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SIMULTANEOUS THERMOGRAVIMETRIC-MASS SPECTROMETRIC STUDY ON THE CO-COMBUSTION OF COAL AND SEWAGE SLUDGES

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To combust coal together with a small percentage (<10%) of sewage sludge may be an option for the management of these wastes. Combustion of two different sewage sludge, one semianthracite coal and several sludges-coal blends (containing different dried mass% of each of the two sewage sludges) were studied by simultaneous TG/MS dynamic runs carried out at 5°C min^{-1} in the temperature range 100–800°C. No interactions have been observed between coal and sludge during the blends combustion. Neither the combustion process, neither the studied emissions have changed appreciably for the mass% of sludge in the blends considered in this work.

Keywords: *co-combustion, mass spectrometry, sewage sludge, thermogravimetry*

Introduction

Sewage sludges are unavoidable wastes derived from the regular activities of wastewater treatment plants. The estimated average production of sewage sludges may be said to be about 40–60 g dry matter/inhabitant/day for urban sewage plants [1]. Production is expected to rise as investment in environmental management increases and more municipal wastewater is treated to even higher standards [2]. Addressing the high production volumes, both current and forecasted, the adequate management of sludges produced at sewage plants is a fundamental need.

Between 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. The necessity of looking for alternative routes for sewage sludge valorisation is the evident. Among these options, this research work deals with the possibility of carrying out co-combustion of sewage sludges with coal.

It must also be said that relevant advantages in the utilization of alternative fuels, such as sewage sludges, may lead to a gradual replacement of the overuse of the traditional fossil fuels. The coal-biomass co-combustion is one of the most promising short-term options for the use of renewable fuels [3]. Sewage sludges coming from wastewater treatment plants may have a considerable potential as an additional fuel source, showing a null cost level in comparison to other non-renewable and even renewable energies.

Nevertheless one of the main difficulties encountered for carrying out sludges combustion is probably public opposition [4]. In this sense co-combustion of sewage sludges together with coal in existing power plants seems to be better considered by society. On the other hand, from an economic point of view, jointing combustion of sludges and coal in power plants allows for the use of existing infrastructures, already equipped with appropriate devices for gaseous emission control and staffed with qualified personnel [5]. Because of this, currently, maybe the most attractive solution for the disposal of sewage sludge is its co-combustion with coal, which is not free of important restrictions, such as HCl, NO_x and toxic trace elements emissions [6–8].

Thermogravimetric analysis (TG) is one of the most commonly used techniques to study the primary reactions of decomposition of solids [9–11]. This kind of analysis not only provides a means for the preliminary assessment of fuel values in sludges [5] but also allows for an ‘a priori’ knowledge of initial and final temperatures for their combustion as well as other relevant data such as maximum reactivity temperature or total combustion time. This information can be very useful to forecast combustion efficiency, residence time, excess air, boiler design, etc. On the other hand, the use of different heating rates during the combustion runs makes it possible to determine the kinetics of the processes. For the combustion and co-combustion of sewage sludge with coal, some TG results have been published [8, 12–16], but differences between sludges and the consequent modifications of the coal combustion process make it imperative to get deeper in this matter.

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In this context, this work tries to make an appraisal to the thermal behaviour of sludge during combustion, both alone and together with coal. Modifications of the coal combustion and emissions related to the addition of small quantities of sewage sludges are to be studied. The present work is particularly interesting in a geographic area such as León (Spain), which has a long mining tradition and a good number of power plants and where schemes for sewage sludge management have not been implemented yet.

Experimental

Materials

For this study, a semianthracite coal and two different sewage sludges have been used. The semianthracite, which has been labelled as 'C', comes from the north coalfield of León (Spain) and it is usually exploited in thermal power stations. Two different urban sewage sludges have been used for the co-combustion with coal tests. Both the sludges were obtained from two urban wastewater treatment plants where an aerobic suspended-growth treatment process is carried out. These sludges come, in one case, from the urban wastewater treatment plant of a very low industrialized town (labelled as 'SSL') and, in the other case, from the urban wastewater treatment plant of a city with a higher degree of industrialization (labelled as 'SSV'). In their respective wastewater treatment plant of origin, SSL and SSV are submitted to stabilization, by anaerobic digestion, dehydration and thermal drying in their respective wastewater treatment plants of origin. The SSL and SSV samples used for this TG/MS study were dried.

The procedure for the determination of the proximate analyses and calorific value corresponding to the coal and both the sludges here used is described elsewhere [17]. For the elemental determination, a LECO equipment model CHN-600 was used to determine the carbon, hydrogen and nitrogen content. In the case of sulphur, a LECO equipment, model SC-132 was used.

Data found in literature about the practice of coal and sewage sludge co-combustion talk about dried sludge percentages in mixtures with coal that are usually below 10%, having been recommended not to exceed the 5% [6, 18]. In this research work, the dried sludge mass% in the coal-sludge blends have been chosen to be 2, 5 and 10%.

TG/MS analysis

Combustion of all the samples was performed in the furnace of the thermogravimetric equipment under temperature control. Each of the samples was submitted to a dynamic run carried out at heating rate of 5°C min^{-1} up to 850°C. 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.

Thermogravimetric analysis was carried out in a TA Instruments equipment, model SDT2960, able to simultaneously register DSC-TGA signals so both mass loss and heat flow profiles were obtained during combustion. Simultaneously, gaseous emission analysis was carried out in a Balzers, model GSD 300, mass spectrometer coupled to the gas off-take from the thermal analysis equipment.

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). During combustion, a mass spectrometer coupled to the thermobalance was used to monitor the gaseous emissions corresponding to m/z=44, 46 and 64. Those m/z values account mainly for CO_2, NO_2 and SO_2 as most probable parent molecules [9, 17, 19] which are especially problematic species from an environmental point of view [6].

Results and discussion

Characterization of materials

Depending on the type of wastewater, the wastewater and the sludge process of treatment in the wastewater treatment plant, sewage sludge has variable characteristics that, in any case, differ substantially from those of a bituminous coal.

The results of the elementary and proximate analysis for the two sludge samples together with the coal are shown in Table 1. These analyses procedure is described elsewhere [14]. The following can be observed:

- Coal ash yield is much lower than those of the sewage sludge samples. Thus, ash yield varies from 31.2 to 53.8 mass% for the sewage sludge samples, while it is 17.7 mass% for coal. Also, sewage sludge samples yield higher amount of volatiles,

Table 1 Proximate analysis, elementary analysis, and calorific values for the sludges (SSL, SSV) and the coal (C) used in combustion studies

Sample	Moisture/%	Volatiles*/%	Ashes*/%	C*/%	H*/%	N*/%	S*/%	O*/%	HHV*/J g^{-1}
SSL	4.3	58.0	31.2	38.2	4.3	4.5	0.9	20.9	17606
SSV	3.9	42.8	53.8	22.7	3.3	3.1	1.6	15.5	9480
C	1.2	10.6	17.7	73.5	3.2	1.6	2.2	1.8	28870

HHV – high heat value, *dry basis

ranging from 42.8 to 58.0 mass%, while the coal sample yields 10.6 mass%. Obviously, sewage sludge samples show much lower fixed-carbon values (22.7 and 38.2 mass%) than coal (73.5 mass%).

- Higher calorific values of the sewage sludge samples on dry basis are low, similar to a low rank coal and varying from, around 9.5 to around 17.6 MJ kg^{-1}, while the coal sample has a heating value of around 28.9 MJ kg^{-1}.
- In relation to the elementary analysis, SSL sludge has a higher hydrogen content and nitrogen (4.3 and 4.5 mass%, respectively) than SSV (3.3 and 3.1 mass%), while SSV samples show a higher content of sulphur (1.6 mass%) than SSL (0.9 mass%). The hydrogen and nitrogen values are lower in the coal (3.2 mass% for hydrogen, 1.6 mass% for nitrogen) than in sludges. But, on the contrary, the sulphur content is higher in the coal (2.2 mass% for sulphur).

TG results

The DTG and DSC results obtained from the temperature programmed combustions of the samples are shown in Figs 1 and 2, respectively. The results corresponding to the coal (C) are shown together with those of the two sludges here used and their respective blends. Figures 1a and 2a represent, in that order, the DTG and DSC curves for SSL and Figs 1b and 2b those for SSV. In Table 2, the characteristic parameters of the combustion profiles are shown.

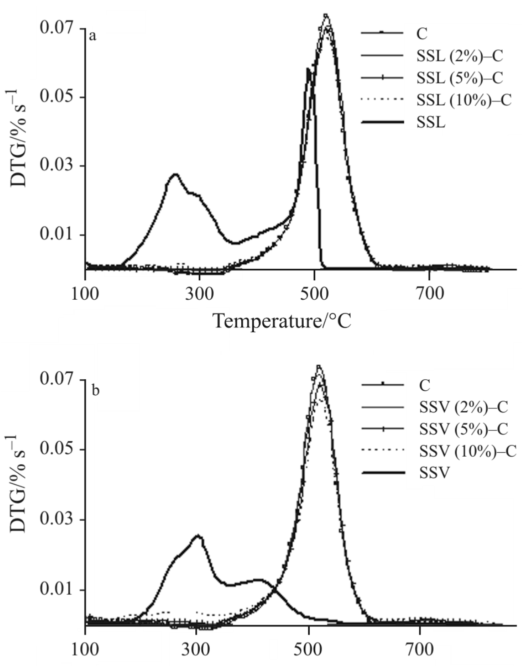

Fig. 1 Combustion and co-combustion DTG curves for coal (C), sludge and its blends. Two sludges were used for this study: a – SSL and b – SSV

As it may be seen, the coal shows the typical combustion profile (DTG curve) of a semianthracite coal, with one peak comprised between 355 and 620°C, with a maximum mass loss rate of 0.073% s^{-1} at 520°C, the result of thermal decomposition and loss of volatiles as well as char gasification [20]. Also, a net mass gain was observed during coal combustion that is due to oxygen chemisorption. In the case of sludge, the combustion profiles vary in a different way for the two sludges here used. Both for SSL and SSV, and differently than for coal, the sludge combustion interval may be divided in two stages. In the case of SSL, the first peak is at 255.5°C (0.026% s^{-1}) and it is comprised between 144 and 364°C and the second one is at 487°C (0.055% s^{-1}) and it is comprised between 364 and 522°C. Differently, for SSV sludge, the two stages are extended from 158 to 361°C and from 361 to 572°C and respectively, the peak values are 0.024% s^{-1} at 304°C and 0.012% s^{-1} at 410°C. In the combustion profiles of sludge, the first stage must be mainly attributed to the reaction of air with volatile matter and more reactive structures while the second one is due to reaction with more complex structures. For both sludges, the chemisorption stage observed in the coal combustion profile has not occurred.

The combustion profile of C is very different from those of SSL and SSV, but, also, the shape of the

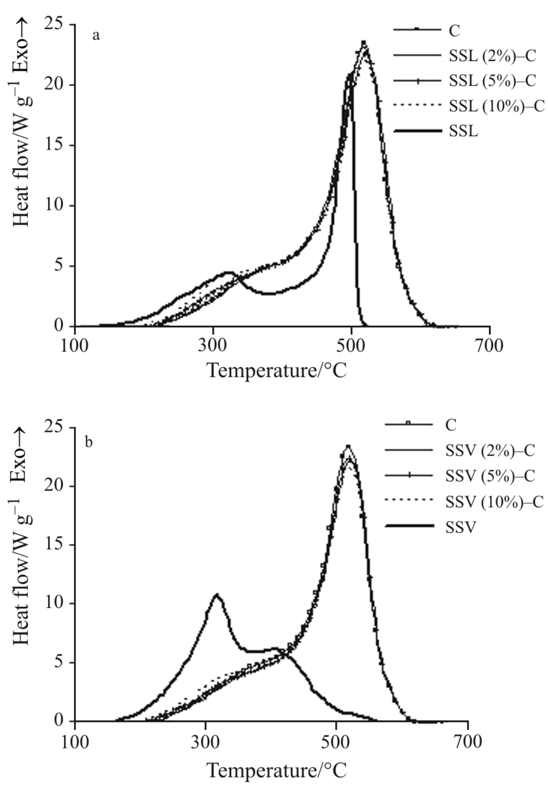

Fig. 2 Combustion and co-combustion DSC curves for coal (C), sludge and its blends. Two sludges were used for this study: a – SSL and b – SSV

curves corresponding to the combustion runs is very different for the sludges. Nevertheless, the blends containing 2, 5 and 10% of sludge behave analogous to coal, except for the progressive disappearance of the chemisorption stage and a slight decrease of the maximum mass loss rate. Table 2 shows that T_v is lower for sludge blends than for coal as chemisorption is not present, nevertheless, as it may be seen in Fig. 1, the combustion is parallel with that of coal so the T_m corresponding to the blends are all around 520°C. As can be seen for the T_f values in Table 2, the final combustion temperature is the same for coal than for the blends so no a practical interaction between blend components occurs.

DSC curves shown in Fig. 2 are in correspondence with the DTG curves. It may be observed that the chemisorption stage found for coal is exothermic and both for the coal and its blends with no matter which sludge, exothermicity starts around 200°C and ends at 620°C. This is not true for sludges, for which a chemisorption stage does not occur. Both for SSL and SSV, a DSC curve showing two peaks occur. In equivalence to the DTG curves, the second peak is more exothermic than the first one for SSL and just on the contrary for SSV. Nevertheless there is not association with the DTG and DSC peaks values. Comparing the first mass loss stage for SSL and SSV, a bigger magnitude occurred for SSL, which is not true for the DSC peaks. It seems that the calorific value of the more reactive fraction contained in SSV is higher than that of SSL.

The enthalpies and characteristic temperatures corresponding to the DSC curves displayed in Fig. 2 are shown in Table 3. Results on the enthalpies corresponding to co-combustion of coal together with SSL or SSV are very similar to this on the combustion of coal alone (33.35 kJ g^{-1}) and are between 31.02 and 33.25 kJ g^{-1}. Temperature for maximum heat release during combustion is more similar to this corresponding to C for SSL than for SSV. Anyway, for the small sludge percentage in the co-combustion with coal used in this study (<10%), energy released during co-combustion resembles that released during coal combustion as it may be seen in DSC curves.

Table 2 Characteristic parameters obtained from burning profiles of coal (C), SSL and SSV sludges and their respective blends

Sample	T_v/°C	T_m/°C	T_f/°C	DTG_{max}/% s^{-1}	t_q/s
C	355	520	620	0.073	4830
SSL	144	487	522	0.055	4535
SSL (2%)–C	220	520	620	0.072	4830
SSL (5%)–C	205	520	620	0.070	5006
SSL (10%)–C	200	520	620	0.067	5071
SSV	158	304	572	0.024	4982
SSV (2%)–C	220	520	620	0.071	4830
SSV (5%)–C	210	520	620	0.068	4956
SSV (10%)–C	200	520	620	0.064	5072

T_v – onset temperature for volatile release and mass loss, T_m – temperature of maximum mass loss rate, T_f – final combustion temperature detected as mass stabilization, DTG_{max} – maximum mass loss rate, t_q – burning time; time interval from the moment the dried sample starts to lose mass until the moment combustion ends and mass stabilizes

Table 3 Characteristic parameters obtained from DSC profiles for the combustion of coal (C), SSL and SSV sludges and their respective blends

Sample	T_i/°C	T_{max}/°C	T_e/°C	HF_{max}/W g^{-1}	ΔH/kJ g^{-1}
C	220	580	620	23.73	33.35
SSL	144	496	522	19.94	17.13
SSL (2%)–C	220	520	620	23.65	33.25
SSL (5%)–C	205	520	620	22.49	33.04
SSL (10%)–C	200	520	620	21.34	32.37
SSV	158	318	572	10.10	16.90
SSV (2%)–C	220	520	620	22.31	31.08
SSV (5%)–C	210	520	620	22.30	31.33
SSV (10%)–C	200	520	620	21.43	31.02

T_i – onset temperature for energy release and peak integration, T_{max} – temperature of maximum energy release during combustion, T_e – final combustion temperature, HF_{max} – maximum heat flow, ΔH – enthalpy from the DSC combustion profile

Both DTG and DSC curves corresponding to coal and sludge are evidence for the necessity of very different combustors to combust them separately. Nevertheless, this is not true for the blends containing a percentage of sludge equal or smaller than 10%. For these blends, the same furnace used for the combustion of coal may be employed. This option does not involve the high costs of building a new biomass plant compared to indirect co-combustion system.

MS results

For simultaneous thermal/gas analysis TG was coupled with MS to obtained deeper information about the combustion behaviour of coal, sludge and their blends. The *m*/*z* signals reported are 44, 46 and 64, which more probable parent molecules are CO_2, NO_2 and SO_2. Data were normalised so each compound (ion) detected by MS has its own response factor [21] and thus the intensities of the same compound may be compared for the different samples.

Figures 3–5 represent the emission of CO_2, NO_2 and SO_2, respectively, upon temperature programmed combustions carried out.

In the case of the CO_2 emission during the combustion of the samples, Figs 3a and b resembles the corresponding mass loss curves (Figs 1a and b) related to the oxidation of the carbonaceous matter in the case of the blends. This is not true for the chemisorption stage observed in the coal DTG curve neither for the two different sludges here used. In the case of SSL, the emission of CO_2 during the first stage of the combustion is not as important as the first peak in the corresponding DTG curve. For SSV sludge, emission of CO_2 is higher during the first stage of mass loss

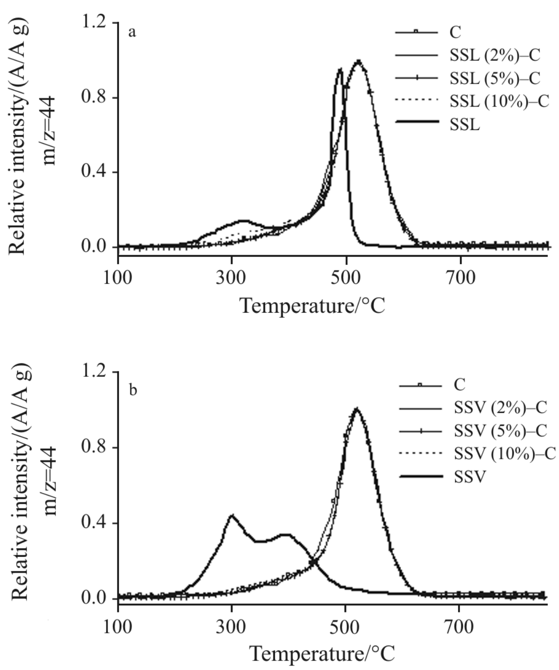

Fig. 3 CO_2 evolution curves followed by MS during the combustion and co-combustion of coal (C), sludge and its blends. Two sludges were used for this study: a – SSL and b – SSV

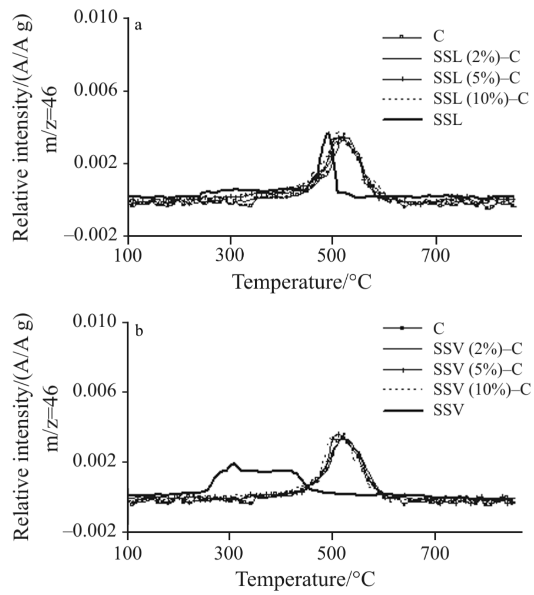

Fig. 4 NO_2 evolution curves followed by MS during the combustion and co-combustion of coal (C), sludge and its blends. Two sludges were used for this study: a – SSL and b – SSV. Note: the scale ratio is 1:100 with respect to Fig. 3

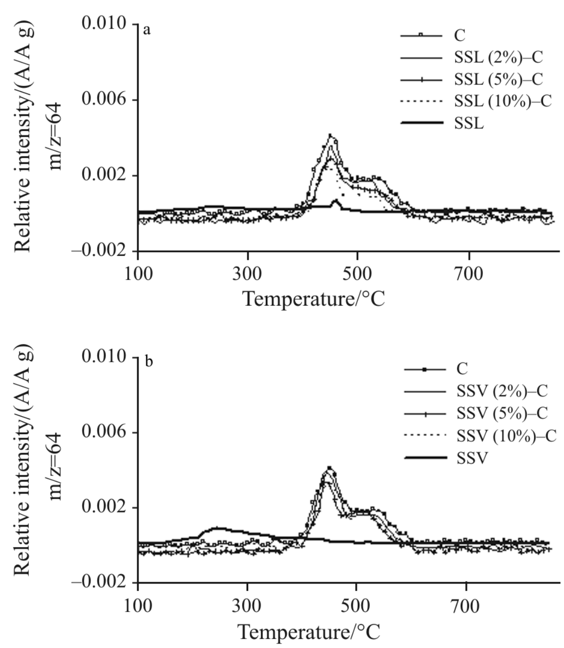

Fig. 5 SO_2 evolution curves followed by MS during the combustion and co-combustion of coal (C), sludge and its blends. Two sludges were used for this study: a – SSL and b – SSV. Note: the scale ratio is 1:100 with respect to Fig. 3

than during the second one. For all samples, maxima in the CO_2 emission occur at the same temperature that T_m showed in Table 2. Although the trends are the same, there is not proportionality between peak values in the emission of CO_2 and in the DTG curves. Blends showed mass loss peaks slightly lower than coal, which is not true in the case of the CO_2 emission during the temperature programmed combustions. CO_2 emission is coincident for coal and blends here considered except for its occurring at slightly lower temperatures for the blends. Combustion is a chemical process, an exothermic reaction between a substance and an oxidizer gas, to release heat. As the fuel is the organic carbon content of the substance and the oxidizer is the O_2, CO_2 is emitted during heat releasing so the profiles of curves of Figs 3a and b resemble Figs 2a and b. Nevertheless, the same as for the combustion profiles (Figs 1a and b) compared with the emission of CO_2 (Figs 3a and b) may be said about the corresponding DSC curves (Figs 2a and b). This is due to an incomplete oxidation of the organic matter in the sludges that produces an increase in mass and a low emission of CO_2; the sum of these factors is similar and a small mass loss is registered.

With respect to the *m*/*z*=46, for which, most probable parent molecule is NO_2, differences between coal and both SSL and SSV may be seen in Figs 4a and b, respectively. Again the maxima occur at around the same temperature than for mass loss during the temperature programmed combustions. In the case of NO_2, the values of the emission peaks are slightly higher for the blends than for coal, which is related to the nitrogen content in sludge. Anyway, despite its high nitrogen content, emissions of NO_2 are lower than experienced from coal combustion, which has been observed by some other authors [6] for NO_x. As for CO_2, NO_2 emissions are very different for SSL and SSV, but differences are not so remarkable for the blends with the same sludge content.

Figures 5a and b shows the relative intensity of the *m*/*z*=64, which most probable parent molecule is SO_2, during the temperature programmed combustions carried out. Emissions associated to the combustion of coal are much larger than for sludge, which is especially true in the case of SSL as for the sulphur content. Also, SO_2 emissions during the combustion of the blends are notably lower than for coal, even when the sludge content in the blend is 2%. Also, it seems that emission of SO_2 occurs during a smaller range of temperature for the blends than for coal. Finally, on the contrary of CO_2 and NO_2 emissions, in the case of SO_2, maxima occur at lower temperatures than the corresponding mass loss peaks in the DTG curves for all the samples.

Conclusions

Differences were found between the combustion profiles (DTG) of a semianthracite coal and sewage sludge samples. In general, for the combustion of sludge: 1) the organic matter combustion shifts to lower temperatures than for coal; 2) the temperature range of combustion is broader than for coal; 3) the combustion is more complex than for coal and comprises two stages and not only one. In the DSC curves, these facts may be also seen, although there is not parallelism between the mass loss and the energy releasing during the sludge combustion. Again, big differences arise from the experimental DSC curves corresponding to coal and sludge.

As for the coal-sludge blends with a percentage of sludge equal or minor than 10%, experimental results demonstrate that the previous differences get out of sight. DTG curves for the blends are comparable to that for coal and decreasing of the energy release during combustion of coal owed to adding of sludge (in a percentage of 10% or less) is barely visible. Also, no interaction has been observed between the original materials during the combustion process.

Both the DTG and the DSC curves corresponding to the temperature programmed combustion of coal-sludge blends are very similar to those corresponding to coal, no matter which is the sludge when its percentage in the blend is 10% or less. Also, for the blends combustions, emission of CO_2 is very alike to that corresponding to the coal, while emission of NO_2 is slightly higher and that of SO_2 lower. Differences between coal and sewage sludge combustion are significant but they get screened in blends, even for different sludges. Sewage sludge and coal co-combustion may play an important role for sewage sludge disposal accounting for not big extra costs. Perhaps an intensive research about this option together with flow of information may enhance the confidence of the public.

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