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Kinetic studies of urban solid residues and leachate from sanitary landfill

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Abstract Urban solid residues are constituted of food remaining, grass leaves, fruit peelings, paper, cardboard, rubber, plastic, etc. The organic fraction formed represents about 50% during the decomposition yields biogas and leachate, which are sources of pollution. Residue samples were collected from the landfill in different and cells from several ages and the corresponding leachate, both after treatments, were submitted to thermal analysis. Kinetic parameters were determined using Flynn–Wall–Ozawa method. The linear relation between the two kinetic parameters (ln A and E) was verified for organic residue urban's samples, but not for leachate's sample. The occurred difference can be attributed to the constituents present in leachate.

Keywords Kinetic parameters · Landfill · Leachate

Introduction

Last century marked the appearance of a large variety of products that provided an improvement in our life and increased people's life style, improved the economy.

The appearance of new medicine, electrical items, industrialized foods, disposable products like diapers, toys, clothes, furniture, domestic utensils and vehicles brought comfort to human beings as well as the increased the amounts of residues. The variety of objects found in the garbage was variable and the physical composition varied from city to city. The physical composition of garbage in 2006, at São Carlos (SP-Brazil), was 58.7% organic matter (OM), paper and cardboard 6.4%, long life 0.9%, fine plastic 6.2%, hard plastic 2.8%, Al 1.6%, and others 21.6% [1].

The organic matter is also biggest fraction found at urban residues, responsible for the decomposition of the same, generating gases and an unpleasant dark liquid that can percolate among the residues and contaminate the subterranean water sheets.

Thermogravimetric analysis is used to study the thermal decomposition of solids residues from composting systems [2, 3].

The leachate and residue samples were analyzed by thermogravimetry (TG and DTG) to provide information on this thermal decomposition and kinetic study.

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Kinetic aspects

The kinetic parameters can be determined by non-isothermal thermogravimetric (TG) experiments and can be mathematically described by kinetic triplet (E, log A and $f(\alpha)$) with one unique stage of solid reaction [4].

The concentration (C) for reactions state solid often can be expressed by physical propriety (x) chosen to represent the studied system, in accordance with Eq. 1, t represents time, initial time ($t = 0$) and end time ($t = \infty$).

$$\alpha_t = \frac{(x_t - x_0)}{(x_\infty - x_0)} \quad (1)$$

Equation 2 represents results from the constant heating rates (β), which relate the rate of temperature variation (T) in function with the time (t): (dT/dt)

$$\beta = \frac{dT}{dt} \quad (2)$$

The variation rate of α as a function of the time can be expressed though differential Eq. 3.

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (3)$$

The kinetic parameters E (kJ mol^{-1}) and A (s^{-1}) can be determined by the Flynn–Wall–Ozawa isoconversional method [5, 6] using Doyle's approximation, $p(x)$ [7] and the equation is given below:

$$\ln \beta = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5{,}331 - 1{,}052\,E/RT \quad (4)$$

A, E, β and R are exponential factor, activation energy, heating rates and molar gases constant, respectively. The pre-exponential factor, A, can be calculated from the equation below, considering the first-order reaction.

$$A = \frac{\beta E}{R T_m^2} \exp\left[\frac{E}{R T_m}\right] \quad (5)$$

The present research objectives the determination of kinetic parameters waste samples and leachate collected from São Carlos sanitary landfill by analyzing their TG/DTG curves and implementing the Flynn–Wall–Ozawa isoconversional method (Método ASTM E-698) [8].

Experimental

São Carlos sanitary landfill was chosen for this research because it is located in an easy-access region and retrieves class IIA solid residues from it [9]. São Carlos' location in São Paulo's state can be seen in Fig. 1.

The urban solid residues withdrawn from the sanitary landfill were buried from 1999 up to 2006 and collected in two stages. The samples were retreat from de cells, as it is shown in Fig. 2 to a depth of 3 m in five different points, after turning a representative sample by means of quartering, according to, NBR 10007 of 2004 was taken [11].

The samples were dried, ground, sieved and conserved in a desiccator. The initial mass for the thermoanalytical experiments was 7 mg according to previous studies in case of heterogeneous samples [2, 12].

The sanitary landfill in São Carlos (Fig. 2) shows where the samples were collected between 1999 and 2006.

Leachate samples were collected and stored in the accumulation tank and conserved at 4 °C. After 12 h, leachate was lyophilized to remove the water content [12]. Then solid product was submitted for thermal analysis.

The equipment used for the thermogravimetric analysis was a SDT 2960 simultaneous DTA/TGA from TA Instruments, Newcastle, Delaware, USA.

Fig. 1 São Paulo state map. City where withdrawal of urban solids residues and lechate, to be used in the research [10]

Fig. 2 Sanitary landfill sight indicating the cells, where were going accomplished the residues samples collected

Results and discussions

The TG/DTG curves for the kinetic studies from the residues were performed at a heating rates of 10, 15 and 25 °C min^{-1} and at a heating rates of 5, 10 and 20 °C for the organic phases (OP) of leachate. The experimental conditions were: nitrogen flow 50 mL min^{-1}; initial temperature 30 °C and final temperature 600 °C for the residues and 30–1,200 °C for the organic phase (OP). The TG curve for sample S_1 (solid residue of the 1999) is shown in Fig. 3 and the TG curve for OP sample can be seen in Fig. 4.

The TG curves of sample S_1 and OP show a first mass-loss step of 0.3–0.5% up to 200 °C, which can be attributed to the sample dehydration. Successive losses can be seen up to 600 °C, which are probably due to mass losses arising from the thermal decomposition of the organic compounds. Similar results were presented in [12–14].

The residue sample S_2, disposed in the Landfill in 2000 and collected to analysis in 2004, presented larger quantity of OM, date obtained through the second mass loss from TG curve, due the presence of leachate effused on the cells (method used in the epoch as treatment form of leachate).

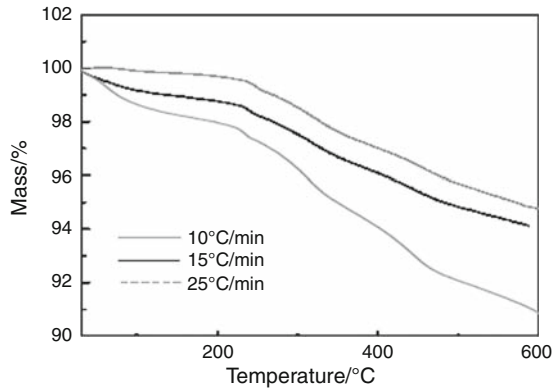

Fig. 3 The TG curves of the 1999 (S_1) waste retrieved from the São Carlos sanitary landfill used heating rates of 10, 15 and 25 °C min^{-1}

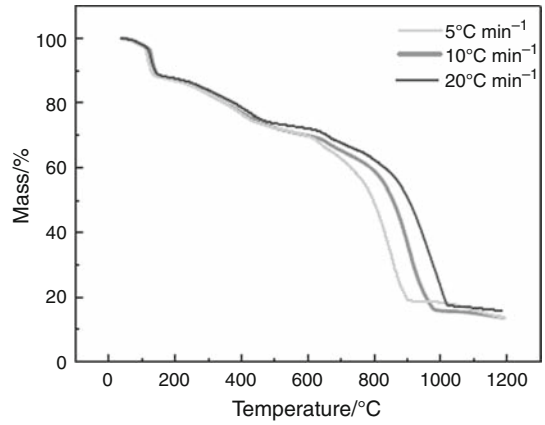

Fig. 4 TG leachate curves (OP) obtained under a nitrogen atmosphere using a heating rate of 5, 10, and 20 °C min^{-1}

S_6 and S_8 residue samples of 2004 and 2006, collected in 2006, presented the same amount of OM, being this fact expected to new residues, when compared with residues of 1999.

It was verified that as the residue is older, the amount of OM is less and consequentially higher the final residue originated from the thermal analysis.

The most intense DTG peak for kinetic study was selected for each heating rate in the temperature range of 215–260 °C for solid residue and 100–200 °C for OP, which corresponds to the second mass loss. The DTG curves from sample S_1 (1999) were at a heating rates of 5, 10 and 20 °C min^{-1} and can be seen in Fig. 5 and OP in Fig. 6.

The kinetic parameters E (kJ mol^{-1}) and A (s^{-1}) (see in Table 1) were determined implementing the Flynn–Wall–Ozawa isoconversional method using Doyle's $p(x)$ approximation.

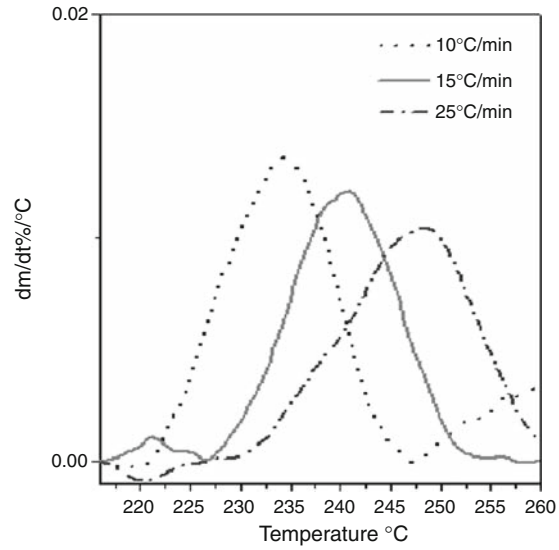

Fig. 5 The DTG curves of sample S_1 retrieved from the São Carlos sanitary landfill were at heating rates of 10, 15 and 25 °C min^{-1}

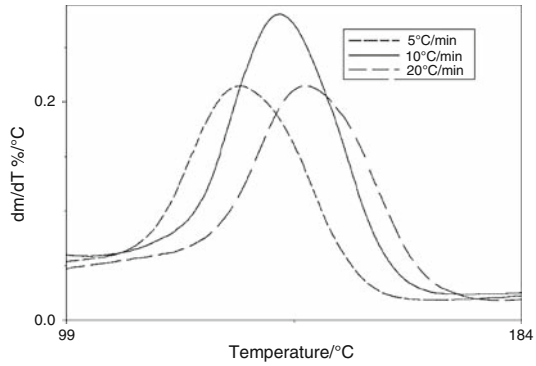

Fig. 6 The DTG curves of OP sample heating rates of 5, 10 and 20 °C min^{-1}

From a computer program and using different values of T values for a fixed value of α, it was possible to determine the pre-exponential factor, A, and the activation energy E.

Table 1 shows β, ΔT, the activation energy, the standard deviation and ln A for all the samples retrieved from the sanitary landfill. The activation energy values (S_2, S_3, S_4, S_5, S_6, S_7 and S_8) are probably the result of simple events, since these energies have standard deviation values $\leq$10,

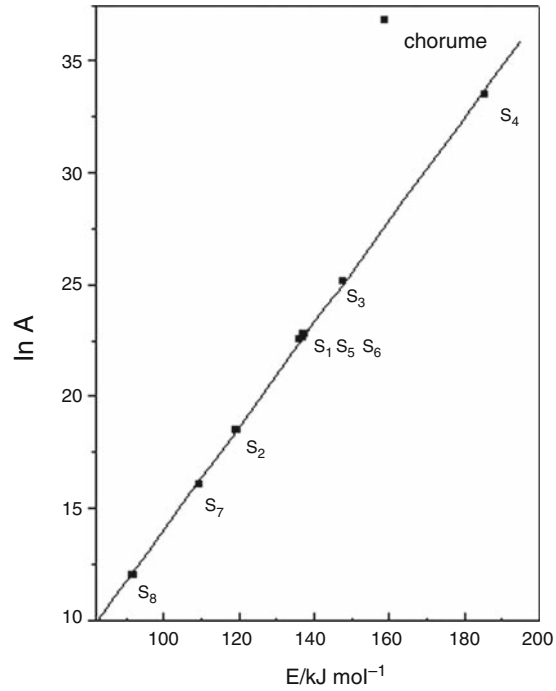

Fig. 7 The average of ln A as a function of average of the activation energy for samples S_1, S_2, S_3, S_4, S_5, S_6, S_7, S_8 and OP (leachate)

Table 1 Heating rate, ΔT (temperature change of the studied step), average activation energy and ln A for all the samples

Samples	β/°C min^{-1}	ΔT/°C	Energy/kJ mol^{-1}	In A/min^{-1}
S_1 1999	10.01	224.0–254.5	$E_1 = 137.0 \pm 14.8$	22.65 ± 3.68
	15.05	224.7–259.1		
	25.73	224.1–259.0		
S_2 2000	10.03	218.6–246.8	$E_2 = 147.0 \pm 7.8$	25.16 ± 2.00
	15.05	227.3–252.7		
	25.77	230.6–261.1		
S_3 2001	10.02	215.0–250.0	$E_3 = 119.4 \pm 7.7$	18.42 ± 2.09
	15.00	216.0–265.0		
	25.36	228.0–267.0		
S_4 2002	9.99	215.0–260.8	$E_4 = 185.6 \pm 8.7$	33.51 ± 2.46
	15.02	223.5–264.5		
	25.21	223.8–272.1		
S_5 2003	10.03	214.1–246.8	$E_5 = 137.3 \pm 2.9$	22.81 ± 0.93
	15.04	222.0–253.4		
	25.40	229.6–263.3		
S_6 2004	10.03	213.7–247.5	$E_6 = 136.2 \pm 6.2$	22.56 ± 1.40
	15.04	224.1–253.1		
	25.58	227.6–259.8		
S_7 2006	10.03	217.7–248.8	$E_7 = 91.9 \pm 1.9$	12.03 ± 0.39
	15.04	227.5–258.2		
	25.18	230.4–266.4		
S_8 2006	10.02	216.3–248.3	$E_8 = 109.4 \pm 4.8$	16.08 ± 0.93
	15.04	229.2–258.0		
	25.42	232.8–264.4		
CSC (OP)	10.01	107.0–170.0	$E_9 = 159.4 \pm 15.4$	36.85 ± 3.89
	15.02			
	20.01			

characteristic of less complex reactions following the behavior described by Arrhenius.

Figure 7 shows that kinetic compensation effect (KCE), where a variation in E corresponds to charge in A.

From the graphic ln A vs. E, Fig. 7 shows a straight line for the points referring to sanitary landfill residues, however, the values for leachate do not follow the same pattern. The KCE was observed in thermal decomposition of cellulosic materials at air atmosphere [15].

Conclusions

The results of the kinetic study indicate that the thermal decomposition reaction analyzed is due to the presence of the components having the same basic organic composition and that the difference in activation energy is probably caused by the presence of inorganic compounds in the samples of solid residues.

The leachate sample was left apart because its components reacted differently during the thermal decomposition and matrix absence the existence of the different catalyst in the sample.

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