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KINETIC OF THERMAL DECOMPOSITION OF RESIDUES FROM DIFFERENT KINDS OF COMPOSTING

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Abstract

Non-isothermal kinetic parameters regarding to the thermal decomposition of the ligninocellulosic fraction present in compost from urban solid residues (USR) obtained through stack covered (SC) with composted material, comes from the usine in composing of Araraquara city, São Paulo state, Brazil, and from stack containing academic restaurant organic solid residues (SAR). The samples were periodically revolved round 132 days of composting.

Results from TG, DTG and DSC curves obtained on inert atmosphere indicated that the lignocellulosic fraction present, despite the slow degradation during the composting process, is thermally less stable than other substances originated during that process. The lignocellulosic fraction decomposition, between 200 and 400°C, were kinetically evaluated through non-isothermal methods of analysis.

By using the Flynn–Wall and Ozawa isoconversional method, the medium activation energy, E_a, and pre-exponential factor, lg$A$, were 283.0±14.6, 257.6±1.3 kJ mol^{-1} and 25.4±0.8, 23.2±0.2 min^{-1}, to the SC and SAR, respectively, at 95% confidence level.

From E_a and lg$A$ values and DSC curves, Malek procedure could be applied, suggesting that the SB (Šesták–Berggren) kinetic model is suitable for the first thermal decomposition step.

Keywords: composting, household solid residue, kinetic parameters, urban solid residues

Introduction

The urban and household solid residues

The classical destinations to urban garbage, in Brazil, are the scrap yards (76%), incineration (0.1%), sanitary bank (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 use as manure. This way, composting has been a hopeful alternative to minimize the organic garbage [2].

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

TG and DSC curves did not indicate changes in the first thermal decomposition step to the formed composted from 20 days; thus, the components present in that step do not suffer any significant alteration along the process of maturation. The alterations verified for the components only occurred in a second step in the TG-DSC curves [4].

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

The lignocellulosic fraction is one of the main structural components in the organic fraction of the USR and it is present from raw to 132 days 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]:

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

For dynamic data obtained at a constant heating rate $\beta=\mathrm{d}T/\mathrm{d}t$, the kinetic triplet values are inserted in Eq. (1) to obtain the transformation:

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

The dynamic experiments can be more convenient to carry out if 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 discussed in [8], but non-isothermal kinetic analysis was applied by other researchers [9–12].

The activation energy from dynamic data may be obtained from isoconversional method of Flynn, Wall and Ozawa [13–15] using the Doyle's approximation of $p(x)$ [16], 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 [17]:

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

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 a given 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.

The test proposed by Málek [18–21] is based on this equation and on 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 [18].

The aim of this work is the kinetic evaluation of the thermal decomposition of lignocellulosic fraction in the 132 days compost which comes from urban solid residues stack covered with pre-composted material, and from academic restaurant organic solid residues stack. Based on the TG, DTG and DSC curves, the suitable kinetic model was proposed to describe the first thermal decomposition step.

Experimental

The household solid garbage (HSG) has been obtained but not through selective collection. In the 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 manually removed. The organic parts are sent to a 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 speed up the composting process, the stack was covered with a thin layer of pre-composted material [22].

The organic solid residues from academic restaurant were disposed in a shelter, covered with a thin layer of grass and the material was periodically revolved.

The 132 days 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 glass flask.

TG/DTG experiments were performed by using a module of thermal analysis, SDT 2960, from TA Instruments, under nitrogen dynamic atmosphere and heating rates at 5, 10 and 20°C min^{-1}. DSC curves were obtained by using a DSC 2910 from TA Instruments in a dynamic atmosphere of nitrogen and heating rate at 5, 10 and 20°C min^{-1}. The E_a and lg$A$ 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 10°C min^{-1}, Figs 1a–b, show a first mass loss up to 180°C, which corresponds to the dehydration between 2–4% to SC and SAR, respectively. The next step, due to the thermal decomposition of the lignocellulosic compounds, shows successive mass losses up to 600°C, which are well defined to SAR sample. However, the defined step between 600 and 900°C, ascribed to the organic compounds originated during the composting process, can only be seen to the SC sample. The residues to each step of the thermal decomposition present different masses, depending on the stack originated sample. The residues at 900°C, 76–79 and 56–64%

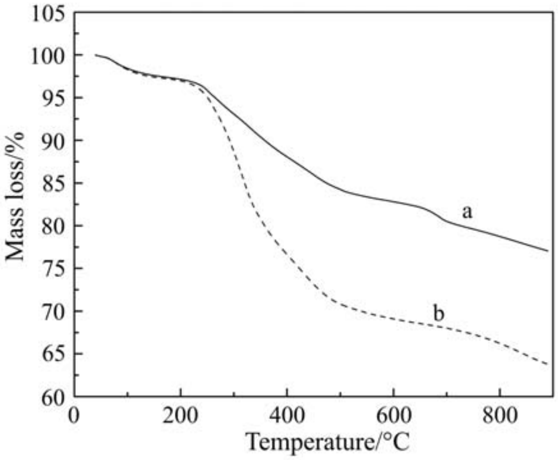

Fig. 1 TG curves in nitrogen atmosphere at 10°C min^{-1}: a – SC and b – SAR

to SC and SAR, respectively, correspond probably to the carbonaceous materials and to the amount of mineralized residue, Table 1.

Table 1 TG and DSC data

Stack	Heating rate/ °C min^{-1}	TG		DSC
		Δm/%	T_i–T_f/°C	T_{peak}/°C
SC	5.01	2.14 12.23 2.38 –	43.3–168.3 168.3–567.3 567.3–694.5 T>694.5	50.7, 238.0, 297.8, 447.6, 573.8
	9.99	2.49 13.70 3.60 –	48.1–175.5 175.5–584.1 584.1–745.2 T>745.2	58.4, 71.9, 246.2, 318.9, 463.8, 574.5
	19.99	2.14 15.29 3.43 –	48.1–173.1 173.1–588.9 588.9–759.6 T>759.6	73.4, 247.5, 366.3, 467.6, 574.8
SAR	5.01	3.00 19.48 7.60 –	43.3–168.5 168.8–382.2 382.2–598.6 T>598.6	52.4, 241.3, 289.2, 434.6, 573.9
	9.98	3.59 20.0 7.59 –	45.7–168.3 168.3–399.0 399.0–632.4 T>632.4	60.8, 245.9, 295.1, 442.3, 574.5
	19.97	3.33 25.00 10.00 –	48.1–173.1 173.1–403.8 403.8–646.6 T>646.6	67.5, 258.4, 313.8, 462.5, 575.2

DSC curves, in a nitrogen atmosphere and at 10°C min^{-1}, Figs 2a–b and Table 1, show good agreement to TG curves, in which, to the first step an endothermic peak at 50–73°C is ascribed to the dehydration reaction followed by another one at 238–259°C due to the thermal decomposition of the lignocellulosic compounds. Between 290 and 470°C two broad endothermic peaks are 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 that the reduced metal formed in the previous step has melt.

Kinetic parameters

The Wall–Flynn–Ozawa method [13–15] could be applied to the TG curve at an 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 lg$A$, with 95% confidence level,

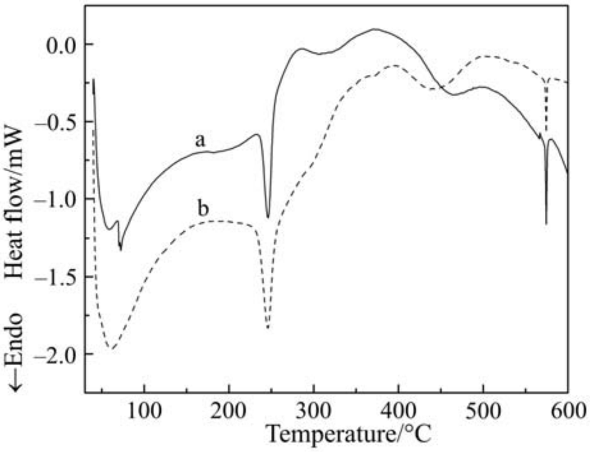

Fig. 2 DSC curves in nitrogen atmosphere at 10°C min^{-1}: a – SC and b – SAR

were 283.0±14.6, and 257.6±1.3 kJ mol^{-1}, and 25.4±0.8 and 23.2±0.2 min^{-1} to SC and SAR, respectively.

Once known the E_a values and α *vs*. T(K) 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 [18], the suitable model to the thermal decomposition process between 200 and 400°C was the Šesták–Berggren (SB) model in which $f(\alpha)=\alpha^{m}(1-\alpha)^{n}$ [23]. The kinetic exponent value, n, could be obtained from the slope of the $\ln[y(\alpha)]\ln[\alpha^{p}(1-\alpha)]$ plot. The second kinetic exponent value, m, could be calculated by the relation $m=np$, where $p=\alpha_m/(1-\alpha_m)$.

From the known E_a, lg$A$, α–T relation and $f(\alpha)$, their values were applied in Eqs (2) and (7) and the corresponding simulated $\mathrm{d}\alpha/\mathrm{d}T$ and ϕ *vs*. temperature could be calculated. The plot of normalized ϕ *vs*. T(°C) and $\mathrm{d}\alpha/\mathrm{d}T$ *vs*. T(°C), regarding simulated and experimental data, show that they are very close to each other, Figs 3–6.

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

Stack	m	n	α_m	α_p
SC	0.35	0.79	0.31	0.60
SAR	0.49	0.94	0.34	0.57

Several models may be involved to the other steps of the thermal decomposition, which could have different activation energies, and consequently $f(\alpha)$ could not be calculated.

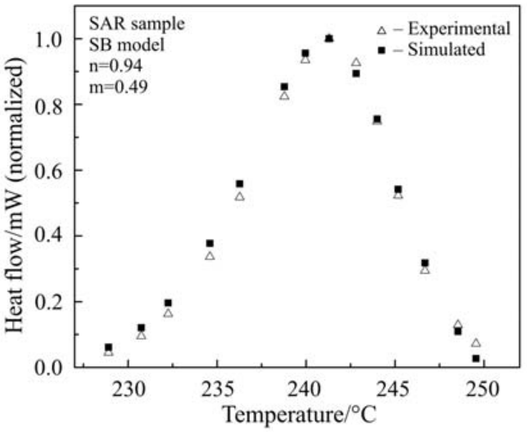

Fig. 3 Experimental/simulated normalized DSC curves of SC

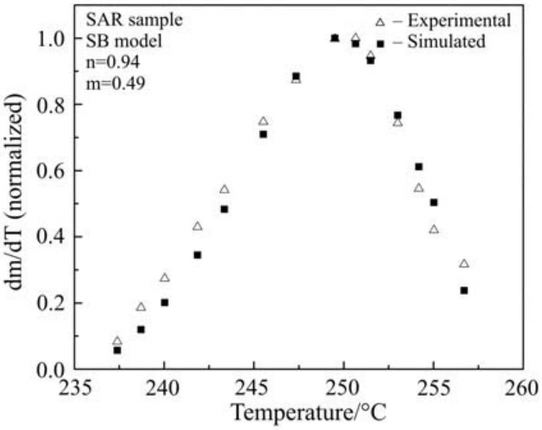

Fig. 4 Experimental/simulated normalized DTG curves of SC

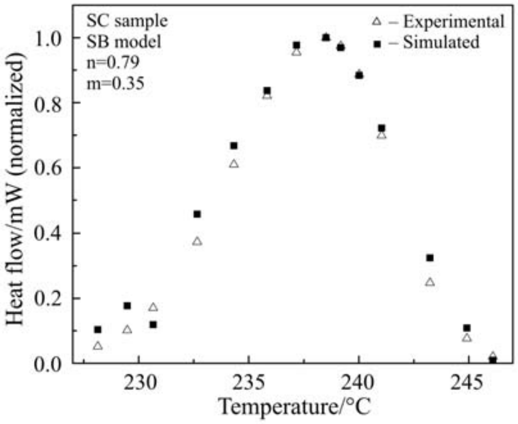

Fig. 5 Experimental/simulated normalized DSC curves of SAR

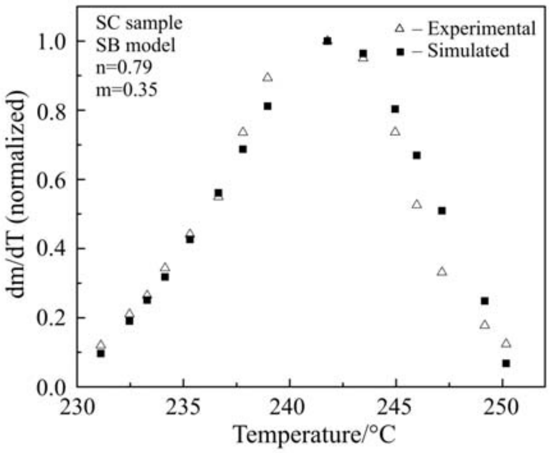

Fig. 6 Experimental/simulated normalized DTG curves of SAR

Conclusions

From the results presented, the SB kinetic model seemed to be a suitable model to describe the thermal decomposition of the step containing lignocellulosic material.

The two different kinds of stacks showed small differences in the aspect of the TG and DSC curves; however, the kinetic exponent seems to be similar and the values of *m* indicate a low heterogeneity degree. This aspect is interesting once known the complexity in the composition of the samples.

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