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NON-ISOTHERMAL THERMOGRAVIMETRIC ANALYSIS OF THE COMBUSTION OF TWO DIFFERENT CARBONACEOUS MATERIALS

Coal and sewage sludge

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The combustion of two different sewage sludges and a semianthracite coal was studied and compared by thermogravimetric analysis. Non-isothermal thermogravimetric data were used to evaluate the Arrhenius parameters (activation energy and the pre-exponential factor) of the combustion of these carbonaceous materials. The paper reports on the application of model-free isoconversional methods for evaluating and comparing the corresponding activation energy of the combustion process.

Keywords: *coal, combustion, kinetics, sewage sludge, thermogravimetric analysis*

Introduction

Sewage sludge (biosolids) is an unavoidable byproduct of wastewater treatment. It has valuable attributes but can be odorous and often contains unpleasant constituents that restrict its further use. Land application provides a means of supplying nutrients, such as nitrate and phosphorus, and organic matter (OM) that could be both agriculturally useful and environmentally appropriate [1]. However, the reduced availability of land, the increased public concerns over food chain safety, and the associated uncertainties and costs of reuse have required water utilities to explore alternative management options that can contribute to a more sustainable biosolids strategy [2].

Among the several ways of disposing of sewage sludge which could be considered, it always must be tried, when possible, to make use of this waste material properties and characteristics so to turn it into a resource. Combusting and co-combusting biosolids with fuels could provide one secure outlet, among others, and generate income through energy recovery. The changing energy policy climate lends support, in principle, to the use of biomass and locally generated waste as fuel, as part of a move toward the low carbon economy. However, the classification of biosolids as ‘waste’ has constrained its onward use [3, 4]. Research on sewage sludge combustion and information campaigns are probably the first step to overcome reticence.

Some published works have shown that safe co-combustion of sewage sludge is feasible from energy, economic and environmental points of view and allows the use of existing infrastructures [2, 5–8]. Thermogravimetric analysis (TG) has been used to study both sewage sludge and coal burning providing a preliminary assessment of its fuel value and the initial and final combustion temperatures as well as other relevant data such as maximum reactivity temperature or total combustion time [6, 9–14]. This information is basic to estimate combustion efficiency, residence time, excess air, boiler design, etc. Conversely, there is not much information on the kinetics of the process which is also critical when projecting sewage sludge co-combustion with coal. The kinetic studies of thermally induced reactions in solids, such as the combustion of carbonaceous materials, may be performed by thermal analysis methods which measure a change in an extensive property, generally, mass (thermogravimetry, TG) [15]. Differences between sludge and coal make it necessary to further study the kinetic aspects of combustion.

The main purpose of this work was to approach the kinetics of sewage sludge and coal combustions via thermogravimetric measurements. The procedure to treat the non-isothermal TG data was carried out by the application of Ozawa–Flynn–Wall [16, 17] and Vyazovkin [18] kinetic models. These models allow the calculation of the activation energy of the process using dynamic integral TG curves obtained with several heating rates and make it possible to compare the results for sewage sludge and coal combustions.

Theory

The rate of heterogeneous solid-state reactions can generally be described by:

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$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \qquad (1)$$

where t is time, $k(T)$ the temperature-dependent constant and $f(\alpha)$ a function called the reaction model, which describes the dependence of the reaction rate on the extent of reaction, α.

The temperature dependence of the rate constant is described by the Arrhenius equation. Thus, the rate of a solid-state reaction can generally be described by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Ae^{-\mathrm{E/RT}}f(\alpha) \qquad (2)$$

where A is the pre-exponential Arrhenius factor, E the activation energy and R the gas constant.

For dynamic data obtained at a constant heating rate ($\beta=\mathrm{d}T/\mathrm{d}t=$constant), this term is inserted in Eq. (2) so the above rate expression can be transformed into nonisothermal rate expressions describing reaction rates as a function of temperature at a constant β:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{1}{\beta}Ae^{-\mathrm{E/RT}}f(\alpha) \qquad (3)$$

Integrating up to conversion, α, Eq. (3) gives:

$$\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=g(\alpha)=\frac{A}{\beta}\int_{\mathrm{T_0}}^{\mathrm{T}}e^{-\mathrm{E/RT}}\mathrm{d}T \qquad (4)$$

Kinetics analysis is traditionally expected to produce an adequate kinetic description of the process in terms of the reaction model and the Arrhenius parameters. These three components ($f(\alpha)$, E, and A) are known as the 'kinetic triplet' [19].

Many methods exist for the analysis of solid-state kinetic data [20]. These methods may be classified according to the experimental conditions selected and the mathematical analysis performed. Experimentally, either isothermal or non-isothermal methods are employed. Among the mathematical approaches, two kinds of methods may be considered: model-fitting and isoconversional (free model).

Initially, kinetic studies were usually carried out under isothermal conditions [20, 21] and the concepts of solid-state kinetics were established on the basis of these experiments. However, in isothermal experiments the sample requires some time to reach the experimental temperature. This is problematic, especially when, under isothermal conditions, a solid-state process has its maximum reaction rate at the beginning of the transformation. Even though the non-isothermal experimental technique is advantageous from this point of view, it accounts for computational difficulties associated with the kinetic analysis.

In the model-fitting mathematical approach, the $f(\alpha)$ term is determined by fitting various reaction models to experimental data. Then, the $k(T)$ can be evaluated by the chosen form of $f(\alpha)$. Traditionally, model-fitting methods have been the first and most popular ones, especially for isothermal experiments. Although they were widely used because their capacity to directly determine the kinetic triplet, they account for two main problems. The first is that non-isothermal experiments give both $k(T)$ and $f(\alpha)$, but not in a separate form. In this way, almost any $f(\alpha)$ can satisfactorily fit data by varying the Arrhenius parameters so to compensate for the difference between the assumed form $f(\alpha)$ and the right but unknown kinetic model. Thus, this method cannot provide a unique reaction model. The second problem is that only a single pair of Arrhenius parameters results from each application of the model-fitting method. Nevertheless, most of solid-state reactions are not simple one-step processes, so a combination of serial and parallel elementary steps may result in activation energy that changes during the course of the reaction. Consequently, model-fitting methods have lost popularity while isoconversional methods have gained it, as they can compute kinetic parameters without modelling assumptions [22–24].

Model-free isoconversional methods allow estimating the activation energy as a function of α without pre-fixing the reaction model. The essential assumption is that the reaction rate for a constant extent of conversion, α, depends only on the temperature [16, 25–27]. Hence, constant E values may be expected in the case of single-state process, while in a multi-step one E varies with α due to the variation in the relative contributions of the single step to the overall reaction rate.

In non-isothermal kinetics, several isoconversional methods may be used. To use these methods, a series of experiments has to be conducted at different heating rates [28, 29]. These methods have been used to study the thermal decomposition kinetics of residual carbonaceous materials such as low rank coal [30, 31], rubber [32], sugarcane bagasse [33], residues from composting [34] or urban solid residues composting [35].

The activation energy from dynamic data may be obtained from isoconversional method by Flynn, Wall and Ozawa [16, 26, 36] using the Doyle's approximation of $p(x)$ [37], which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates.

$$\ln(\beta)=\ln\left(\frac{AE}{Rg(\alpha)}\right)-5.331-1.052\frac{E}{RT} \qquad (5)$$

The activation energy E may be estimated by plotting $\ln(\beta)$ *vs.* $1/T$.

Vyazovkin developed another isoconversional method that allows both simple and complex reactions to be evaluated [38]. From Eq. (4), and since $E/2RT \approx 1$, the temperature integral can be approximated by:

$$\int_{T_0}^{T} e^{-E/RT} dT \approx \frac{R}{E} T^2 e^{-E/RT} \tag{6}$$

Substituting the temperature integral and taking the logarithm, we have that:

$$\ln\frac{\beta}{T^2} = \ln\left(\frac{RA}{Eg(\alpha)}\right) - \frac{E}{R}\frac{1}{T} \tag{7}$$

To use this method, it is necessary to obtain at least three different heating rates (β), the respective conversion curves being evaluated from the measured TG curves [39]. For each conversion value (α), $\ln(\beta/T^2)$ plotted *vs.* $1/T$, gives a straight line with slope $-E/R$, and thus the activation energy is obtained as a function of the conversion.

In order to determine the reaction order, Avrami's theory was extended to describe non-isothermal cases, where variation of the degree of conversion with temperature and heating rate can be described as:

$$\alpha(T) = 1 - \exp\left(\frac{-k(T)}{\beta^n}\right) \tag{8}$$

Taking the double logarithm of both sides of Eq. (8), with $k(T)=Ae^{-E/RT}$, gives:

$$\ln[-\ln(1-\alpha(T))] = \ln A - \frac{E}{RT} - n\ln\beta \tag{9}$$

Hence, a plot of $\ln[-\ln(1-\alpha(T))]$ *vs.* $\ln\beta$, which is obtained at the same temperature from a number of isotherms taken at different heating rates, should yield straight lines whose slope will have the value of the reaction order or the Flynn–Wall–Ozawa exponent n [16, 17]. Additional details of the method applied to study the process are described elsewhere [40].

Experimental

Materials

For this study, a semianthracite coal and two different sewage sludges have been used. The semianthracite, which has been labelled as 'SA', comes from the north coalfield of León (Spain) and it is exploited in thermal power stations. Two different urban sewage sludges have been used for comparison. Both of them come from urban wastewater treatment plants where an aerobic suspended-growth treatment process is carried out. In one case, the sludge is from the urban wastewater treatment plant of a very low industrialized town (labelled as 'SS_L') and, in the other case, from the urban wastewater treatment plant of a city with a higher degree of industrialization (labelled as 'SS_V'). In their respective wastewater treatment plant of origin, SS_L and SS_V went through a stabilization treatment by anaerobic digestion, dehydration and thermal drying. Before thermogravimetric analysis, these samples were analysed to determine the main properties that affect to thermal conversion. Moisture content was determined gravimetrically by the oven drying method. Higher heating value (HHV) at a constant volume was measured by means of an adiabatic oxygen bomb calorimeter. Proximate determinations were made according to modified procedures from ASTM D 3172 to 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). For the elemental determination, a LECO equipment model CHN-600 was used to determine the carbon, hydrogen and nitrogen content. Sulphur was determined by means of a LECO equipment, model SC-132.

TG analysis

Thermogravimetric analysis was carried out in a TA Instruments equipment, model SDT2960. Combustion of the samples was performed in the furnace of the thermobalance under controlled temperature.

Each of the samples was submitted to four different dynamic runs carried out at heating rates (β) of 0.083, 0.167, 0.417, 0.667 K s^{-1} up to 1273 K. All dynamic runs were carried out on a pan containing 25±1 mg of the corresponding sample and a reference crucible containing calcined calcium oxide. Oxidising atmosphere inside the furnace during temperature-programmed combustion was got by means of a continuous airflow of 100 cm^3 min^{-1} at a gauge pressure of 1 atm (101 KPa). Six different percentages of conversion were considered for the kinetic evaluation of the combustion of each of the carbonaceous materials here studied.

Results and discussion

Characterization of materials

Sewage sludge from different origin may have different properties which depend on the type of wastewater, the kind of treatment/s given to wastewater and to sludge itself in the purification plant. Sludge properties may not differ much from those of a low rank brown coal but, in any case, substantially differ from those of a bituminous coal.

The results of the elementary and proximate analysis for the coal and the sewage sludge here used are shown in Table 1. It must be pointed out that the ash yield of SA (17.7 mass%) is much lower than those of SS_L (31.2 mass%) and SS_V (53.8 mass%). Furthermore, sewage sludge samples yield higher amount of volatiles, ranging from 42.8 mass% (SS_V) to 58.0 mass% (SS_L), while the coal sample yields 10.6 mass%. Also, SS_V and SS_L show much lower fixed-carbon values, 22.7 and 38.2 mass% respectively, than coal (73.5 mass%).

About the HHV corresponding to sewage sludge, it is similar to those of a low rank coal and vary from around 9.5 MJ kg^{-1} for SS_V to around 17.6 MJ kg^{-1} for SS_L, while the coal sample has a heating value of around 28.9 MJ kg^{-1}.

Finally, in the elementary analysis, SS_L sludge show a higher hydrogen and nitrogen contents (4.3 and 4.5 mass%, respectively) than SS_V (3.3 and 3.1 mass%), while SS_V samples show a higher content of sulphur (1.6 mass%) than SS_L (0.9 mass%). In the coal, the hydrogen and nitrogen contents (H 3.2 mass% and N 1.6 mass%) are lower than in sludge. But, on the contrary, the sulphur content is higher in the coal (2.2 mass%).

TG results

The TG curves obtained from the temperature programmed combustions of the samples at the heating rates (β) of 0.083, 0.167, 0.417 and 0.667 K s^{-1} are depicted in Fig. 1. The mass loss during combustion is shown for the semianthracite coal (SA) and the sewage sludges SS_L and SS_V. For all the heating rates, the coal burning starts and ends at higher temperatures than for the two sewage sludge, especially than SS_V.

Six different percentages of conversion are pointed out in each curve. For both SA and SS_L, these percentages are 20, 30, 40 50, 60 and 70%. For the sewage sludge SS_V, which had a higher ash yield than SS_L and much higher than SA, the percentages of conversion considered are 13, 20, 27, 34, 41 and 48%.

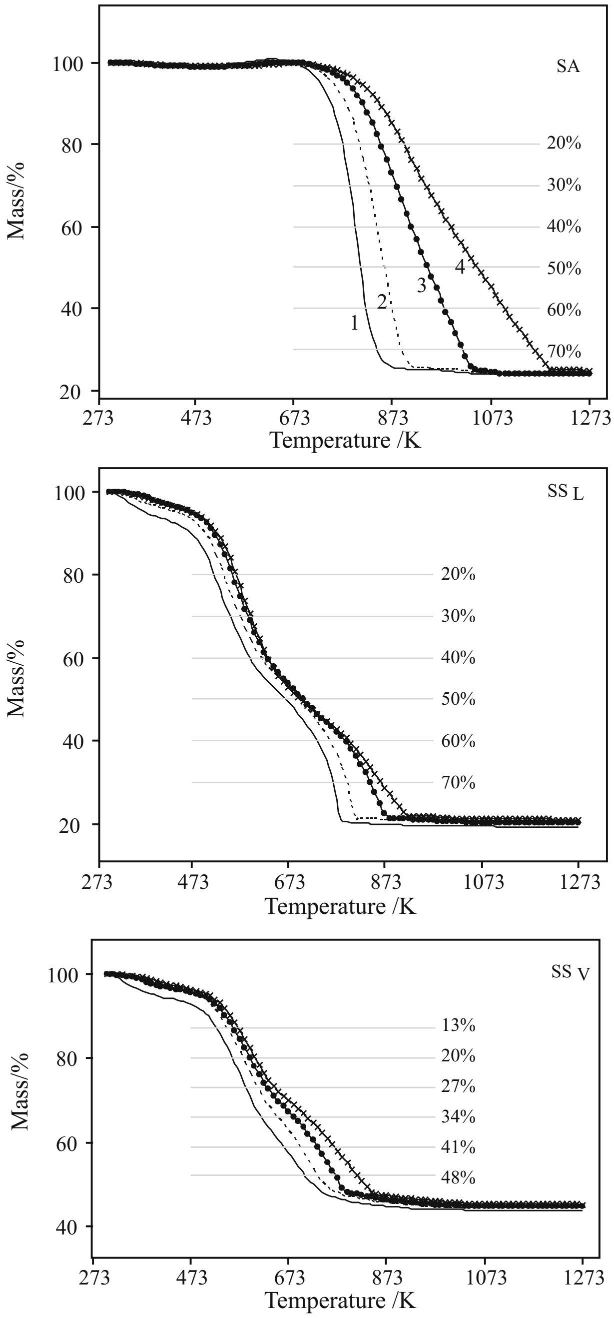

Fig. 1 TG curves corresponding to the combustion of a semianthracite coal (SA), and two sewage sludges (SS_L and SS_V) at 1 – 0.083, 2 – 0.167, 3 – 0.417 and 4 – 0.667 K s^{-1}

Table 1 Proximate analysis, elementary analysis, and calorific values for the semianthracite coal (SA) and the two different sewage sludge (SS_L, SS_V)[a]

Sample	Moisture/ content/%	Volatiles/ %	Ashes/ %	C/ %	H/ %	N/ %	S/ %	O/ %	HHV/ %
SA	1.2	10.6	17.7	73.5	3.2	1.6	2.2	1.8	28.9
SS_L	1.3	58.0	31.2	38.2	4.3	4.5	0.9	20.9	17.6
SS_V	3.9	42.8	53.8	22.7	3.3	3.1	1.6	15.5	9.5

[a] Dry basis, HHV=high heat value

The plots of logβ *vs.* 1/T corresponding to the several conversion degrees (α) of the process are shown in Fig. 2 for SA, SS_L and SS_V. As it may be seen there is a linearity for the several conversion percentages so the activation energy E may be calculated from the corresponding slope according with the Ozawa–Flynn–Wall kinetic method employed [16, 26, 36, 37]. The slopes of linear fittings showed in Fig. 2, together with the corresponding correlation coefficients (R^2) are shown in Table 2. As it may be seen R^2 are higher than 0.96 in all cases.

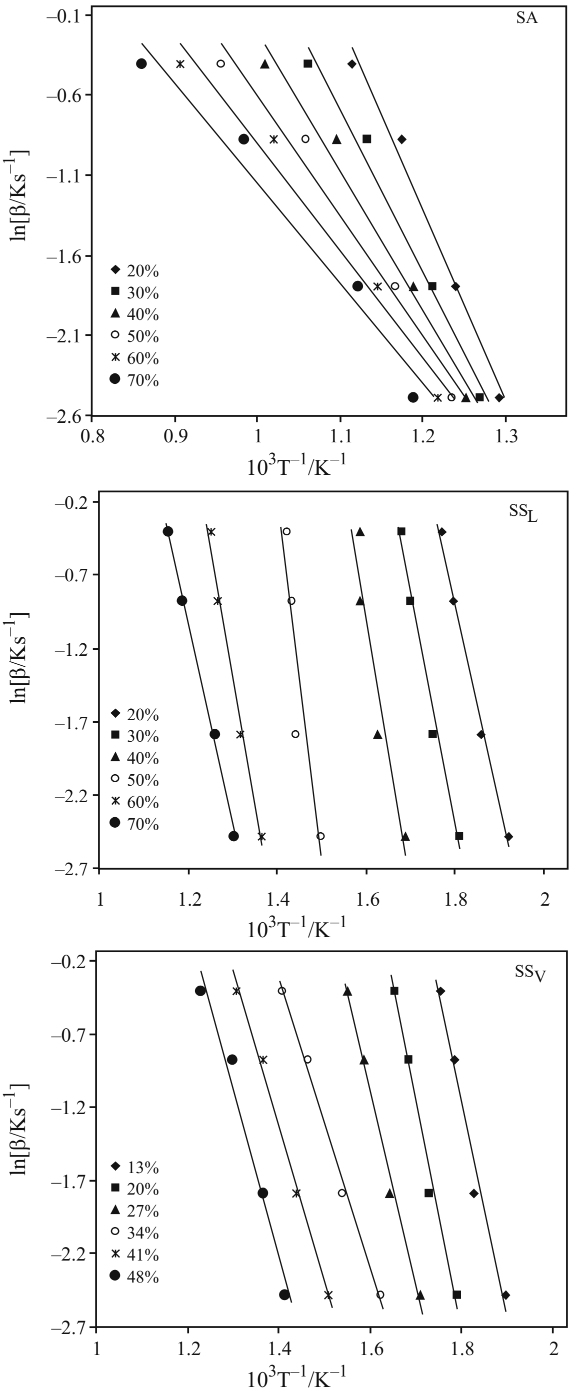

Fig. 2 Curves of fitting to kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages corresponding to the combustion of a semianthracite coal (SA), and two sewage sludges (SS_L and SS_V) at different heating rates

Figure 3 shows the plots of ln(β/T^2) *vs.* 1/T to the several conversion degrees (α) corresponding to SA, SS_L and SS_V combustion. According with the Vyazovkin method [18, 38], straight lines with the angular coefficient –E/R were obtained. The slopes of linear fittings showed in Fig. 3, together with the corresponding correlation coefficients (R^2) are shown in Table 3. In this case, R^2 are higher than 0.89 in all cases.

It may be seen, both in Figs 2 and 3, that linearity corresponding to SA samples is not as good as that corresponding to SS_L or SS_V. This may be due to the heating rate range used in this study, which may be appropriate for sewage sludge samples but large enough to cause that the kinetic mechanism has changed to some extent in the case of the coal sample.

As indicated in Table 4, the values of E calculated by the two methods presented a great accordance although the Ozawa–Flynn–Wall method gave slightly higher values than the Vyazovkin one in all cases. The activation energy corresponding to the semianthracite coal SA is lower than that corresponding to both the sewage sludge. However, sewage

Table 2 Slopes and correlation coefficients (R^2) corresponding to linear fittings in Fig. 2 together with the resultant activation energy (E) values

Sample	Conversion/ %	Slope	R^2	E/ kJ mol^{-1}
SA	70	–6.2614	0.9677	49.5
	60	–6.6848	0.9753	52.9
	50	–7.4718	0.9763	59.1
	40	–8.6217	0.9798	68.2
	30	–10.172	0.9848	80.4
	20	–11.882	0.9859	93.9
SS_L	70	–13.713	0.9970	108.4
	60	–17.942	0.9857	141.9
	50	–25.106	0.9763	198.5
	40	–18.651	0.9076	147.5
	30	–15.811	0.9813	125.0
	20	–13.556	0.9906	107.2
SS_V	48	–11.342	0.9703	89.7
	41	–10.589	0.9932	83.7
	34	–9.904	0.9928	78.3
	27	–13.33	0.9909	105.4
	20	–15.506	0.9805	122.6
	13	–14.689	0.9684	116.1

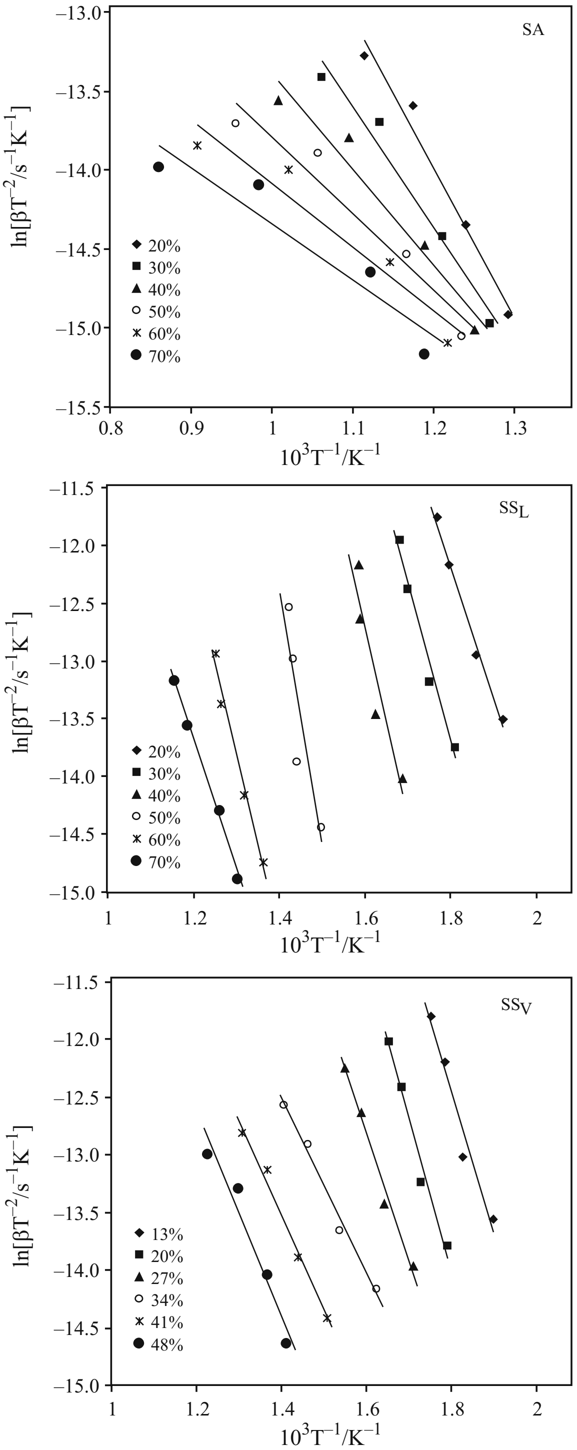

Fig. 3 Curves of fitting to kinetic model proposed by Vyazovkin to various conversion percentages corresponding to the combustion of a semianthracite coal (SA), and two sewage sludges (SS_L and SS_V) at different heating rates

Table 3 Slopes and correlation coefficients (R^2) corresponding to linear fittings in Fig. 3 together with the resultant activation energy (E) values

Sample	Conversion/%	Slope	R^2	E/ kJ mol^{-1}
SA	70	−3.5353	0.8945	29.4
	60	−4.0202	0.9272	33.4
	50	−4.857	0.9409	40.4
	40	−6.0549	0.9720	50.3
	30	−7.6511	0.9720	63.6
	20	−9.4042	0.9769	78.2
SS_L	70	−11.263	0.9955	93.6
	60	−15.563	0.9812	129.4
	50	−22.83	0.7736	189.8
	40	−16.441	0.8843	136.7
	30	−13.621	0.9750	113.2
	20	−11.371	0.9866	94.5
SS_V	48	−8.9696	0.9524	74.6
	41	−8.2784	0.9887	68.8
	34	−7.6506	0.9880	63.6
	27	−11.118	0.9871	92.4
	20	−13.314	0.9737	110.7
	13	−12.504	0.9569	104.0

sludge SS_L and SS_V have shown quite different E values. Although SS_V had a higher ash yield and a lower fixed carbon value than SS_L, the activation energy corresponding to its combustion is lower than that corresponding to SS_L.

For the computation of the reaction order, the plots of $\ln[-\ln(1-\alpha(T))]$ *vs.* $\ln\beta$ have been represented in Fig. 4. The values of n as a function of temperature for SA, SS_L and SS_V combustion are shown in Table 5. The value of n varies differently with temperature for each of the three carbonaceous materials. The values ranged from close to zero (pseudo zero-order reaction) for SS_L to 1.4 for SA and are dependent on the extent of the reaction, i.e., not constant during the reaction which is evidence of the multiple step process. The semianthracite coal SA showed higher n values than both the sewage

Table 4 Values of activation energy obtained by Ozawa–Flynn–Wall and Vyazovkin models

Sample	Activation energy*/kJ mol^{-1}	
	Ozawa–Flynn–Wall model	Vyazovkin model
SA	67.3	49.2
SS_L	138.1	126.2
SS_V	99.3	85.7

*The activation energy E was calculated as arithmetic average of the several E values obtained for different conversion degrees shown in Figs 2 and 3

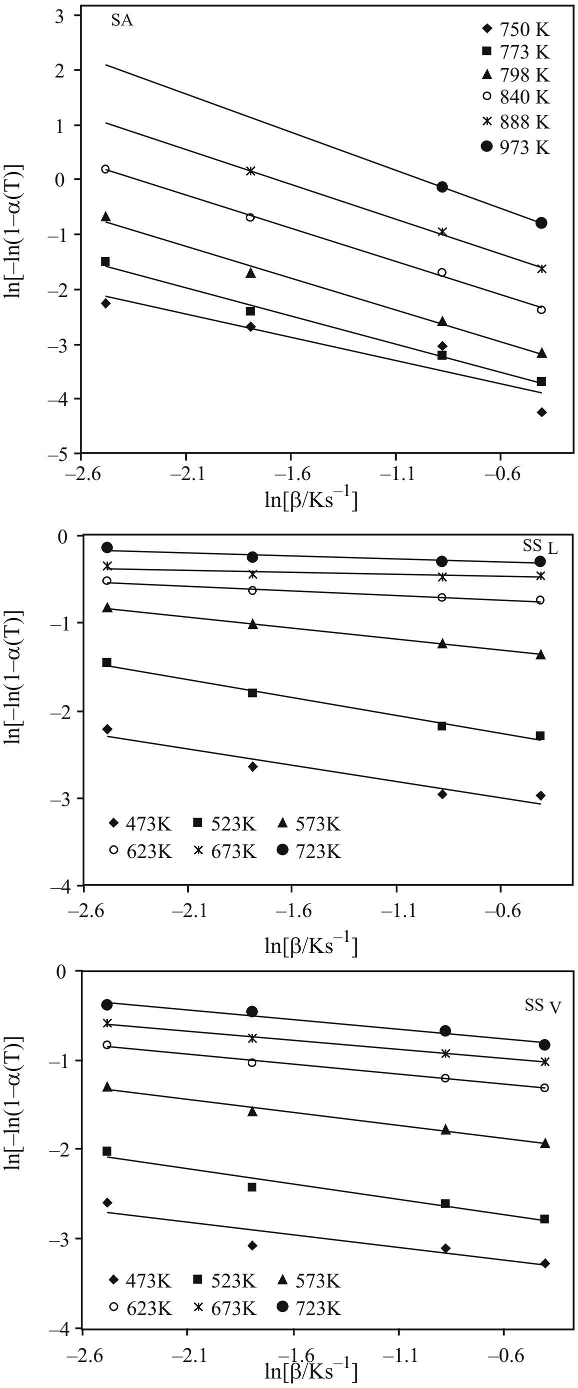

Fig. 4 Curves of fitting corresponding to the reaction order *n* for different temperatures along the combustion of a semianthracite coal (SA), and two sewage sludges (SS_L and SS_V) at different heating rates

Table 5 Reaction order (*n*) as a function of temperature for the semianthracite coal SA and the sewage sludge SS_L and SS_V

Temp./K	SSA	Temp./K	SS_L	SS_V
750	0.85	473	0.37	0.28
773	1.03	523	0.41	0.34
798	1.16	573	0.25	0.29
840	1.21	623	0.10	0.22
888	1.27	673	0.05	0.21
973	1.38	723	0.07	0.22
Average *n*	1.15	Average *n*	0.21	0.26

sludge in the temperature range of combustion. In general, the order of reaction was lower for the sewage sludge SS_V than for SS_L but the maximum *n* occurred at 523 K for both the sewage sludge.

It is worth noting that although *n* is dependent on the type of carbonaceous material, for a specific material its value is not integral (fractional order), which indicates the complexity of the degradation process of all these materials. The Flynn–Wall– Ozawa exponent *n* was found to follow the opposite trend of the activation energy *E*, i.e., the higher the *n* values the lower the *E* values. However, there is not a linear relationship between *n* and *E*. Thus, in this study, coal, which was the least thermally stable material, had the highest reaction order. However, both sewage sludges showed similar reaction orders while *E* values were not comparable.

Conclusions

Differences were found between the combustion of the carbonaceous materials studied: coal and sewage sludge. The TG curves are in correspondence with the proximate analysis of the materials studied. The Ozawa–Flynn–Wall method and the Vyazovkin one showed concurrence in the calculation of the activation energies, although the first one gave slightly higher values. The activation energy corresponding to the semianthracite coal SA (E~50 kJ mol^{-1}) was lower than those corresponding to urban sewage sludge. Still, the two sewage sludge here studied showed quite different *E* values and the corresponding to SS_V (E~100 kJ mol^{-1}) were lower than the corresponding to SS_L (E~130 kJ mol^{-1}).

The reaction order was found to vary along the reaction pathway. Both the *n* values and its dependence of temperature diverged for the different carbonaceous materials. In all cases, the lower the activation energy *E*, the higher the *n* values. The averaged *n* value corresponding to the semianthracite coal SA was 1.15 while the corresponding to sewage sludge SS_L and SS_V were 0.21 and 0.26, respectively.

This work shows that combustion of the carbonaceous materials studied is a complex process characteristic for each kind of material. Differences between the coal and sewage sludge combustion are noteworthy but, anyway, differences between different sewage sludge are not negligible at all. No generalist conclusions may be launched about the sewage sludge combustion or co-combustion with coal, as for each kind of sewage sludge may be different. However, the present study proves that thermogravimetric analysis is a very useful tool for a first and fast assessment of the materials when planning co-combustion of sewage sludge together with coal in existing infrastructures.

References

1 I. Vogeler, S. R. Green, T. Mills and B. E. Clothier, Soil Till. Res., 89 (2006) 177.
2 E. Cartmell, P. Gostelow, D. Riddell-Black, N. Simms, J. Oakey, J. Morris, P. Jeffrey, P. Howsam and S. J. Pollard, Environ. Sci. Technol., 40 (2006) 649.
3 J. F. Enright, ‘Waste’ or ‘Product’? That is the question. In Biodegradable and Residual Waste Management; K. Papadimitriou, E. I. Stentiford, Eds, CalRecovery Europe Ltd.: Leeds, 2004, p. 311.
4 G. Zheng and J. A. Kozinski, Fuel, 79 (2000) 181.
5 J. Werther and T. Ogada, Prog. Energy. Combust., 25 (1999) 55.
6 M. B. Folgueras, R. M. Díaz, J. Xiberta and I. Prieto, Fuel, 82 (2003) 2051.
7 H. Yao and I. Naruse, Energ. Fuels, 19 (2005) 2298.
8 P. Stasta, J. Boran, L. Bebar, P. Stehlik and J. Oral, Appl. Therm. Eng., 26 (2006) 1420.
9 M. V. Kök and C. Keskin, J. Therm. Anal. Cal., 64 (2001) 1265.
10 M. Otero, C. Díez, L. F. Calvo, A. I. García and A. Morán, Biomass Bioenergy., 22 (2002) 319.
11 L. F. Calvo, M. Otero, B. M. Jenkins, A. I. García and A. Morán, Thermochim. Acta, 409 (2004) 127.
12 F. E. Ndaji, W. A. T. Ellyatt, R. Malik and K. M. Thomas, Fuel, 78 (1999) 301.
13 R. Font, A. Fullana, J. A. Conesa and F. Llavador, J. Anal. Appl. Pyrol., 58-59 (2001) 927.
14 L. F. Calvo, M. E. Sanchez, A. Morán and A. I. García, J. Therm. Anal. Cal., 78 (2004) 587.
15 R. López-Fonseca, I. Landa, M. A. Gutiérrez-Ortiz and J. R. González-Velasco, J. Therm. Anal. Cal., 80 (2005) 65.
16 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
17 J. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
18 S. Vyazovkin and A. I. Lesnikovick, Russ. J. Phys. Chem., 62 (1988) 1525.
19 M. J. Staring, J. Mater. Sci. (2007) in press.
20 S. Vyazovkin and C. A. Wight, Int. Rev. Phys. Chem., 17 (1998) 407.
21 G. N. Lewis, Z. Phys. Chem., 52 (1905) 310.
22 S. Vyazovkin and C. A. Wight, Thermochim. Acta, 340–341 (1999) 53.
23 A. Khawam and D. R. Flanagan, Thermochim. Acta, 429 (2005) 93.
24 A. Khawam and D. R. Flanagan, J. Phys. Chem. B, 109 (2005) 10073.
25 H. Friedman, J. Polym. Sci., C 6 (1965) 195.
26 J. H. Flynn and L. A. Wall, J. Res. Natl. Bur. Stand. Sect., A 70 (1966) 487.
27 S. Vyazovkin and D. Dollimore, J. Chem. Inf. Comput. Sci., 36 (1996)42.
28 A. Khawam and D. R. Flanagan, Thermochim. Acta, 436 (2005) 101.
29 S. Vyazovkin, J. Comput. Chem., 18 (1997) 393.
30 M. V. Kök, J. Therm. Anal. Cal., 79 (2005) 175.
31 M. Günes and S. Günes, Energy Sources, 27 (2005) 749.
32 R. M. B. Moreno, E. S. Medeiros, F. C. Ferreira, N. Alves, P. S. Gonçalves and L. H. C. Mattoso, Plastics, Rubber Compos., 35 (2006) 15.
33 B. Ramajo-Escalera, A. Espina, J. R. García, J. H. Sosa-Arnao and S. A. Nebra, Thermochim. Acta, 448 (2006) 111.
34 A. R. Silva, M. S. Crespi, C. A. Ribeiro, S. C. Oliveira and M. R. S. Silva, J. Therm. Anal. Cal., 75 (2004) 401.
35 M. S. Crespi, A. R. Silva, C. A. Ribeiro, S. C. Oliveira and M. R. Santiago-Silva, J. Therm. Anal. Cal., 72 (2003) 1049.
36 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
37 C. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
38 S. Vyazovkin and N. Sbirrazzuoli, Anal. Chim. Acta, 355 (1997) 175.
39 S. Vyazovkin and C. A. Wight, Ann. Rev. Phys. Chem., 48 (1997) 125.
40 E. S. Medeiros, R. M. B. Moreno, F. C. Ferreira, N. Alves, A. E. Job, P. S. Gonçalves and L. H. C. Mattoso, Prog. Rubber Plast. Recycl. Technol., 19 (2003) 189.

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