Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 3, 823–826

NON-ISOTHERMAL KINETIC FOR LYOPHILIZED LEACHATE FROM SANITARY LANDFILL AND COMPOSTING USINE

Evaneide Nascimento Lima, Marisa Spirandeli Crespi[*]*, C. A. Ribeiro and Sonia de Almeida*

Universidade Estadual Paulista, Instituto de Química, Departamento de Química Analítica, R. Prof. Francisco Degni, s/n, CP 355
CEP 14801-970, Araraquara, SP, Brazil

Leachate samples from a sanitary landfill of Araraquara city and composting usine of Vila Leopoldina, São Paulo, Brazil were lyophilized to remove the water content. TG/DTG curves at different heating rates were recorded. The second step of the thermal decomposition of leachate from the Araraquara landfill (CB_1), from the composting usine from Vila Leopoldina (CB_2) from the organic phase extracted (FO) and aqueous phase (FA) were all kinetically evaluated using the non-isothermal method.

By Flynn–Wall isoconversional method the following values were obtained: E=234±3.65 kJ mol^{-1} and log$A$=29.7±0.58 min^{-1} for CB_1; E=129±1.66 kJ mol^{-1} and log$A$=11.8±0.10 min^{-1} for CB_2; E=51.6±1.35 kJ mol^{-1} and log$A$=6.09±0.09 min^{-1} for FO and E=76.91±6.33 kJ mol^{-1} and log$A$=8.88±0.7 min^{-1} for FA with 95% confidence level. Applying the procedures of Málek and Koga, SB kinetic model (Šesták–Berggren) is the most appropriate to describe the decomposition of CB_1, CB_2, FO and FA.

Keywords: *kinetic parameters, leachate, non-isothermal kinetic*

Introduction

Concerning the treatment of the solid waste residue is a large trouble to find a suitable place for its deposition. It is known that 90.000 tons of domestic waste is produced daily in Brazil (BNDES) and a small portion (10%) is placed to the sanitary landfill, which is the most suitable solution according to ABRELPE [1].

The solid residue deposition in sanitary landfills yields a liquid, called to leachate. The leachate is a dark liquid containing a high polluting load, with low biodegradability and presence of heavy metals [2]. Besides, leachate contains organic contaminants and high concentration of inorganic salts such as NaCl and carbonates [3]. So its variable composition gives rise to the characteristics of residues that are deposited.

When water, originating mainly from the rain, percolates through these residues, several organic and inorganic substances are loaded into the leachate. The leachate can drain the superficial hydric collections and thus, they may infiltrate into subterraneous layers [4].

Thermogravimetric analysis is used to study the thermal decomposition of solids originating from urban solid residues, such as from the maturation of the compound from which it comes [5, 6].

In this work leachate samples were analyzed by thermogravimetry (TG) to provide information on its thermal decomposition. Applying different heating rates, kinetic parameters of the decomposition could be determined.

Kinetic considerations

By using non-isothermal TG experiments, the thermal decomposition of the substance can be mathematically described by the kinetic triplet (E, log$A$ and $f(\alpha)$). A solid-state Arrhenius-type reaction can be expressed by the general equation [7–10]:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (1)$$

where the fractional degradation (α) and temperature (T) is dependent on a constantly increasing heating rate (β). Accordingly, the isoconversional F–W–O method that is the angular and linear coefficient of a plot of logβ *vs.* $1/T$ at an α being both different and constant, thus providing the E and A values, respectively [7–10].

In order to calculate the best fit kinetic model, which describes well the degradation of leachate the $y(\alpha)$ and $z(\alpha)$ functions were defined.

Koga utilized the generalized time introduced by Ozawa in order to calculate the $y(\alpha)$ and $z(\alpha)$ functions from non-isothermal and isothermal thermogravimetric data for a solid-state reaction, since E and log$A$ are known [11–14].

$$y(\alpha)=\frac{d\alpha}{d\theta}=Af(\alpha) \qquad (2)$$

$$y(\alpha)\theta=f(\alpha)g(\alpha)=z(\alpha) \qquad (3)$$

The maximum value of the normalized $y(\alpha)$ and $z(\alpha)$ functions taken from the α plot is an indication

---

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

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

of the kinetic model function and kinetic exponents that theoretically represents better the studied process [15–17].

Experimental

Leachate samples were collected from a sanitary landfill and from composting usine and they were lyophilized to remove the water content.

Samples were submitted to liquid-liquid extraction to obtain the organic and aqueous phases. For this, 1000 mL of leachate and 60 mL of dichloromethane were used to separate the organic phase. The aqueous phase was used again in the extraction with another 60 mL of dichloromethane, hence obtaining the other organic phase. This procedure is repeated three times for the same extraction. At the end of this process three organic phases were obtained then were lyophilized. The resulted solids were submitted to thermal analysis.

TG/DTG curves for the kinetic studies were performed using a SDT 2960 simultaneous DTA-TG unit from TA Instruments under dynamic nitrogen atmosphere (50 mL min^{-1}) and with about 9 mg initial sample mass. 5, 10 and 20°C min^{-1} heating rates from 40 up to 1200°C were applied. The second thermal decomposition step of the leachate from landfill (CB$_1$), from composting usine (CB$_2$), from the extracted organic phase (FO) and the aqueous phase (FA) were kinetically evaluated using the non-isothermal method.

Results and discussion

TG curves of samples CB$_1$ and CB$_2$ showed the same mass losses. CB$_2$ originates from a controlled maturation process of the compost and CB$_1$ from the uncontrolled decomposition of the waste. Probably, the samples contain similar components since they are derived from the degradation of urban solid residues.

TG curves of leachate in nitrogen at 5, 10 and 20°C min^{-1} heating rates are shown in Fig. 1. The first mass loss at 40°C related to humidity loss. The second step at 195°C corresponds to the dehydration of the sample, followed by the third one at 550°C due to the decomposition of free organic substances in the form of the metal complexes that are present in a suspension of particles under the surface of the leachate. The last mass loss step is attributed to the decomposition of carbonates (700°C), mainly CaCO$_3$, originating from the thermal decomposition of organic metal-complex substances.

For the organic phase and the aqueous phase, four thermal decomposition steps were observed. The first two steps are attributed to the dehydration reactions and the two other ones to the decomposition of the organic compounds.

Attainment of kinetic parameters

The kinetic parameters, E and log$A$, for the CB, FO, FA samples along with the thermal degradation were calculated (Fig. 1) using the Flynn–Wall isoconversional method from experimental TG-DTG curves and software (TGAKin V4.0A) developed by Blaine [18]. For each conversional fraction calculated, α, E and the corresponding log$A$ is obtained from the lnβ *vs.* 1000/T plot with 95% confidence level. The average of the kinetic parameters, E and log$A$ for each α corresponding to each defined temperature interval are presented in Table 1.

When E and log$A$ values are known, the next step is to evaluate the appropriate kinetic model represented by the $f(\alpha)$ function. Using the procedures by Málek and Koga [19, 20] for the DTG data, $y(\alpha)$ and $z(\alpha)$ *vs.* α are plotted, defined from Eqs (2) and (3), respectively, and the α^*_y and α^*_z maximum are determined for the decomposition reactions of CB$_1$, CB$_2$, FO and FA as shown in Table 1. Figure 2 shows the maximum values $\alpha^*_y=0.10$ and $\alpha^*_z=0.58$ for the decomposition reaction of the CB$_1$ sample.

From the α^*_y and α^*_z values it was found that the most suitable model that describes well the thermal decomposition of CB$_1$, CB$_2$, FO and FA is the autocatalytic SB model represented by the $f(\alpha)=\alpha^m(1-\alpha)^n$ function. The kinetic exponent 'n' (Table 1) can be obtained from the inclination of the $\ln[(\mathrm{d}\alpha/\mathrm{d}t)\exp(E/RT)]$ *vs.* $\ln[\alpha^p(1-\alpha)]$ plot of α values between 0.2 and 0.8. The second kinetic exponent 'm' can be calculated from the $m=np$ equation, where $p=\alpha^*_y/(1-\alpha^*_y)$, which may indicate the heterogeneity of the sample.

From the studied events, the largest value of $m=0.52$ was observed for the FA sample.

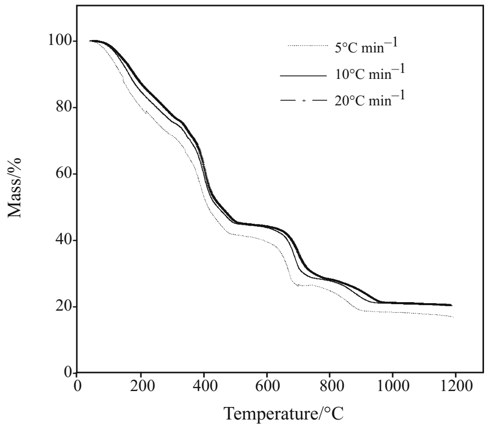

Fig. 1 TG curves of the CB$_1$ sample, m~9 mg, 5, 10 and 20°C min^{-1}, nitrogen atmosphere (50 mL min^{-1})

Table 1 E and log$A$ (average values), maximum of the functions $y(\alpha)$ and $z(\alpha)$ (α^*_y, and α^*_z) and kinetic exponents (m and n)

Samples	T_i–T_f/°C	E/kJ mol^{-1}	log$A$/min^{-1}	α^*_y	α^*_z	m	n
CB$_1$	120–173	234±3.65	29.7±0.58	0.10	0.58	0.16	1.46
CB$_2$	150–228	129±1.66	11.8±0.10	0.08	0.57	0.13	1.51
FO	98–152	52±1.35	6.09±0.09	0.30	0.38	0.47	1.13
FA	74–204	77±6.33	8.88±0.70	0.31	0.47	0.52	1.00

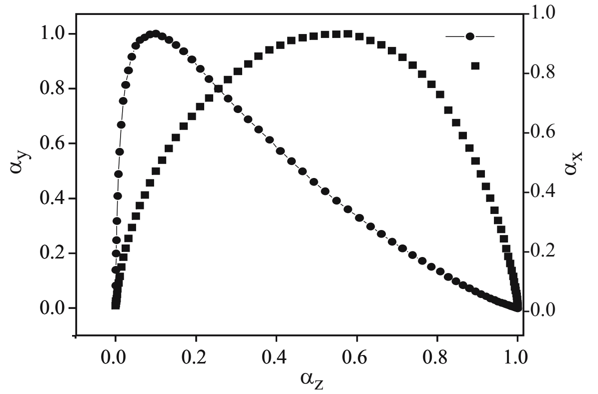

Fig. 2 The α_y and α_z functions calculated from TG CB$_1$ sample

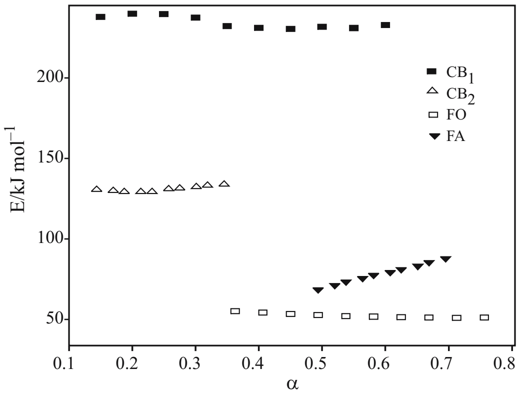

Fig. 4 Activation energy relation with conversion degree to CB$_1$, CB$_2$, FO and FA samples

The functions of the SB kinetic model (Šesták–Berggreen) for the thermal decomposition are $f(\alpha)=\alpha^{0.16}(1-\alpha)^{1.46}$ for CB$_1$, $f(\alpha)=\alpha^{0.13}(1-\alpha)^{1.51}$ for CB$_2$, $f(\alpha)=\alpha^{0.47}(1-\alpha)^{1.13}$ FO and $f(\alpha)=\alpha^{0.52}(1-\alpha)^{1}$ for the FA samples.

If E, log$A$ and α-T relationships are known, $f(\alpha)$ can be calculated from dα/dT *vs.* T and compared to the experimental DTG data (Fig. 3). The overlapping of the normalized experimental and calculated (simulated) DTG curves indicates the probable kinetic parameters found to thermal event under analysis.

Considering Fig. 4, it can be seen that E values for all samples are approximately constant in the $0.1<\alpha<0.85$ range. Furthermore, it can be seen that E=234±3.65 kJ mol^{-1} for the CB1 sample within the same interval and can be taken as representative data. The difference lower by 10% in the activation energy values regarding α indicate that the reaction can be considered as relatively simple to describe by Eq. (1) for the studied α interval.

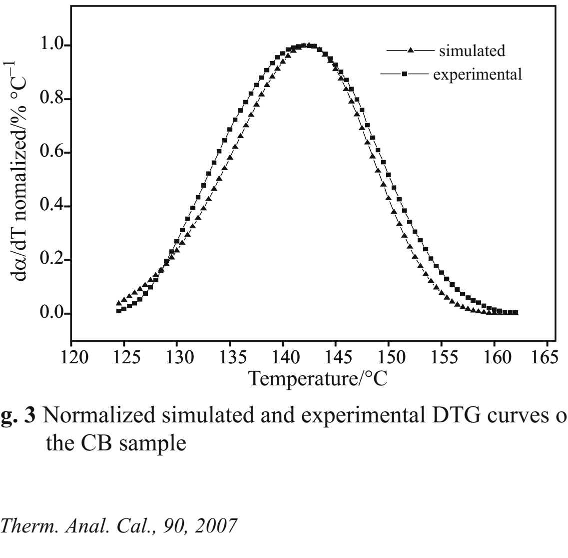

Fig. 3 Normalized simulated and experimental DTG curves of the CB sample

For heterogeneous reactions, E and A lost their relevance since they are not applied as reaction order and concentration. In the literature the E parameter is treated as dependent on several experimental factors such the sample size, particle size, heating rate, presence of impurities and the purging atmosphere around the sample [21–23]. It is possible to show the linear relationship between E and A, known as KCE (kinetic compensation effect), where a variation in E corresponds to change in A, expressed mathematically as ln$A$=a+bE [21].

Figure 5 shows that KCE was observed for all the samples.

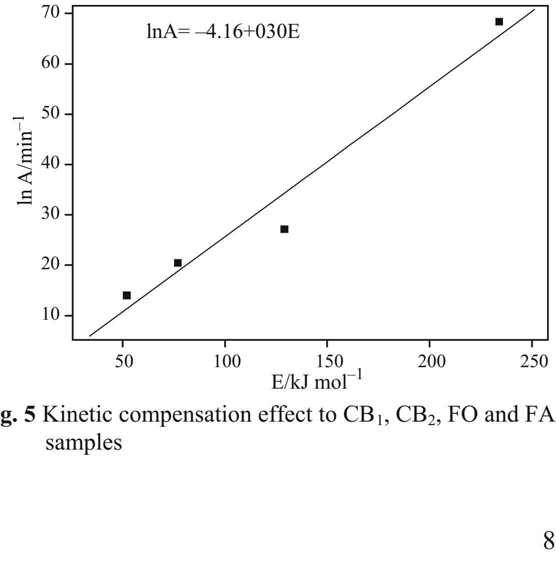

Fig. 5 Kinetic compensation effect to CB$_1$, CB$_2$, FO and FA samples

Conclusions

Kinetic parameters (activation energy, E, and the pre-exponential factor, log$A$) were determined for the thermal decomposition of leachate samples (CB_1 and CB_2) and the solid residues for their organic and aqueous phases (FO and FA). Flynn–Wall isoconversional method was used in the investigated temperature interval. The values of E and log$A$ associated with the Málek and Koga procedures allowed to predict an autocatalytic Šesták–Berggreen (SB) model. This model yields two kinetic exponents, n and m, where m is related to the heterogeneity of the samples representing the complexity of the studied urban solid residue components.

Acknowledgements

The authors are grateful to CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for their financial support.

References

1 F. Alves, Saneamento Ambiental n°103, março/abril, 2004.
2 <http://www.curupira.org.br/notícias/dezembro-2003/materia-dezo3-6.htm> Acessado em 10/10/04.
3 D. Trebouet, P. S. Jaquen and F. Quemeneur, Water Res., 35 (2001)2935.
4 C. L. S. Sisinno and J. C. Moreira, Cad. Saúde Pub., 12 (1996).
5 A. N. Garcia and R. F. Marcilla, Thermochim. Acta, 254 (1995) 277.
6 A. R. Silva, M. S. Crespi, C. A. Ribeiro, S. C. Oliveira and R. S. Silva, J. Therm. Anal. Cal., 75 (2004) 401.
7 J. H. Flynn and J. Wall, Polym. Lett., 4 (1996) 323.
8 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
9 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
10 T. Ozawa, Polym., 12 (1971) 150.
11 T. Ozawa, Bull. Chem. Soc. Jpn., 57 (1984) 639.
12 T. Ozawa, Thermochim. Acta, 100 (1986) 109.
13 N. Koga, Thermochim Acta, 258 (1995) 145.
14 N. Koga, S. Takemoto, T. Nakamura and H. Tanaka, Thermochim. Acta, 283 (1996) 81.
15 J. Málek, J. Sesták, F. Roquerol, J. M. Rouquerol, J. M. Criado and A. Ortega, J. Thermal Anal., 38 (1992) 71.
16 J. Málek, T. Mitisuhash and J. M. Criado, J. Mater Res., 16 (2001) 1862.
17 J. Šesták and G.Berggren, Thermochim. Acta, 3 (1971) 1.
18 R. L. Blaine, DuPont Thermal Application Brief. Du Pont, 1980.
19 J. H. Flynn, J. Wall. NBS A Phys. Ch., 70 (1966) 487.
20 C. D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
21 T. P. Prasad, S. B. Kanungo and H. S. Ray, Thermochim. Acta, 203 (1992) 503S.
22 J. R. MacCallum and M. V. Munro, Thermochim. Acta, 203 (1992) 457.
23 M. B. Dantas, Dissertação de Mestrado, Departamento de Química, Universidade Federal da Paraíba 2006, p. 116.

Received: May 17, 2007
Accepted: May 24, 2007
OnlineFirst: August 31, 2007

DOI: 10.1007/s10973-006-8167-0