential factor, log$A$=21.4, 22.5, 22.7 min^{-1}, to the ST, SR and SM, respectively.

From E_a and log$A$ values and DSC curves, Málek procedure could be applied, suggesting that the SB (Šesták–Berggren) kinetic model is the appropriated one to the first thermal decomposition step.

Keywords: composting, kinetic parameters, thermal behavior, urban solid residues

Introduction

The urban solid residues

The classical destinations to urban garbage, in Brazil, are being the scrap yards (76%), incineration (0.1%), sanitary banks (10%) and composting (0.9%) [1]. In Brazil, the amount of organic garbage is around 57% of the total volume regarding the household solid garbage (HSG) which can propitiate its utilization as manure. Thus, composting has been a hopeful alternative to minimize the organic garbage [2].

Composting consists of biological reactions in the organic garbage through thermophilic micro-organism under aerobic conditions [3].

TG and DTA curves did not indicate any significant changes in the first thermal decomposition step to the formed composted from 20 days on; thus, the components present in that step don't suffer any significant alteration along the process of matura-

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[*] Author for correspondence: E-mail: crespims@iq.unesp.br

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tion. The alterations were verified for the components which decompose in a second step in the TG-DTA curves [4].

The first step in TG curves to the composted product was ascribed to the thermal decomposition of cellulosic materials, whose thermal stability is around 300°C [5].

The cellulosic fraction is one of the mainly structural components in the organic fraction of the USR and it is present from raw material up to 132 days of composted material.

Kinetic aspects

The mathematical description of the data from a single step solid state decomposition is usually defined in terms of a kinetic triplet, as activation energy, E_a, Arrhenius parameters, A, and an algebraic expression of the kinetic model in function of the fractional conversion α, $f(\alpha)$, which can be related to the experimental data as follows [6]:

$$\frac{d\alpha}{dt}=A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

For dynamic data obtained at a constant heating rate, $\beta=dT/dt$, this new term is inserted in the Eq. (1) to obtain the transformation:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

The dynamic experiments can be more convenient to carry out whether compared to running isothermal experiments and the reason for this is that it takes time to reach an isothermal temperature. It means that for a short but significant period, the system is subjected to an uncontrolled temperature regime [7]. However, any disagreement between the kinetic triplets obtained from dynamic and isothermal experiments has been argued in literature [8].

The activation energy from dynamic data may be obtained from isoconversional method of Flynn, Wall and Ozawa [9–11] using the Doyle's approximation of $p(x)$ [12], which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates, plotting $\ln\beta$ *vs.* $1/T$:

$$\ln(\beta)=\ln\left[\frac{AE}{Rg(\alpha)}\right]-5.331-1.052\frac{E}{RT} \tag{3}$$

The pre-exponential factor is evaluated taking into account that the reaction is a first-order one and can be defined as [13]:

$$A=\frac{\beta E}{RT_m^2}\exp\left(\frac{E}{RT_m}\right) \tag{4}$$

The kinetic interpretation through DSC curves, by isothermal or non-isothermal methods, is based on the relation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{\phi}{\Delta H_\mathrm{c}} \tag{5}$$

where ϕ is the heat flow normalized per sample mass and ΔH_c corresponds to the enthalpy change associated with this process.

The rate of the kinetic process can be expressed by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha) \tag{6}$$

The kinetic equation for any kind of model can be written as:

$$\phi=\Delta H_\mathrm{c} A\exp\left(-\frac{E_\mathrm{a}}{RT}\right)f(\alpha) \tag{7}$$

where $f(\alpha)$ is an algebraic expression for a given model.

The test proposed by Málek [14–17] is based on this equation and the $y(\alpha)$ and $z(\alpha)$ functions. Under non-isothermal conditions these functions are given by:

$$y(\alpha)=\phi\, A\exp\left(\frac{E_\mathrm{a}}{RT}\right) \tag{8}$$

$$z(\alpha)=\phi T^2 \tag{9}$$

These functions exhibit their maximum at α_m and α_p, respectively, which allows to find the kinetic model [14].

The aim of this work is to show the kinetic evaluation of the thermal decomposition of urban solid residues obtained by different dispositions, based on the TG, DTG and DSC curves and to propose the suitable kinetic model to describe the first thermal decomposition step.

Experimental

The household solid garbage (HSG) has not been obtained through selective collect. In a first moment, it is sent to a composting and recycling mill where the HSG is stored in a reception trench and after that the material is put on a roller where metals, glasses and other inorganic parts are removed by hand. The organic parts are sent to composting yard where they are stacked.

Six tons of organic residues disposed in a triangular form with 2.5, 5 and 1.2 meters to base, width and height, respectively, were used. In order to obtain the aeration, (a) six drilled PVC tubes were disposed in a transversely in the stack (ST); (b) the stack was periodically revolved (SR) and (c) brushwood were disposed in the stack (SM) [18].

The 132-day samples containing 3 kg of material were collected, then they were mixed, homogenized and a portion was withdrawn, dried in air, ground and packed in a glass flask.

The TG/DTG experiments were performed by using a module of thermal analysis, SDT 2960, from TA Instruments under nitrogen dynamic atmosphere of 100 mL min^{-1}, sample mass around 10 mg, alumina crucible and heating rates at 5, 10 and 20°C min^{-1}. DSC curves were obtained by using a DSC 2910 from TA Instruments under a dynamic atmosphere of nitrogen of 100 mL min^{-1}, sample mass around 3 mg, open aluminum pan and heating rates at 5, 10 and 20°C min^{-1}. The E_a and log$A$ were calculated by using the softwares TGAKin V4.04 and DSCASTMKin V4.08 from TA Instruments.

Results and discussion

TG and DSC curves

TG curves in a nitrogen atmosphere and at 20°C min^{-1}, Figs 1a–c, show a first mass loss up to 183°C, which corresponds to the dehydration between 2–5%, followed by consecutive mass losses up to 550°C, initially ascribed to the thermal decomposition of the cellulosic compounds and afterwards to the organic compounds originated during the composting process. After this, a third step which does not decompose completely up 900°C, produces carbonaceous materials and some amount of mineralized residue, Table 1.

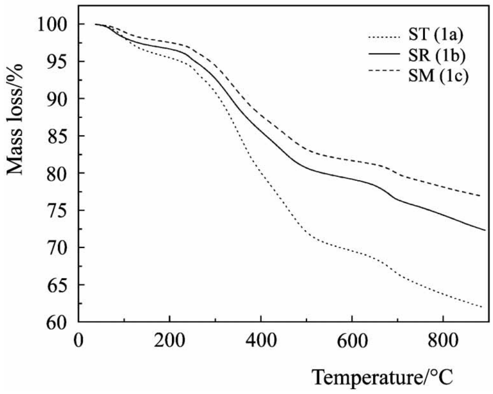

Fig. 1 TG curves in a nitrogen atmosphere to the 132-days composted material: a – stack with drilled PVC tubes – ST, b – revolved stack – SR and c – stack with material of structure – SM

DSC curves in a nitrogen atmosphere, Figs 2a–c and Table 1, show agreement to TG curves, in which, to the first step an endothermic peak at 52–55°C is ascribed to the dehydration reaction followed by another one at 231–239°C attributed to the thermal decomposition of the cellulosic compounds. Between 444 and 451°C a broad endothermic peak can be observed ascribed to the thermal decomposition reaction of the organic fraction from composting process. A sharp endothermic peak at 574°C can be observed and it may indicate a kind of melting of reduced metal formed in the previous step.

Table 1 TG and DSC data

STACK	Heating rate/°C min^{-1}	TG		DSC
		Δm/%	T_i–T_f/°C	T_{peak}/°C
ST	5.01	2.4, 1.7 7.3, 5.4 –	43.3–165.9, 165.9–250.0 250.0–389.4, 389.4–572.1 T>572.1	51.9, 239.3, 451.1, 575.0
	9.98	3.6, 2.5 10.1, 7.4 –	43.3–173.1, 173.1–264.4 264.4–401.4, 401.4–581.7 T>581.4	59.2, 237.6, 456.2, 574.3
	19.99	4.1, 2.6 13.6, 8.3 –	48.1–182.7, 182.7–271.6 271.6–416.0, 416.0–580.1 T>580.1	70.8, 242.2, 473.8, 575.0
SR	5.01	3.1, 2.0 9.7, 4.8 –	40.9–163.5, 163.5–250.0 250.0–413.5, 413.5–572.1 T>572.1	55.3, 231.0, 443.6, 574.1
	10.04	3.0, 2.1 9.3, 5.7 –	43.3–180.3, 180.3–257.2 257.2–406.3, 406.3–572.1 T>572.1	59.3, 248.4, 452.5, 574.4
	20.07	3.0, 2.1 11.4, 5.8 –	40.4–187.5, 187.5–262.5 262.4–426.9, 426.9–576.9 T>576.9	73.6, 245.7, 471.3, 575.2
SM	5.01	3.4, 2.3 11.2, 6.6 –	40.9–165.9, 165.9–252.4 252.4–394.2, 394.2–572.1 T>572.1	54.0, 232.3, 445.3, 573.9
	9.98	3.4, 2.3 11.2, 4.9 –	43.3–173.1, 173.1–262.1 262.1–413.5, 413.5–581.7 T>581.7	73.3, 235.9, 458.9, 574.3
	19.98	2.2, 1.7 8.8, 5.3 –	48.1–175.5, 175.5–266.8 266.8–415.9, 415.9–588.9 T>588.9	70.6, 240.5, 464.0, 575.3

Kinetic parameters

The Wall–Flynn–Ozawa method [9–11] could be applied to the TG and DSC curves in the interval of 200–400°C in order to obtain the activation energies and the respective pre-exponential factor to each α. The average E_a and log$A$, which changed less than 10% in value, were 248, 257 and 259 kJ mol^{-1}, and 21.4, 22.5 and 22.7 min^{-1}, to ST, SR and SM, respectively.

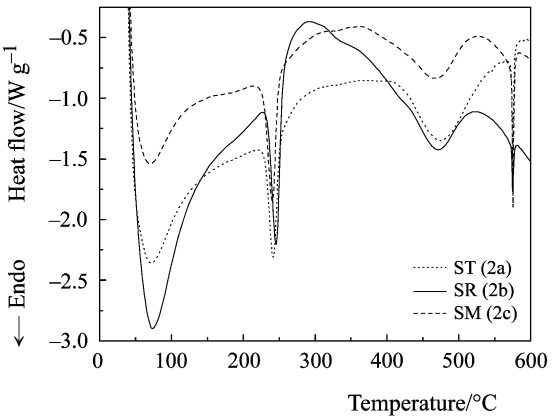

Fig. 2 DSC curves in a nitrogen atmosphere to 132 days composted material: a – stack with drilled PVC tubes – ST, b – revolved stack – SR and c – stack with material of structure – SM

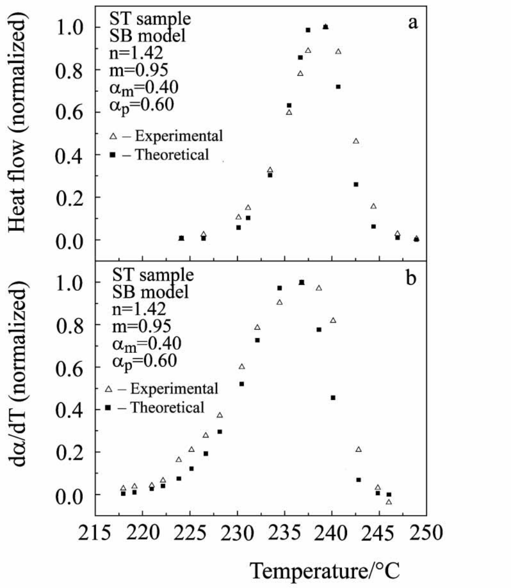

Fig. 3 Experimental and theoretical normalized curves a – DSC and b – DTG regarding to the thermal decomposition step at 215–250°C

Once known the E_a values and α *vs.* T from DSC curves, the plots of $y(\alpha)$ and $z(\alpha)$ *vs.* α could be obtained to each compound and consequently the values of α_m and α_p were determined, Table 2.

Through α_m and α_p values found [14], the suitable model to the thermal decomposition process between 200 and 400°C was the Šesták–Berggren (SB) in which $f(\alpha)=\alpha^m(1-\alpha)^n$ [19]. The kinetic exponent value, n, could be obtained from the slope of the ln[y(α)]ln[$\alpha^p(1-\alpha)$] plot. The second kinetic exponent value, m, could be calculated by the relation $m=np$, where $p=\alpha_m/(1-\alpha_m)$.

Table 2 Maxima y(α) and z(α) function at 5°C min^{-1} and kinetic exponents to SB model (n, m)

STACK	m	n	α_m	α_p
ST	0.95	1.42	0.40	0.60
SR	0.44	0.68	0.39	0.59
SM	0.90	1.14	0.44	0.60

From the known E_a, log$A$, α–T relation and f(α), their values were applied in the Eqs (2) and (7) and the corresponding theoretical dα/dT and ϕ *vs*. temperature could be calculated. The plots of both normalized ϕ *vs*. T(°C) and dα/dT *vs*. T(°C), concerned with theoretical and experimental data, show that they are very close to each other, Figs 3a–b.

To the other steps of the thermal decomposition, the mechanisms show to be complex, that is, they involved several steps, which could have different activation energies, and consequently f(α) could not be calculated.

Conclusions

From the results presented, the SB kinetic model seemed to be suitable to describe the first step of the thermal decomposition to the composted urban solid residues, which is related to the decomposition of the cellulosic products.

The different treatment to the same material (USR) has not shown significant influence in the shapes of TG and DSC curves, however, the kinetic exponent to revolved stack shows lower values for m and n when compared to ST and SM. It might have occurred due to the homogeneity of the sample.

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