J Therm Anal Calorim (2011) 105:461–465
DOI 10.1007/s10973-011-1390-3

Relation between kinetic parameters for reactions of organic matter degradation in waste environmental matrix

Sonia de Almeida · Giseli Bernabé · Marisa S. Crespi · Clóvis A. Ribeiro · Evaneide Nascimento Lima

ESTAC2010 Conference Special Issue

Abstract The organic fraction of urban solid residues disposed of in sanitary landfills during the decomposition yields biogas and leachate, which are sources of pollution. Leachate is a resultant liquid from the decomposition of substances contained in solid residues and it contains in its composition organic and inorganic substances. Literature shows an increase in the use of thermoanalytical techniques to study the samples with environmental interest, this way thermogravimetry is used in this research. Thermogravimetric studies (TG curves) carried out on leachate and residues shows similarities in the thermal behavior, although presenting complex composition. Residue samples were collected from landfills, composting plants, sewage treatment stations, leachate, which after treatment, were submitted for thermal analysis. Kinetic parameters were determined using the Flynn–Wall–Ozawa method. In this case they show little divergence between the kinetic parameter that can be attributed to different decomposition reaction and presence of organic compounds in different phases of the decomposition with structures modified during degradation process and also due to experimental conditions of analysis.

Keywords Kinetic · Landfill · Leachate · Composting · KCE

S. de Almeida (✉) · G. Bernabé · M. S. Crespi ·
C. A. Ribeiro · E. N. Lima
São Paulo State University—UNESP, IQ/CAr, Rua Francisco Degni, s/n, Araraquara, SP, Brazil
e-mail: avopsalmeida@ig.com.br

Introduction

The daily urban garbage production in the State of São Paulo, Brazil is approximately 26,000 tons/day, causing sanitation, environmental, and social problems. Dissemination of illnesses, the contamination of the ground and superficial water and air pollution are environmental impacts that can be caused by not treating these residues and by its inadequate final disposal. Data in the 2009 inventory show that for São Paulo State, Brazil, the index quality of landfill residues (IQR) is inadequate 1.0%, controlled 15.0%, and in an adequate situation 83.9% [1].

The generation of urban solid residues (USR) is directly related to habits, customs, culture, and the purchasing power of the people.

The physical composition of the waste varies from city to city, however, the raw substance used in the confection of these objects is practically the same one. In São Carlos city (Brazil), the composition of the organic matter (OM) present in the waste is around 60%, and it consists of alimentary residues, pruning residues, weeds, and finally microorganisms. The garbage collected in the city is disposed of in the Sanitary landfill of São Carlos. The OM suffers anaerobic decomposition in the sanitary landfill generating biogas and the leachate that are pollution sources. [2].

The leachate constitutes a great environmental problem, because it is a source of diverse organic and inorganic contaminants, therefore needing treatment [3].

The non decomposed OM, humic substance, remains mixed with the ground and its components. The technique used for determination of the organic matter in ground was thermogravimetry [4]. This technique also has been used to study the thermal behavior of residues proceeding from the aerobic decomposition (composting) of URS [5].

Composting is an aerobic, exothermic, bio-oxidation process, of a heterogeneous organic substratum in the solid state, carried out by a complex population of microorganisms, characterized for having as an end product water and CO_2. This has a simultaneous release of organic substance that stabilizes after the maturation. The substratum hygienic cleaning is a function in the rise of the temperature during the decomposition process and of the exposition time of the substratum [6].

The end product is known as compost and was been widely used in agriculture since remote times, already being known and used by the Greeks and Romans, but only from 1920, has the composting process scientifically studied.

The compost can be obtained from diverse substrata as: weeds, sugar cane trash, rinds of trees, wood waste, agro-industrial residues, waste of animals, and others [6].

The aeration, pH, humidity, temperature, structure, and C/N relation are important factors during the composting process. The presence of oxygen in adequate amounts guarantees the transformation of carbohydrates in dioxides of carbon and water. The excess oxygen can dry up the stack and cool the substratum mass in the composting process. The aeration can be increased in the end of the process to reduce the humidity to about 40% [6].

Humidity is another important factor in the composting process and must be around 60% to guarantee the quality of the compost [6].

The reaction of aerobic decomposition depends on the size of particles, the smaller the pieces the faster the biochemical reaction will take place [6].

The pH influences the microbiological activity of the composting process, an important parameter in the accompaniment of all processes. During the composting, the pH changes between 6 and 9 [7].

The result of the analysis of the compost disclosed the convenience of the use of thermal methods to supply simple, fast, and trustworthy information on the stabilization of the OM in the process of agro-industrial treatment of residues by means of composting. The possibility to analyze the entire sample makes the method a routine tool in the control of the composting process [8].

Composting is one of the processes most efficient for the stabilization from sludge of sewage for agriculture [6].

Research of the IBGE shows that in 2008, Brazil had 30.2 million in domiciles bonds to the sewage net, with an increase of four points percentile than in 2007. This percentage increases of 51.1 (2007)–52.5% (2008). In this year, the region of the North of Brazil still had 1.6 million domiciles without collecting net or septic fossil [9].

The quality of aquatic life depends on the industrial and domestic effluents that the rivers and seas receive daily, therefore it is very important to treat these effluents before reaching the rivers. The SABESP, Basic Sanitation Company of the São Paulo State, Brazil, is the company responsible for the service of basic sanitation for the cities in the interior and for the capital of the state, of the 645 cities it works in 366, and around 26 million inhabitants they are benefited by attending of its services. [10].

The treatment of sewage used in the great stations is for activated sludge, a process that was developed in England in 1914. It is widely used for treatment of domestic and industrial sewage. The crude sewage and the activated sludge are mixed and aerated in aeration tanks. After this procedure, the sludge is sent for the secondary decanter, where the solid part is separated from the treated sewage. The sediment sludge returns to the aeration tank and another part is removed for specific treatment, reducing the volume by up to 30% (anaerobic or aerobic) [10].

The amount of sludge (bio solid) produced per person is around 160–190 g/day [6]. This material can be incorporated into the ground, since it does not cause damage to the environment. The ETE sludge presents around 50% of organic material that could be mixed into the ground causing, the appearance of earthworms, an important role in the conditioning of the physical properties of the ground [6].

The molecules in a humidification process contained in the garbage, in the sludge of sewage contain the origins of humic substances.

The humic substances are of a heterogeneous nature and of raised molar mass formed by the products of the decomposition of animals and vegetables presenting a high content of aromatical rings and oxygen due to the presence of acid groupings and esters. The humic substances are formed by the insoluble fraction in alkaline mean (humin), by the soluble fraction in alkaline mean (humic acid) and by the soluble fulvic acids in acid mean (carbohydrates, amino acids) [11].

The kinetic thermal degradation of samples in the solid state has been studied, using curves TG/DTG, from the beginning of the thermal degradation of the ambient matrix.

Isoconversional methods can be classified as differential and integral. They are well known because they allow us to estimate the activation energy, E, pre-exponential factor, A, independently from the kinetic model reaction $f(\alpha)$.

The kinetic parameters E (kJ mol^{-1}) and A (s^{-1}) can be determined by the Flynn–Wall–Ozawa isoconversional method [12, 13].

$$\ln\beta = \ln\left(\frac{AE}{R(\alpha)}\right) - 5.331 - 1.052\,E/RT \quad (1)$$

A, β, and R are pre-exponential factor, heating rate, and gas constant, respectively.

The linear relation obtained through the ln β versus 1/T plot allows determining the activation energy value by the angular coefficient.

The pre-exponential factor A can be calculated using the equation bellow, considering zero order reaction [14]:

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

For small intervals in temperature and the same extension and reactions in a series of experiments using different heating rates, activation energy can be described as:

$$E = -\frac{R}{0.4567} \frac{\mathrm{d}\log\beta_j}{\mathrm{d}\left(1/T\right)} \cong -2.19R \frac{\mathrm{d}\log\beta_j}{\mathrm{d}\left(1/T\right)} \quad (3)$$

The heterogeneous kinetic reaction dependence with the temperature is normally represented by Arrhenius classic law.

$$K = A\exp^{[-E/RT]} \quad (4)$$

where A = frequency factor and E = activation energy.

In a similar group, reaction rates for example, using a similar sequence of reactants, catalytic or solvents, many researches have reported a linear correlation between the frequency factor and activation energy. So the change in the Arrhenius parameter is compensated by a correspondent change in the other.

This behavior is frequently referred as Kinetic Compensation Effect (KCE) that is usually expressed as: ln$A = aE + b$, where a and b are constants, characteristics of a particular group of reactions in which the relation is applied [15].

The average values of E and ln$A$ found were respectively 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 the residues from plant compost USR and food compost from the school restaurant [16].

The landfill residues, leachate, compost, sludge of sewage presented an individual linear relation between the two kinetic parameters (ln$A$ and E) that is called the KCE.

This study has as the objective to use the kinetic parameters to analyze the similarity of the degradation reactions of OM, in the samples of USR, and leachate collected from the sanitary landfill of São Carlos, SP; of plant waste compost and sludge from STS, food compost from the city of Araraquara, SP and humic substances collected from Arachá river, AM, Brasil.

Experimental

The sample of the sanitary landfill residue of São Carlos [17, 18] was removed in 2004 from the cell formed in the year of 2000. The collection was carried through five different points, 10 m distant ones from the others, in a depth of 3 m. A representative sample, called (S_2), was obtained after the mixture of the residues and after the quartering, in accordance with the Norm Technical Brazilian Association [19].

A sample was dried, triturated, bolted, and conditioned in a dissector. The initial mass for the thermal analysis was of 7 mg.

The TG and DTA curves were obtained using a TA Instruments Model SDT 2960 analyzer whit alumina pan, sample mass of around 7 mg, in a nitrogen atmosphere at a flow rate of 100 mL min^{-1}, and heating rate of 5, 10, and 15 °C min^{-1}.

Results and discussions

The TG curves were obtained under nitrogen atmosphere, heating rates of 10, 15, and 25 °C min^{-1}, nitrogen flow of 50 mL min^{-1}, with initial temperature of 30 °C and final of 600 °C. TG curves obtained S_2 (2000) sample could be observed through the Fig. 1.

The TG curves, Fig. 1, show the first step of mass loss up to 200 °C that can be attributed to the dehydration of the sample (0.5%). After 200 °C and with successive losses until 600 °C, occurred probable mass losses relating to the

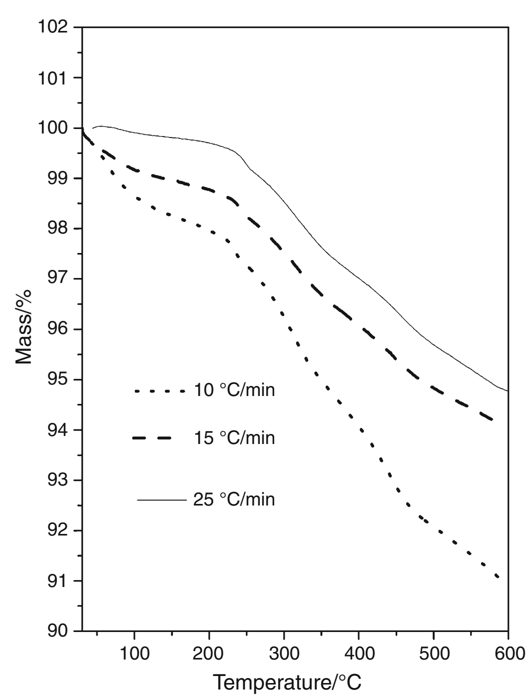

Fig. 1 TG curves of residues retired from São Carlos sanitary landfill (S_2). Conditions: nitrogen atmosphere (50 mL min^{-1}), 10, 15, and 25 °C min^{-1} heating rates, and alumina pan

thermal decomposition of lignocellulosic compounds present in organic matter, a similar result was obtained through other researches [20, 21].

For the kinetic study, the most pronounced DTG peak was selected to each heating rate, correspondent to the second mass loss in the temperature range of 215–260 °C.

Curves DTG of the S_2 residue (2000) for the heating rates 10, 15, and 25 °C min^{-1} can be seen in Fig. 2. The kinetic parameters *E* (kJ mol^{-1}) and *A* (s^{-1}) were determined through the Flynn–Wall–Ozawa isoconversional method by using *p*(*x*) Doyle's approximation.

Through a computational program and using different *T* values to fixed α, it was possible to determine the pre-exponential factor *A* and activation energy *E*. *E* versus α (conversion degree) plot S_2, the sample can be seen in Fig. 3.

By means of graph *E x* α, the same trend was verified in keeping the activation energy constant with the increase of the conversion degree, probably due the occurrence of simple events.

Literature also reports values of the kinetic parameter of Arrhenius for residues of cellulose around 200 kJ mol^{-1}, which are close to the value found for S_2 and humic substance [15, 22].

Ln*A* and *E* data from the wooden samples, residues of foods, domiciles, leachate, and of sewage sludge were also analyzed in this research (Table 1).

The residues of different origins showed evidenced linear correlation between the pre-exponential factor and

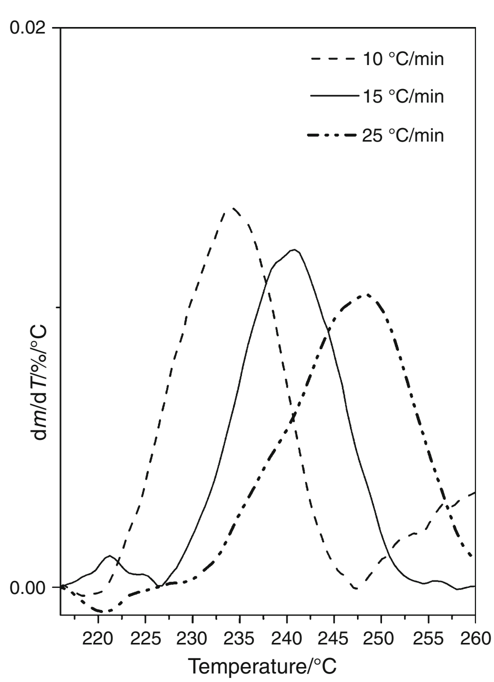

Fig. 2 DTG curves of S_2 sample retired from São Carlos sanitary landfill in heating rates 10, 15, and 25 °C min^{-1}

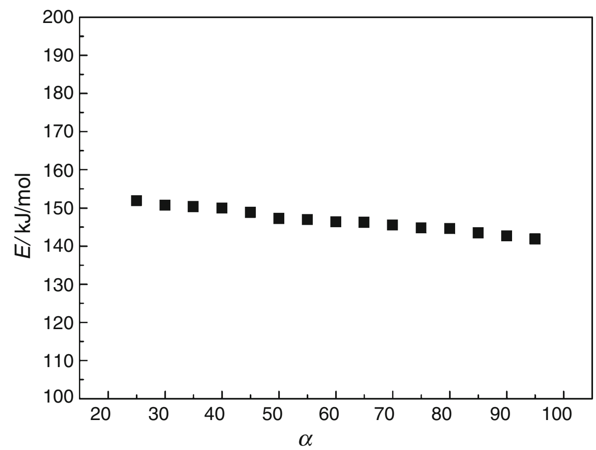

Fig. 3 Activation energy in function of decomposed fraction, α, plot of S_2

Table 1 *E* and ln*A* values to samples from other environment matrix

Samples	Energy/kJ mol^{-1}	ln*A*/min^{-1}
Landfill	147.0	25.2
Humic substance	165.9	47.2
Wood (tea tree)	42.7	6.3
UR (compost)	283.0	33.6
SM (compost)	259.0	52.3
Leachate (PA)	76.9	18.9
Sludge (STS)	125.0	19.9

Heating rate, Δ*T* (temperature change of the studied step), average activation energy and ln*A* to the samples: landfill (S_2), humic substance, wood, composting of the domestic residue revolved (UR), and stack with material of structure (SM), of leachate (PA) and of sewage treatment station sludge

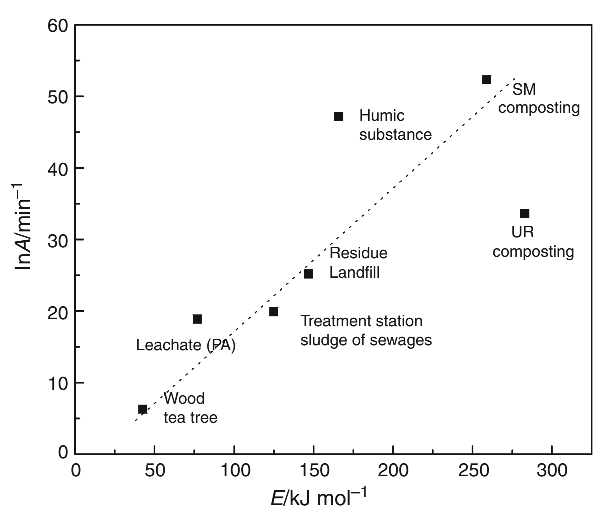

Fig. 4 ln*A* average in function of average of activation energy to landfill (S_2), humic substance, wood, composting of the domestic residue revolved (UR), and stack with material of structure (SM), of leachate aqueous phase and of sewage treatment station sludge

the activation energy, this behavior is known as KCE and it was observed at the beginning of the OM decomposition ($T = 200–400$ °C) in all the cited studies [15, 23–25]. The effect of kinetic compensation, that is usually expressed as: $\ln A = aE + bc$, where a and b are constants, characteristics of a particular group of reactions, carrying a change in ln$A$ is compensated by a corresponding change in the other.

Figure 4 shows the ln$A$ (min^{-1}) versus E (kJ mol^{-1}) graph for the analyzed samples where a linear trend of the express values was observed, even though all the matrixes presented individual KCE. This relation refers to the beginning of the degradation of the organic matter. Although the samples originated from different matrixes, the organic content is similar. The different activation energy values observed for these samples are due to the presence of organic matter at different stages of the decomposition. Molecular modifications occurred during all the degradation process and also from different experimental conditions of the analyses.

Conclusions

The kinetic study carried out indicated that the matrix presented simple events separated by the presence of one basic organic composition, but, when analyzed together they showed a trend of linearity. The relation between the two kinetic parameters (ln$A$ and E) of different samples is due to experimental conditions and the presence of organic components in different periods of degradation and modified molecular structures during these different processes of degradation, either in sanitary landfill or in the composting process, in rivers, or in sewage treatment station sludge.

Acknowledgements The authors thank Instituto de Química de Araraquara, UNESP; Academia da Força Aérea (AFA) Pirassununga, SP and Fundação de Apoio à Ciência, Tecnologia e Educação (FACTE).

References

1. Companhia de tecnologia de saneamento ambiental. Inventário estadual de resíduos sólidos do estado de São Paulo. 2009. http://www.cetesb.sp.gov.br. Accessed 21 July 2010.
2. Lima JD. Gestão de resíduos Sólidos no Brasil. Campina Grande: Inspira Comunicação e Design; 2003
3. Slack RJ, Gronow JR, Voulvoulis N. Household hazardous waste in municipal landfills: contaminants in leachate. Sci Total Environ. 2005;337:119–37.
4. Yyazawa M, Pavan MA, Oliveira EL, Yonashiro M, Silva AK. Gravimetric determination of soil organic matter. Braz Arch Biol Tech. 2000;43:475–8.
5. Pietro M, Paola C. Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process. Thermochim Acta. 2004;413:209–14.
6. Biosssolidos na agricultura. 2nd ed. São Paulo: Associação Brasileira de Engenharia Sanitária e Ambiental—ABES. 2002.
7. Kiehl JE. Manual de compostagem: maturação e qualidade do composto. Piracicaba: Editado pelo autor; 2002.
8. Dell'abate MT. Thermal methods of organic matter maturation monitoring during a composting process. J Therm Anal Calorim. 2000;61:389–96.
9. Instituto brasileiro de geografia e estatística. Pesquisa Nacional de Saneamento. 2008. http://www.ibge.gov.br/home/presidencia. Accessed 21 June 2010.
10. Companhia de tecnologia de saneamento ambiental. http://pt.wikipedia.org/wiki/Companhia_de_Saneamento_B%C3%A1sico_do_Estado_de_S%C3%A3o_Paulo. Accessed 29 July 2010.
11. Rocha JC, Rosa AH. Substâncias húmicas aquáticas: interação com espécies metálicas. São Paulo: UNESP; 2003.
12. Flynn JH, Wall L. General treatment of the thermogravimetry of polymer. Polym Lett. 1966;70A:487–523.
13. Ozawa T. Non-isothermal kinetics and generalized time. Thermochim Acta. 1986;100:109–18.
14. Vyazovkin S. Model-free kinetics. Staying free of multiplying entities without necessity. J Therm Anal Calorim. 2000;83:45–51.
15. Liu N, Zong R, Shu L, Zhou J, FAN W. Kinetic compensation effect in thermal decomposition of cellulosic materials in air atmosphere. J Appl Polym Sci. 2003;89:135–41.
16. Silva AR, Crespi MS, Ribeiro CA, Oliveira SC, Silva MRS. Kinetic of thermal decomposition of residues from different kinds of composting. J Therm Anal Calorim. 2004;75:401–9.
17. São Carlos. In: WIKIPÉDIA: enciclopédia livre. http://pt.wikipedia.org/wiki/Categoria:S%C3%A3o_Carlos. Accessed 13 August 2010.
18. Associação Brasileira de Normas Técnicas. NBR 10.004-resíduos sólidos: classificação. ABNT: Rio de Janeiro; 2004.
19. Associação Brasileira de Normas Técnicas. NBR 10.007-amostragem de resíduos sólidos. ABNT: Rio de Janeiro; 2004.
20. Garcia AN, Marcila A, Font R. Termogravimetric kinetic study of the pyrolysis of municipal solid waste. Thermochim Acta. 1995;254:277–304.
21. Crespi MS, Silva AR, Ribeiro CA, Oliveira SC, Santiago-Silva MRS. Composting of urban solid residues (USR) by different disposition kinetic of thermal decomposition. J Therm Anal Calorim. 2003;72:1049–56.
22. Oliveira LC, Ribeiro CA, Rosa AH, Botero WG, Rocha JC, Romão L PC, Santos A. Thermal decomposition kinetics of humic substance extracted from mi-Rio Negro (Amazon basin) soil sample. J Braz Chem Soc. 2009;20:1003–10.
23. Almeida S, Lima EM, Crespi MS, Ribeiro CA, Salch V. Kinetic studies of urban solid residues and leachate from sanitary landfill. J Therm Anal Calorim. 2009;97:529–33.
24. Lima EN, Crespi MS, Ribeiro CA, Almeida S. Non-isothermal kinetic for lyophilized leachate from sanitary landfill and composting usine. J Therm Anal Calorim. 2007;90:823–6.
25. Capana AS. Caracterização e estudo do comportamento térmico de resíduo (lodo) proveniente de estação de tratamento de água e esgoto no município de Araraquara (Mestrado em Química). Araraquara: Instituto de Química, UNESP; 2009.