

Heating process characteristics and kinetics of sewage sludge in different atmospheres

L.F. Calvo^b, M. Otero^b, B.M. Jenkins^a, A.I. García^b, A. Morán^{b,*}

^a Agricultural Engineering Department, University of California, CA 95616, USA

^b Chemical Engineering Department, University of León, IRENA-ESTIA, Avda. de Portugal 41, León 24071, Spain

Received 28 August 2002; received in revised form 4 June 2003; accepted 17 June 2003

Abstract

The treatment of wastewater generates a by-product, sewage sludge, the disposal of which poses problems. There are, however, a number of options for making use of this residue, including its conversion into a valuable fuel. The aim of this paper is to describe the process of the heating of sewage sludge under different atmospheres of helium and oxygen and to obtain the kinetic parameters by means of a mathematical model, a heating rate of 10 °C/min being used. Measurements were taken by thermogravimetry and mass spectrometry, and proximate and elementary analyses were made of the sludges and their calorific values were determined. Visual observation of the heating profiles shows four stages in the heating process, which have been characterized. The model proposed was found to adequately describe the weight loss of the sludges studied, while making it possible to obtain the kinetic parameters for the differentiated stages in the thermal process but not to establish any clear tendency of the evolution of these parameters with the increase in oxygen in the heating atmosphere.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Sewage sludge; Differential thermal analysis; Kinetic model

1. Introduction

Sewage sludge disposal is becoming a problem due to the increase in municipal wastewater treatment plants to comply with environmental policy. In Europe, the implementation of the Urban Wastewater Treatment Directive 91/171/EEC will cause a major increase in sewage sludge production, expected to be around 8–10 Mt dry matter per year from 2005 on, as the Directive requires the treatment of all sewage discharges from towns with population equivalents of over 2000 [1].

Many different possibilities for the disposal of sludge have been studied, one of the most important being its use as a fertilizer [2–4]. This route is becoming more and more restricted for both regulatory and economic reasons. The conversion of sludge into different materials such as activated carbon has also been suggested by different authors [5]. It has been reported, however that these alternatives will not

be able to deal with the excess of sludge as required in the short term [6].

As a result of all of these limitations, other disposal options have been studied. From the point of view of energy the options mentioned imply a significant waste of sludge's power capacity. Although raw sludge cannot be used as fuel because of its high moisture content, drying it may be considered, because it contains significant amounts of carbon and hydrogen. Many processes exist for converting biomass like sludge into fuel, including biological and thermal ones. The former produce ethanol or methane, and the latter produce heat, solid, liquid, and gaseous fuels, and a wide variety of secondary products [7–9].

As the process of thermochemical conversion of sewage sludge requires exhaustive controls owing to problems of high ash content, fouling and low carbon conversion efficiency, a better understanding of thermal conversion mechanisms is necessary before any successful industrial application can be considered. Information on reaction kinetics would be a preliminary step to that end, and may also be used to describe the mathematical formulation of the reactions and modeling of reactor design [10].

* Corresponding author. Tel.: +1-34-987-291-841;

fax: +1-34-987-291-839.

E-mail address: dfqamp@unileon.es (A. Morán).

Numerous authors have reported kinetic data for fossil fuels [11–13], alternative fuels [14,15] and several solid wastes [16,17]. However, the reaction kinetics of sewage sludge have received a very little attention until recently. Only a few papers have been published: Conesa et al. [18] studied the pyrolysis and combustion of different types of sewage sludge, and Otero et al. [19] analyzed the co-combustion of sewage sludge and coal under different conditions. Again, only a few papers offer kinetic data for sewage sludge heating in different atmospheres. For our study, helium and oxygen were used to simulate the processes of combustion, gasification and pyrolysis.

The aim of this paper is to describe the process of heating sewage sludge in different atmospheres of helium and oxygen and to obtain the kinetic parameters by means of a mathematical model.

2. Materials and methods

2.1. Materials

Representative samples of two kinds of urban sewage sludge were used for this study, designated SLA and SLB. SLA is obtained from the treatment of waste waters from a large city (population about 1.5 million) and SLB comes from a small city (population about 150,000). Both were subjected to stabilization by the same kind of anaerobic digestion as at their original sewage treatment plants and were dehydrated by centrifugation, so any differences in analysis and composition probably result from the dehydration process.

The sludges were then ground to pass through a 0.2 mm screen for feeding to the thermobalance. For the analysis of some properties the material had to be ground to pass through a 420 μm screen.

2.2. Fuel analysis

Before thermogravimetric analysis the sludges were analyzed to determine the main properties affecting thermal conversion. Moisture content was determined gravimetrically by the oven drying method. The highest heating value at constant volume (HHV) was measured using an adiabatic oxygen bomb calorimeter. Fuel was previously sampled in 1 g amounts, pelleted in a hand press to 12.7 mm diameter, and oven-dried to constant weight at $104 \pm 3^\circ\text{C}$ prior to analysis. Proximate determinations were made according to modified procedures ASTM D 3172–D 3175 (Standard Practice for Proximate Analysis of Coal and Coke); E 870 (Standard Methods for Analysis of Wood Fuels), D 1102 (ash in wood), and E 872 (volatile matter in wood); and the methods for refuse-derived fuel (RDF)—E 830 (ash), and E 897 (volatile matter). Volatile concentration was determined under inert conditions using a modified method for sparking fuels in which samples in covered nichrome crucibles

were placed in the front part of the open muffle furnace preheated to 950°C for 6 min to dispel volatiles over a period of more gradual heating, then brought to completion in the closed furnace during an additional 6 min, removed, and cooled under desiccant while still covered and weighed immediately.

For knowing the weight fractions by element of the constituents, sludge samples were sent to a commercial laboratory where standard methods were used.

2.3. Thermogravimetric and mass spectrometry analysis

Thermogravimetric analysis was carried out using a TGA Instrument SDT2960, which is able to provide a continuous measurement of sample weight as a function of time or temperature and also give a DTG signal (rate of weight loss) when used with the appropriate software.

Samples weighing 6–8 mg were placed in a pottery crucible and heated at $10^\circ\text{C}/\text{min}$ from ambient to 650°C . To simulate the combustion, gasification and pyrolysis processes, five different atmospheres were used, all with a flow of 100 ml/min. These were 100% helium, 90% helium/10% oxygen, 95% helium/5% oxygen, 97% helium/3% oxygen and 100% oxygen, and were, respectively, designated Atm100, Atm90, Atm95, Atm97 and Atm0. CO and CO₂ gas emissions were monitored with a Balzers GSD 300 mass spectrometry apparatus in line with the thermal analysis equipment. Instead of nitrogen, helium was used for obtaining the inert atmosphere as N₂ has the same molecular weight as CO, making CO determination possible by mass spectrometry. No appreciable differences were detected in TG profiles.

2.4. Kinetic model

DTG curves are characterized for containing shoulders and/or double peaks because more than one reaction is involved. The best mathematical model for describing overall decomposition is that of independent parallel reactions one [16]. The material consists of several components, each being assumed to decompose independently of the others. The kinetic equation for each single reaction can be described by the following equations:

$$\frac{d\omega_i}{dt} = K_i e^{(-E_i/RT)} (1 - \omega_i)^n \quad (1)$$

$$\omega_i = \frac{m_{0i} - m_{ij}}{m_{0i} - m_{fi}} \quad (2)$$

where ω_i is the reacted mass fraction or normalized mass for reaction i at time j ; R the gas universal constant; T the absolute temperature; K the frequency factor; E the activation energy; n the order of reaction; m_{0i} the initial mass of the sample i ; m_{ij} the sample mass for the reaction i at time j ; and m_{fi} the final mass of the sample in that reaction.

The overall rate of conversion for N reactions can be described by the following equation:

$$-\frac{d\omega}{dt} = \sum_{i=1}^N c_i \frac{d\omega_i}{dt} \quad (3)$$

where c_i is a coefficient that expresses the contribution of each single reaction to the mass global lost.

Eq. (4) allows us to calculate coefficient c_i after determination of the frequency factor, activation energy and order of reaction by the following equation:

$$\frac{d\omega}{dt} = \sum_{i=1}^N c_i K_i e^{(-E_i/RT)} (1 - \omega)^n \quad (4)$$

This model was carried out using Origin6.1. v6.1052(B232) software. We used a non-linear least squares curve fitter performing the Levenberg–Marquardt (LM) algorithm. The way of defining the best fit is to choose the parameters so that the sum of the squares of the deviations of the theoretical curve from the experimental points for a range of independent variables is minimum.

For the optimization of the kinetic parameters the objective functions proposed by two different researchers were considered, one by Conesa et al. [17] and one by Sørum et al. [16]. These depend on the number of points considered in the model. It is not, however, possible to compare their values because the authors do not specify any particular number of points. To avoid that dependence and given that each run has different number of points to be fitted, this will be the number to be considered. These authors' expressions have therefore been divided by the total of points used for the fitting, to give expressions (5) and (6). Expression (5) is obtained from Conesa's expression and is described as

$$\text{OF}_{\text{CC}} = \frac{\sum_i \sum_j [(d\omega/dt)_{\text{exp}ij} - (d\omega/dt)_{\text{calc}ij} / (d\omega/dt)_{\text{exp}j}^{\text{max}}]^2}{N} \quad (5)$$

where i is the value of the variable at time t for reaction j and N the number of points considered in the fit. Subscript “exp” represents the experimental values and subscript “calc” the calculated values. Finally, superscript “max” represents the maximum value obtained for the variable.

Another objective function is obtained from Sørum's expression and it is shown in the following equation:

$$\text{OF}_{\text{SC}} = \frac{\sum_{i=1}^N [(d\omega/dt)_i^{\text{exp}} - (d\omega/dt)_i^{\text{calc}}]^2}{N} \quad (6)$$

Subscript j denotes values of the variable at time t , N the number of points fitted, superscript “exp” represents the experimental values and “calc” the calculated values.

Conesa's modified objective function gives a value of the relative dispersion to the maximum value of $d\omega/dt$ because the fit depends on that maximum value. Sørum's modified objective function would be similar to the regression variance of the fit, showing the dispersion of the experimental values against the calculated values. Both have been divided by the total number of points considered.

3. Results and discussion

SLB has a higher ash content than SLA content owing to a more complete digestion process [22], meaning that the maximum heating value of SLB sludges is lower than that of SLA, so SLB would be less efficient as a fuel (Table 1).

3.1. Thermal analysis of the sludge heating process

Heating profiles at programmed temperatures for the five atmospheres tested are shown in Fig. 1 (SLA) and Fig. 2 (SLB). Atm100 is representative of a pyrolysis process, Atm0 of combustion and the others of gasification. Tables 2 and 3 show results of thermogravimetric analysis, including initial and final temperature of the reactions and the maximum DTG value with the temperature for each reaction.

A visual observation of the thermograms reveals four stages in the sludge heating for which four different temperature zones can be interpreted.

3.1.1. Drying

This stage can be observed in burning profiles showing a loss of mass between ambient temperature at the beginning of the test and about 150 °C, corresponding to a loss of moisture and of the very light volatile materials [23]. In most thermogravimetric analyses, authors often overlook this stage because of the very low moisture content of the sample, so this stage will not be discussed in this paper.

3.1.2. Low temperature region

This stage begins between about 170 and 260 °C depending on the heating atmosphere. The lowest temperature

Table 1
Sewage sludge properties^a

Sludge	Elemental analysis (%)						Proximate analysis (%)			
	C	H	N	S	Cl	O	Moisture	Ash	Volatiles	HHV ^b (MJ/kg)
SLA	36.2	4.5	5.6	1.1	0.1	14.7	7.9	37.9	55.0	15.4
SLB	22.7	3.3	3.1	0.9	0.1	16.1	3.9	53.8	42.9	9.5

^a All values dry basis except moisture.

^b High heating value.

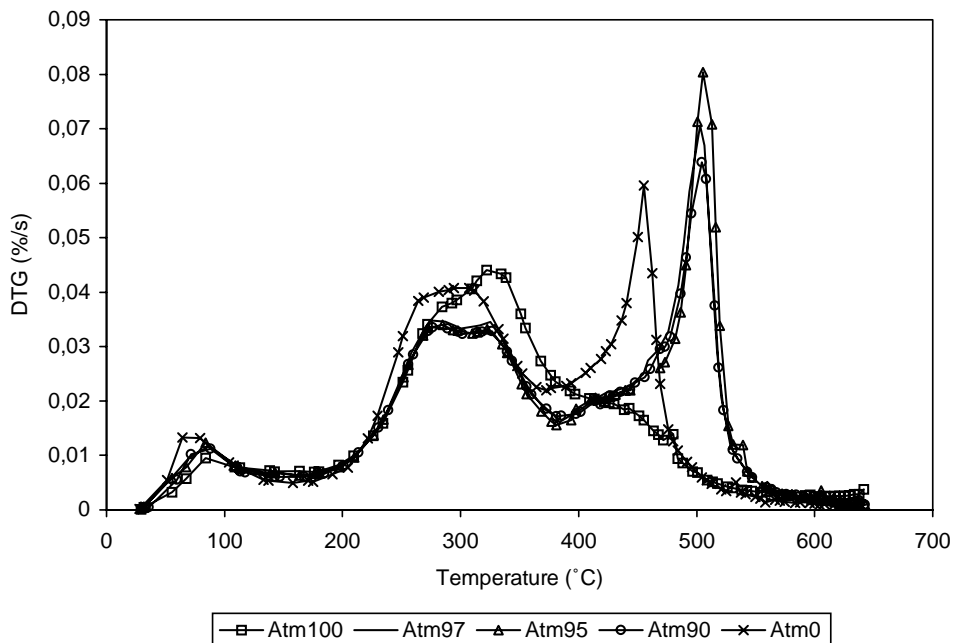


Fig. 1. SLA heating profiles.

required for devolatilization to begin is for Atm90, an atmosphere that simulates a gasification process.

Except for SLB in Atm0, a double peak can be observed in this stage, its first shoulder perhaps identified with biodegradable materials, undigested organics and dead bacteria, together with the emissions of semivolatile compounds. The emission of organic polymers must be represented in the second shoulder as they need higher temperatures to devolatilize [22,23]. For SLB in Atm0, a single

peak is to be observed as heating takes place in a reactive atmosphere and SLB has a lower volatile content.

The highest DTG values for SLA sludge in the first shoulder are obtained in Atm100 at 285 °C and in Atm0 at 271 °C. In the remaining atmospheres, it is obtained at intermediate temperatures. The same tendency can be appreciated in the case of the second peak. This decrease in temperature required for the maximum DTG is a consequence of the presence of oxygen in the heating

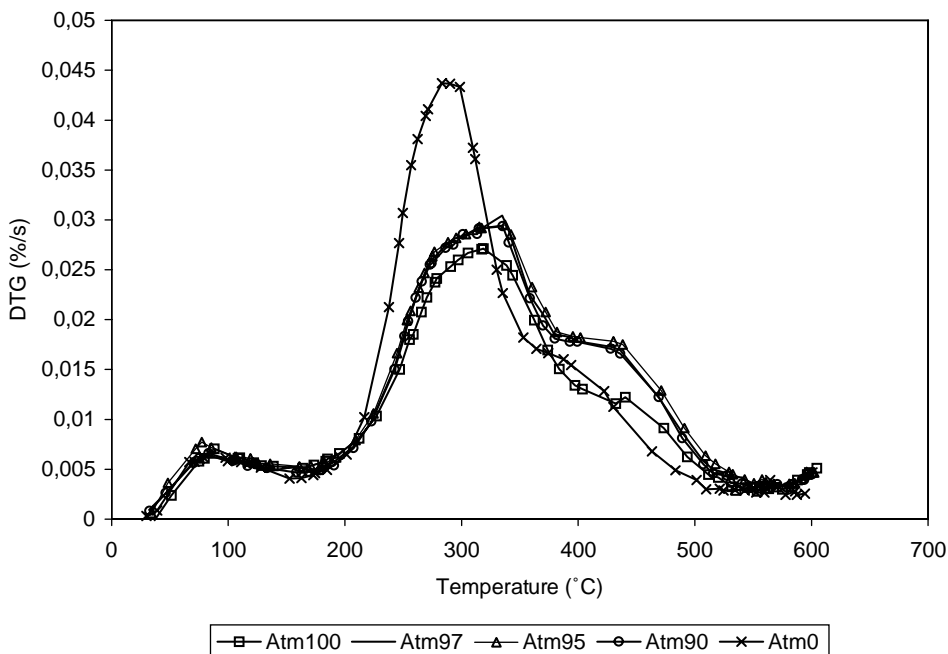


Fig. 2. SLB heating profiles.

Table 2
Results from thermogravimetric analysis for SLA sludge^a

	Atm100	Atm97	Atm95	Atm90	Atm0
LTR Peak I					
T_0 (°C)	239	177	240	165	236
T_f (°C)	327	303	323	330	306
DTG _{max} (%/s)	0.0373	0.0353	0.0326	0.0338	0.0344
$T_{DTG_{max}}$ (°C)	285	280	280	284	271
LTR Peak II					
T_0 (°C)	244	293	318	300	178
T_f (°C)	491	366	342	361	437
DTG _{max} (%/s)	0.0434	0.0338	0.0323	0.0322	0.0408
$T_{DTG_{max}}$ (°C)	333	330	330	331	308
MTR					
T_0 (°C)	277	368	338	363	
T_f (°C)	64	503	506	500	
DTG _{max} (%/s)	0.0197	0.0221	0.0202	0.0209	
$T_{DTG_{max}}$ (°C)	426	434	491	431	
HTR					
T_0 (°C)		399	401	390	374
T_f (°C)		557	604	616	533
DTG _{max} (%/s)		0.0701	0.0811	0.0639	0.0582
$T_{DTG_{max}}$ (°C)		505	509	505	458

^a T_0 : initial temperature of the process; T_f : final temperature of the process; DTG_{max}: largest value of DTG in the considered process; $T_{DTG_{max}}$: temperature associated to DTG_{max}; LTR: low temperature region; MTR: medium temperature region; HTR: high temperature region.

atmosphere, as it is a reactive gas and facilitates devolatilization reactions.

When the test is carried out on SLA sludge in Atm100, DTG_{max} of first peak takes a value of 0.0373%/s, decreasing as atmospheric oxygen content increases, so DTG_{max} in Atm90, for example is 0.0320%/s. Nevertheless, in Atm0,

no such tendency is observed because the fourth stage starts before second stage has ended. Therefore, DTG_{max} detected at the second peak of devolatilization in Atm0 is higher than in Atm90. The same trend is observed for the second peak. The first peak is lower than the second one when the test is run in an inert atmosphere, however, this difference

Table 3
Results from thermogravimetric analysis for SLB sludge^a

	Atm100	Atm97	Atm95	Atm90	Atm0
LTR Peak I					
T_0 (°C)	262	251	258	246	193
T_f (°C)	306	332	337	330	383
DTG _{max} (%/s)	0.0058	0.0279	0.0283	0.0274	0.0440
$T_{DTG_{max}}$ (°C)	294	291	294	292	292
LTR Peak II					
T_0 (°C)	202	249	265	252	
T_f (°C)	437	418	407	410	
DTG _{max} (%/s)	0.0272	0.0304	0.0295	0.0296	
$T_{DTG_{max}}$ (°C)	320	335	337	332	
MTR					
T_0 (°C)	337				
T_f (°C)	537				
DTG _{max} (%/s)	0.0118				
$T_{DTG_{max}}$ (°C)	437				
HTR					
T_0 (°C)		263	263	272	242
T_f (°C)		573	568	577	528
DTG _{max} (%/s)		0.0176	0.0183	0.0168	0.0161
$T_{DTG_{max}}$ (°C)		418	416	425	386

^a T_0 : initial temperature of the process; T_f : final temperature of the process; DTG_{max}: largest value of DTG in the considered process; $T_{DTG_{max}}$: temperature associated to DTG_{max}; LTR: low temperature region; MTR: medium temperature region; HTR: high temperature region.

decreases when the oxygen content of the atmosphere increases, being inverted in Atm0. This can be explained by emissions of organic polymers being more easily removed when the heating atmosphere contains oxygen.

As for SLB sludge, two peaks can be observed except in Atm0. At the first peak, no major differences can be appreciated in the temperature at which DTG_{max} is obtained as SLB has a lower volatiles content than SLA. At the second peak this temperature decreases when oxygen is not a restrictive factor for combustion reactions. The DTG_{max} value continues to fall as oxygen content increases as for SLA. The relationships between the two peaks are similar for the two sludges.

3.1.3. Medium temperature region

A third stage occurs during or after the low temperature region. Weight losses, represented by several peaks, may be produced by reactions between char and volatiles from previous stages [20]. Non-degradable compounds like cellulosic material may also react in this stage [21]. For analysis this stage has been considered as a single reaction.

For SLA sludge, this stage can be differentiated in all tests which have helium in the heating atmosphere. It starts at 277 °C for Atm100 rising to about 325 °C for the other atmospheres. However, for SLB sludge a peak is only to be observed in Atm100, owing to a lower volatile content.

3.1.4. High temperature region

When oxygen is used in the heating atmosphere the initial temperature of this stage is lower because exothermic reactions take place. Consequently, previously released volatiles are burned and the remaining volatiles are emitted. At the same time, there is a rapid oxidation of the rest of the oxidant material in the sample.

Heating in an inert atmosphere (Atm100) produces neither oxidation nor combustion. Weight loss does, however, occur, probably owing to both devolatilization and reactions between char and volatiles from previous stages.

This stage occurs at a lower temperature when the heating atmosphere is 100% oxygen because it is totally reactive and exothermic reactions allow combustion reactions to occur at lower temperatures in the oven. This stage occurs at temperatures about 100 °C higher for SLA than SLB because the char of the latter is less reactive and its ash content is higher.

Mass spectrometry analysis was used to monitor CO and CO₂ gas emissions. Fig. 3, for example, shows the evolution of CO and CO₂ emissions from SLA in Atm100, Atm95 and Atm0. CO was observed to be given off with helium in the heating atmosphere, the greatest emissions being noticed in Atm95. When CO emissions were observed in Atm97 and Atm90, amounts were similar to those registered for Atm95. In 100% oxygen, CO₂ emissions reach the highest values in the medium temperature region, thus bearing out the idea that Atm97, Atm95 and Atm90 simulate a gasification process [24].

The different performances of the two kinds of sludges are probably due to a difference in the original wastewater, as they both underwent a similar anaerobic digestion.

Mass loss during heating is higher for SLA sludge, so gasification or pyrolysis would be the best processes for it. Combustion would be more suitable for SLB sludge as it ignites at 100 °C less than SLA.

3.2. Application of the kinetic model

The frequency factor, activation energy, order of the reaction and mass that reacts for each of the peaks obtained for these parameters are of the same order as those given by other authors for different materials catalogued as biowastes. The contribution of each single reaction to the global mass loss is calculated with Eq. (3). For example, Fig. 4 shows the kinetic fit of SLA and SLB when heated in Atm95. Results of kinetic parameters are shown in Tables 4 and 5.

It will be observed that no clear tendency may be established of the evolution of the kinetic parameters with the

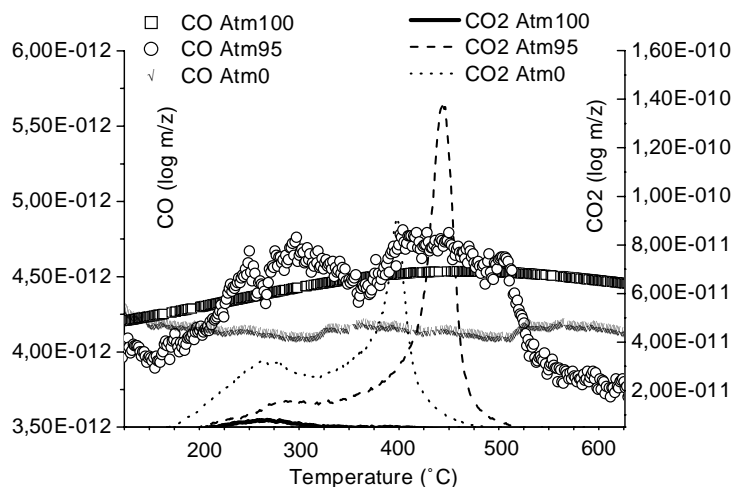


Fig. 3. CO and CO₂ emissions during heating process for SLA and Atm100, Atm95 and Atm0.

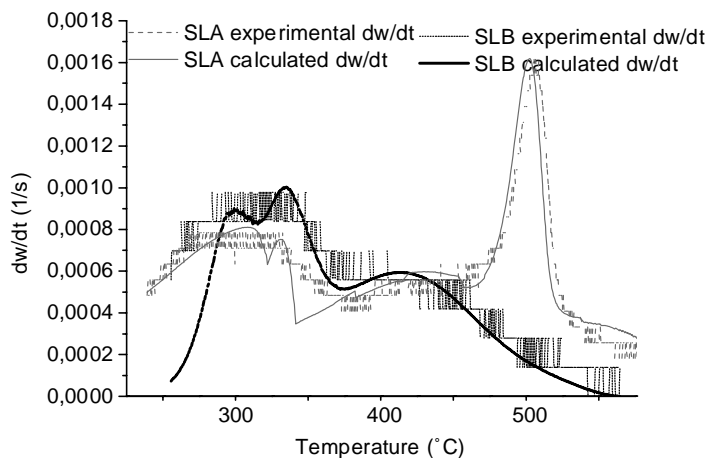


Fig. 4. Kinetic fit of SLA and SLB in Atm95.

increase of oxygen in the heating atmosphere. Some deductions, however, may be made.

For the medium temperature region, the activation energy takes the highest values when oxygen is present in the heating atmosphere a point which must be borne in mind if sludge is to be subjected to a gasification or pyrolysis process. Otherwise, the activation energy value is usually under 200 kJ/mol, although in several cases, mainly for the high temperature region, it exceeded 400 kJ/mol, probably owing to the narrower degradation temperature range and the

higher DTG peak temperature of the combustion reactions. Few data have been published on the degradation of sludge, but activation energies of 97 and 136 kJ/mol have been reported for the pyrolysis in high purity nitrogen of municipal solid wastes [16]. Other authors, such as Conesa et al. [17], for the combustion of other wastes, obtain values in the range 70–252 kJ/min. These values are in the same order that the values shown in this paper.

Frequency factor values are usually lower than the range of 10^{10} s^{-1} , in line with other authors' results [15].

Table 4
Kinetic parameters for SLA sludge^a

	Atm100	Atm97	Atm95	Atm90	Atm0
LTR Peak I					
<i>K</i> (1/s)	3.52E17	6.40E5	2.35E2	6.94E5	1.51E28
<i>E</i> (J/mol)	205	85	51	85	310
<i>n</i>	2.4	0.8	0.5	0.9	2.3
<i>m</i> (g) × 10 ⁻³	0.56	1.05	1.18	1.18	0.15
<i>c</i>	0.05	0.18	0.21	0.24	0.02
LTR Peak II					
<i>K</i> (1/s)	3.56E9	1.14E5	3.50E21	3.87E5	7.46
<i>E</i> (J/mol)	135	86	269	83	39
<i>n</i>	1.7	0.7	0.8	0.5	1.3
<i>m</i> (g) × 10 ⁻³	1.26	0.79	0.29	0.69	2.70
<i>c</i>	0.49	0.17	0.05	0.03	0.70
MTR					
<i>K</i> (1/s)	1.41E8	3.81E4	8.37E4	1.80E11	
<i>E</i> (J/mol)	138	103	96	179	
<i>n</i>	2.5	0.4	1.8	2.6	
<i>m</i> (g) × 10 ⁻³	1.25	1.01	1.36	1.04	
<i>c</i>	0.44	0.68	0.30	0.25	
HTR					
<i>K</i> (1/s)		5.93E7	1.70E27	3.57E14	1.52E18
<i>E</i> (J/mol)		145	434	247	281
<i>n</i>		2.5	2.5	1.8	2.3
<i>m</i> (g) × 10 ⁻³		1.10	1.23	1.12	0.97
<i>c</i>		0.03	0.44	0.25	0.39

^a *K*: frequency factor; *E*: activation energy; *n*: order of reaction; *m*: released mass in the process; *c*: contribution of the single reaction to the mass global lost; LTR: low temperature region; MTR: medium temperature region; HTR: high temperature region.

Table 5
Kinetic parameters for SLB sludge^a

	Atm100	Atm97	Atm95	Atm90	Atm0
LTR Peak I					
<i>K</i> (1/s)	2.67E8	1.81E18	2.27E23	9.37E22	4.87E11
<i>E</i> (J/mol)	120	216	273	267	148
<i>n</i>	2.0	2.0	2.3	2.8	3.8
<i>m</i> (g) × 10 ⁻³	0.10	0.38	0.36	0.31	1.30
<i>c</i>	0.04	0.16	0.21	0.18	0.54
LTR Peak II					
<i>K</i> (1/s)	6.01E7	1.86E14	1.61E20	1.35E14	
<i>E</i> (J/mol)	161	200	257	117	
<i>n</i>	2.4	2.1	2.3	2.5	
<i>m</i> (g) × 10 ⁻³	1.27	0.62	0.49	0.77	
<i>c</i>	0.59	0.28	0.21	0.42	
MTR					
<i>K</i> (1/s)	2.82E26				
<i>E</i> (J/mol)	301				
<i>n</i>	1.5				
<i>m</i> (g) × 10 ⁻³	0.68				
<i>c</i>	0.37				
HTR					
<i>K</i> (1/s)		1.31E5	7.54E3	6.93E13	2.21E10
<i>E</i> (J/mol)		99	84	207	157
<i>n</i>		2.1	1.8	3.8	2.7
<i>m</i> (g) × 10 ⁻³		1.08	1.36	1.10	1.09
<i>c</i>		0.40	0.64	0.40	0.46

^a *K*: frequency factor; *E*: activation energy; *n*: order of reaction; *m*: released mass in the process; *c*: contribution of the single reaction to the mass global lost; LTR: low temperature region; MTR: medium temperature region; HTR: high temperature region.

The order of the reaction is a parameter of the model used. Although authors such as Sørnum et al. [16] or Ebeling and Jenkins [15] suppose in their models that the order of reaction value is 1, several others consider it also to be a model parameter, as in this study. A model that considers this value as a parameter is therefore more representative of the reality of the heating process. From Tables 5 and 6, its value will be observed in most cases to be under 2.5. In comparison with values obtained when the same model is applied to other materials, such as rice straw, reaction order values for sludge kinetics are higher, probably owing to the more complex composition of sludge, originating from urban wastewaters. This supposes a higher number of heating degradation reactions. Similar values for this parameter are reported by others authors, such as Conesa et al. [17], for the combustion of tyre wastes.

Objective function values are shown in Table 6. The most important appreciation is that FO_{cc} and FO_{sc} are lower for SLA than SLB. DTG profiles for SLA show a better definition of shoulders, allowing for a better fit with the model described and, therefore, lower values for the objective functions. When compared, FO_{sc} always gives lower values than FO_{cc} because the latter is obtained by dividing the difference between the experimental and calculated values by the maximum experimental value. If FO_{cc} and FO_{sc} values from sludge heating kinetics are compared with those of other materials, such as agricultural wastes, in experiences realized in our laboratory and not yet published, higher values

Table 6
Objective function values

		FO _{cc}	FO _{sc}
Atm100	SLA	9.21E-3	1.17E-8
	SLB	0.031	3.31E-8
Atm97	SLA	6.88E-3	6.65E-8
	SLB	7.52E-3	1.99E-8
Atm95	SLA	6.46E-3	1.69E-8
	SLB	0.015	3.05E-8
Atm90	SLA	0.021	5.93E-9
	SLB	0.026	2.55E-6
Atm0	SLA	5.72E-3	7.78E-9
	SLB	0.022	3.69E-7

are obtained for the sludge, probably for the reasons already stated.

4. Conclusions

DTG profiles proved the possibility of differentiating four stages in the heating process of sludge when there is oxygen in the atmosphere. Without oxygen (a pyrolysis process) only the first three stages can be differentiated, as the fourth one does not take place. Mass loss during heating is higher for SLA sludge, so it is best suited for gasification or pyrolysis, while combustion would be more appropriate for SLB

sludge as it ignites at a temperature 100 °C lower than SLA sludge.

The model used was found to adequately describe the weight loss of the two kinds of sludge considered. With it we were able to obtain the kinetic parameters (activation energy, frequency factor and order of reaction) for the stages differentiated in the thermal process, although no clear tendency could be established for the evolution of these kinetic parameters with the increase of oxygen in the heating atmosphere.

Acknowledgements

This research was made possible through a grant from the Spanish Administration from the Education and Culture Department given to L.F. Calvo and the Castilla y León Administration for the Project number LE 34/01.

References

- [1] J. Werther, T. Ogada, Sewage sludge combustion, *Prog. Energy Combust. Sci.* 25 (1999) 55–116.
- [2] A. Morán, E. Garzón, J.M. Castaño, J.L. Villarías, Aplicación de lodos de una depuradora de industria agroalimentaria en agricultura, *Revista Técnica del Medio Ambiente*, September 1997, pp. 25–30.
- [3] A.B. Pincince, L.H. Moss J.F. Donovan, M.S. Switzenbaum, Biosolids management: evaluation of innovative processes, in: Project 96-Rem-1, Water Environment Research Foundation, Camp Dresser & McKee Inc., 1998.
- [4] M.J. Martín, M.D. Balaguer, M. Rigola, Valoración de fangos biológicos excedentes de EDARs por transformación en carbón activo, *Tecnología del agua* 184 (1997) 42–48.
- [5] L.F. Calvo, M. Otero, A. Morán, A.I. García, Upgrading sewage sludge for adsorbent preparation by different treatments, *Bioresour. Technol.* 80 (2001) 143–148.
- [6] P.J. Matthews, European progress on the political and economic concerns of sludge disposal—is the future biosolids or ash? in: Proceedings of the EWPCA-NVA Conference on Future of Water Quality Management in Europe, Aquatech, Amsterdam, September 1996.
- [7] E. Rensfelt, Practical achievements in biomass gasification, in: H. Egnéus, A. Ellegard (Eds.), *Bioenergy*, vol. 84, Elsevier, Amsterdam, 1984.
- [8] A.C.M. Beenackers, W.P.M. van Swaaij, Methanol production from biomass, in: H. Egnéus, A. Ellegard (Eds.), *Bioenergy*, vol. 84, Elsevier, Amsterdam, 1984.
- [9] B. Revuz, Biomass ethanol—present technologies, realistic industrial prospects, energy and economic balances, in: H. Egnéus, A. Ellegard (Eds.), *Bioenergy*, vol. 84, Elsevier, Amsterdam, 1984.
- [10] C.T. Bowman, Kinetics of pollutant formation and destrucción in combustion, *Prog. Energy Combust. Sci.* 1 (1975) 33–45.
- [11] M.A. Serio, S. Charpenay, R. Bassilakis, P.R. Solomon, Measurement and modelling of lignin pyrolysis, *Biomass Bioenergy* 7 (1994) 107–124.
- [12] K.N. Ninan, K. Krishnan, V.N. Krishnamurthy, Kinetics and mechanism of thermal decomposition of insity generated calcium carbonate, *J. Therm. Anal.* 37 (1991) 1533–1543.
- [13] L. Campanella, M. Tomassetti, R. Tomellini, Thermoanalysis of ancient, fresh water logged woods, *J. Therm. Anal.* 37 (8) (1991) 1923–1932.
- [14] J.O. Jaber, S.D. Probert, Pyrolysis and gasification kinetics of Jordanian oil-shales, *Appl. Energy* 63 (1999) 269–286.
- [15] J.M. Ebeling, B.M. Jenkins, Physical and chemical properties of biomass fuels, *Trans. ASAE* 28 (3) (1985) 898–902.
- [16] L. Sørum, M.G. Grønli, J.E. Hustad, Pyrolysis characteristics and kinetics of municipal solid wastes, *Fuel* 80 (2001) 1217–1227.
- [17] J.A. Conesa, R. Font, A. Fullana, J.A. Caballero, Kinetic model for the combustion of tyre wastes, *Fuel* 77 (13) (1998) 1469–1475.
- [18] J.A. Conesa, A. Marcilla, J.A. Caballero, R. Font, Comments on the validity and utility of the different methods for kinetic analysis of thermogravimetric data, *J. Anal. Appl. Pyrol.* 58–59 (2001) 617–633.
- [19] M. Otero, C. Díez, L.F. Calvo, A.I. García, A. Morán, Analysis of the co-combustion of sewage sludge and coal by TG-MS, *Biomass Bioenergy* 22 (2002) 319–329.
- [20] S. Gaur, T.B. Reed, Prediction of cellulose decomposition rates from thermogravimetric data, *Biomass Bioenergy* 7 (6–1) (1994) 61–67.
- [21] S. Tia, S.C. Bhattacharya, P. Wibulswas, Thermogravimetric analysis of Thai lignite. I. Pyrolysis kinetics, *Energy Conserv. Manage.* 31 (3) (1991) 265–276.
- [22] M. Otero, L.F. Calvo, B. Estrada, A.I. García, A. Moran, Thermogravimetry as a technique for establishing the stabilization progress of sludge from wastewater treatment plants, *Thermochim. Acta* 389 (2002) 121–132.
- [23] A.B. Singh, A study of reaction kinetics for thermochemical conversion of rice straw, Ph.D. Thesis, University of California, Davis, 1996.
- [24] D.L. Urban, M.J. Antal Jr., Study of the kinetics of sewage sludge pyrolysis using DSC and TGA, *Fuel* 61 (1982) 799–806.