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Thermogravimetric Analysis of Sewage Sludge and Straw Co-Firing

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Abstract

The main objective of this study is to perform thermogravimetric analysis on sewage sludge and straw co-firing at selected proportions. Sewage sludge is a residue from wastewater consisting of organic matter, toxic contaminants and heavy metals [1]. It is estimated that 10 million tonnes of sewage sludge are produced every year in European states, which represents 4.1% of all waste generated in the EU annually – about 250 million tonnes of dry solids [2]. Landfilling is deemed to be the most expensive way to dispose of sewage sludge, with average total costs ranging from EUR 260 to 350 per tonne of dry matter [3]. Straw is a major biomass solid waste from agriculture; it can be considered CO_2 neutral. The availability is wide in Europe that it is estimated to be 33 million metric tonnes [4]. A suite of thermogravimetric analysis and derivative thermogravimetric experiments was performed for this study, followed by the determination of the kinetic parameters and characteristic temperatures for these materials and their blends at different proportions. Through this analysis we can obtain information about the thermal behaviour, energy activation and ash content, and the decomposition of gaseous products can be identified the help of thermal decomposition [5].

Słowa kluczowe: hermogravimetric analysis, sewage sludge, straw,co-firing

1. Introduction

The day-by-day increase in the production and storage of sewage sludge will create a huge environmental crisis, not only in European countries but also round the world. Many countries and universities are working together to find an effective method for the disposal of sewage sludge. Even though there are many methods for disposal, many studies and experiments have proved that thermal technologies present the best results. This study explains the possible combustion of sewage sludge with biomass and the outcomes and consequences. To make the firing more effective and to reduce the emission of hazardous gasses, sewage sludge is mixed with straw at certain proportions. In this study, the experimental proportions of sewage sludge and straw were as follows: 100% straw, 100% sewage sludge, 50% straw and 50% sewage sludge, 30% straw and 70% sewage sludge, 20% straw and 80% sewage sludge and 10% straw and 90% sewage sludge. The experimental analysis was carried out using thermogravimetric analysis (TGA) under two conditions: a heating rate of 10°C/min and of 200°C/min. The thermogravimetric and derivative thermogravimetric curves obtained from the experiments were analysed and the energy activation calculated.

2. Analysis of Sewage Sludge

Sewage sludge contains traces of heavy metals such as chromium, zinc, mercury, lead, nickel, cadmium and copper, which makes sewage sludge unsuitable for direct use in landfills. Sewage sludge has a high density due to its high ash content. The proximate analysis of sewage sludge in dry form was performed; the results are shown in Table 1.

Table 1. Proximate Analysis of Sewage Sludge [6]

Moisture Content	Volatile Content	Fixed Carbon Content	Ash Content
80.2%	56.62%	7.46%	35.9%

Sewage sludge still has a high content of volatile matter, high carbon content and good calorific value, which gives it potential for further utilization in appropriate combustion. The ultimate analysis of sewage sludge was performed; the results are presented in Table 2.

Table 2. Ultimate Analysis of Sewage Sludge, in a Dry Form [6]

C	H	N	O	S
32.52%	4.5%	4.84%	22.52%	6%

3. Analysis of Straw

Straw contains more volatile matter when compared to that of coal and carbon. The unburnt produce pollutants such as carbon monoxide, tar, hydrocarbon, polychlorinated aromatic hydrocarbons and unburnt char particles. Table 3 shows the proximity analysis of wheat straw, while Table 4 shows the ultimate analysis of wheat straw.

Table 3. Proximate Analysis of Straw [7]

Moisture Content	Volatile Content	Fixed Carbon Content	Ash Content
5%	68%	18.6%	8.4%

Table 4. Ultimate Analysis of Straw, in a Dry Form [7]

C	H	N	O	S
43.2%	5.8%	0.178%	52.9%	0.28%

Table 5 shows the calorific value of sewage sludge and straw, as measured by the arrangement of the IKA C 2000 basic bomb calorimeter at Wrocław University of Science and Technology.

Table 5. Calorific Value of Sewage Sludge and Straw

Fuel (dry)	Calorific Value (HHV), in MJ/kg
Sewage sludge	15.7
Straw	18.2

4. Fuel Preparation

The preparation of the fuel for TGA is the most important procedure in the analysis, as we use microscopic particles to test the specimen. The dried sewage sludge from the water plant and the straw should be ground to very fine particles and evenly distributed in order to get accurate results. To prepare fine particulate fuels, the fuel is initially powdered using a milling machine with a nanometre filter. After the fuel is ground with a milling machine, it is collected and sieved using a variety of filter meshes in order to get the fine fuel particles.

Table 6 shows the cumulative distribution of straw and sewage sludge, in per cent, which represents the particle size distribution of the fuel after sieving. Figures 1 and 2 show the cumulative distribution curve for the straw and sewage sludge; Table 7 displays the median value of particle size (d50), which is determined from the screening operation and is defined as the particle size calculated from the sample where 50% of the mass is above and 50% is below [8].

Table 6. Distribution of Fuel (Straw and Sewage Sludge)

Particle Size [nm]	Straw Distribution [%]	Sewage Sludge Distribution [%]	Straw [g]	Sewage Sludge[g]
>250	0.9	2.6	0.9	9.2
106–250	27.6	10.2	28.7	35.9
90–106	7.6	5.6	7.9	19.7
63–90	18.2	11.6	18.9	40.8
25–63	40.0	65.4	41.6	230.1
0–25	5.7	4.5	5.9	15.9
	Total		103.9	351.6

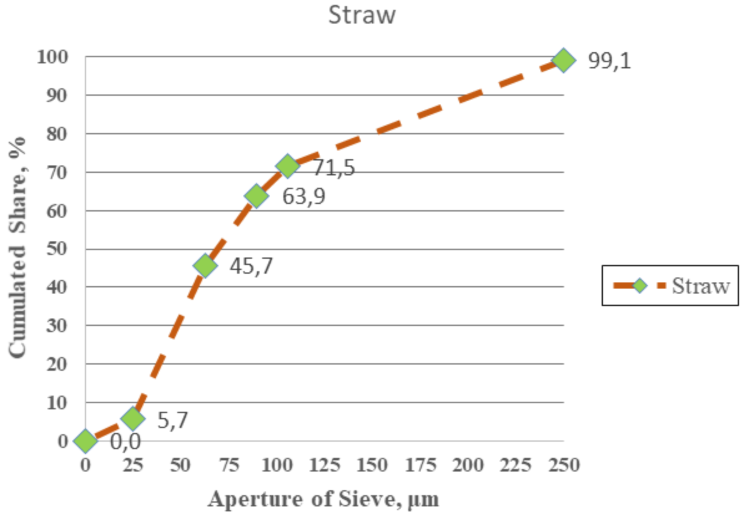

Fig. 1. Cumulative Distribution Curve for Straw

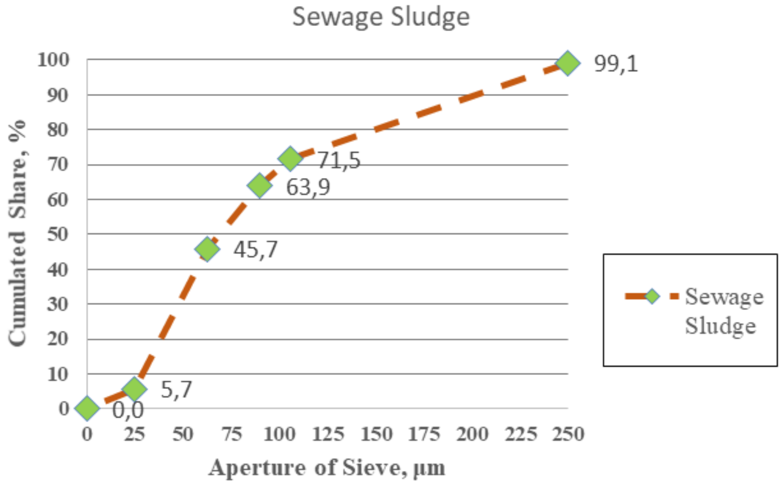

Fig. 2. Cumulative Distribution Curve for Sewage Sludge

Table 7. Median Value of Particle Size Distribution of the Sample

	Straw		Sewage Sludge	
D 50	69	[μm]	65	[μm]

5. Thermogravimetric Analysis

In this report we analyse the behaviour of straw and sewage sludge using TGA. This experiment was carried out at two heating rates:

- HR-10 – 10°C/min rise in temperature,
- HR-200 – 200°C/min rise in temperature.

The following sample compositions were used in the TGA tests:

- 100% Straw,
- 100% Sewage Sludge,
- 50% Straw; 50% Sewage Sludge,
- 30% Straw; 70% Sewage Sludge,
- 20% Straw; 80% Sewage Sludge,
- 10% Straw; 90% Sewage Sludge.

6. Experiment Design and Planning

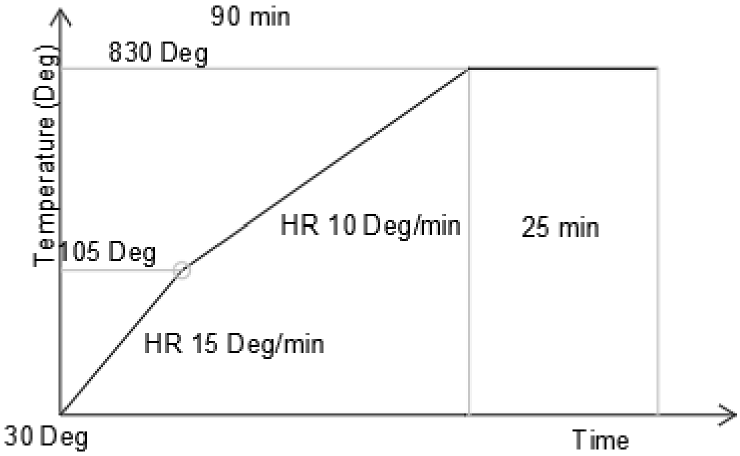

Fig. 3. Planned Programme for HR-10 TGA Analysis (Temperature over Time)

In this experiment the specimens were first tested at HR-10 – a rise in heat of 10°C/min – and then for HR-200 – a rise in heat of 200°C/min. Figures 3 and 4 show the changes in temperature over time during the experiment. Initially, the experiment started at room temperature and increased up to 105°C at a heating rate of 15°C/min in order to quickly remove the moisture content in the fuel. After reaching 105°C, in HR-10 the temperature was increased by 10°C/min gradually up to 830°C, which took 90 minutes. The temperature was held at 830°C for 25 minutes for the fuel to be completely burnt. The final temperature of the experiment was maintained at 830°C in order to ensure that the specimens were completely burnt. In the case of HR-200, after the temperature was increased to 105°C at a rate of 15°C/min, it was further raised to 830°C at a heating rate of 200°C/min, which took 30 minutes. It was then maintained at 830°C for 25 minutes.

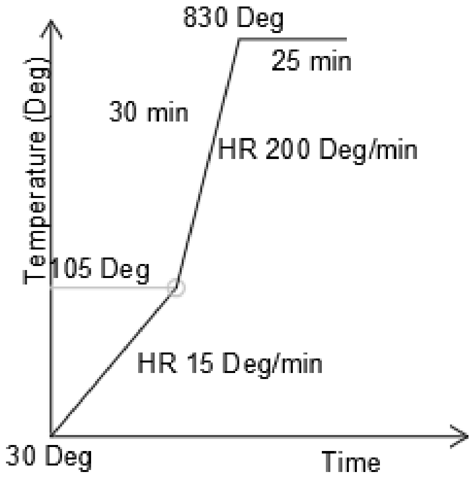

Fig. 4. Planned Programme for HR-200 TGA Analysis (Temperature over Time)

7. Comparison of Temperature and Weight

Figures 5 and 6 show the thermogravimetric curves of various experiments performed in this study for heating rates of 10°C/min and 200°C/min. In the

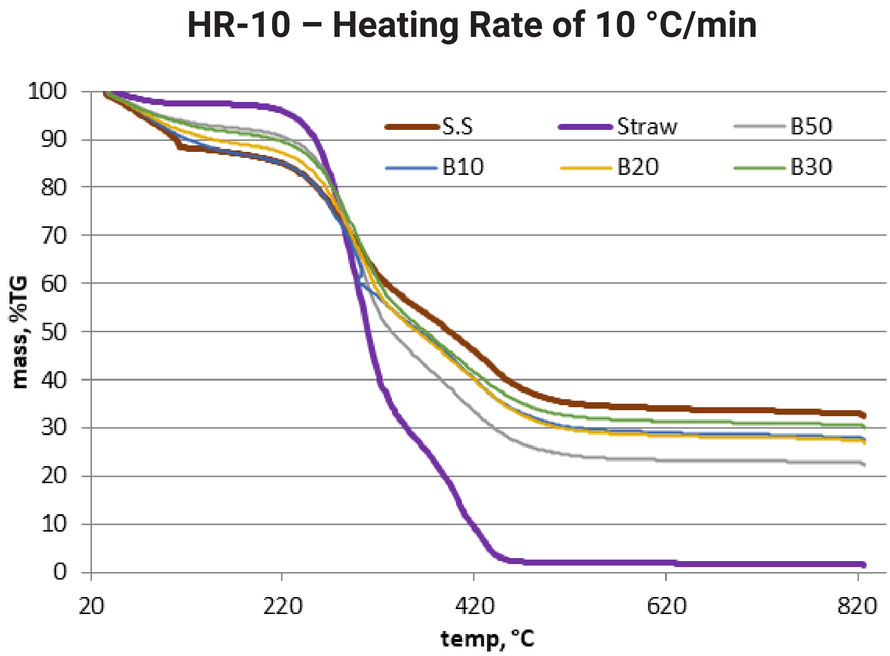

Fig. 5. TGA Comparison of a Heating Rate of 10°C/min

comparison of the two heating rates, they show similar values with difference in temperature. It was also observed that the higher the sewage sludge proportion, the more ash remained. The moisture was more quickly removed from the straw and it combusted very rapidly when compared to the other mixture and raw sewage sludge. Also, the ash content of the 50%/50% fuel mixture was moderate in comparison to that of the other mixtures. The raw sewage sludge had the highest ash content and the complete combustion time was a bit longer than the other specimens at both heating rates.

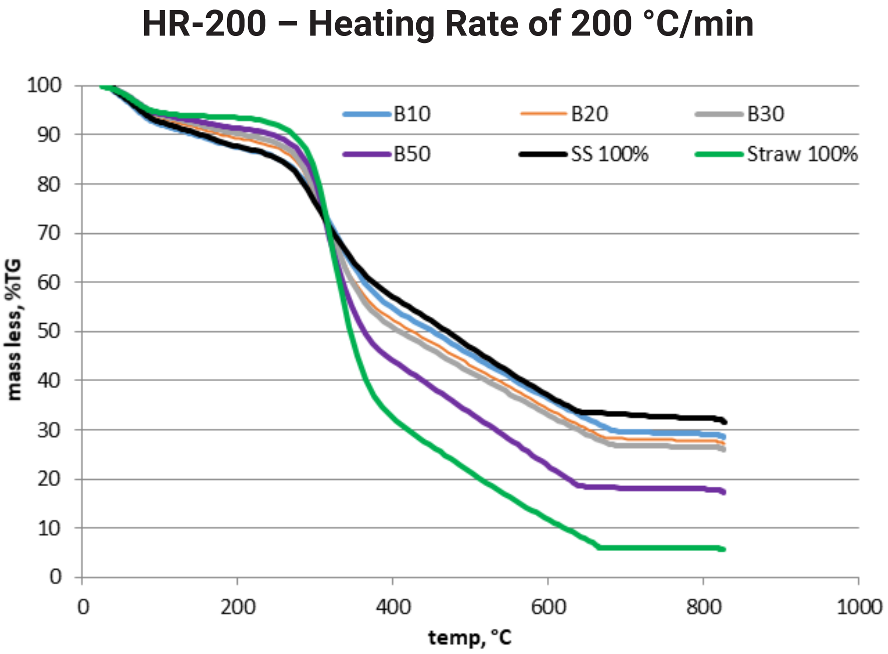

Fig. 6. TGA Comparison of a Heating Rate of 200°C/min

Table 8 presents the activation energy calculated in each experiment. The activation energy is higher for straw and lower for sewage sludge; the 50% proportion of both fuels lies approximately between straw and sewage sludge in terms of activation energy. Tables 9 and 10 show the characteristic temperature of the specimens at the two heating rates, such as the initial temperature of reaction (ITR), peak temperature (PT) and burnout temperature (BT). The heating rate of 10°C/min DTG for all the fuel ratio was observed to have three different peak values due to the slow heating rate.

Table 8. Activation Energy for Samples

Samples	Activation Energy in kJ/(mol K)
Straw	68.604
Sewage Sludge	23.108
50% Straw – 50% Sewage Sludge	50.7
30% Straw – 70% Sewage Sludge	38.7
20% Straw – 80% Sewage Sludge	34.8
10% Straw – 90% Sewage Sludge	31.8

Table 9. Characteristic Temperatures for a Heating Rate of 10°C/min

Characteristic Temperature		Straw 100%	Sewage Sludge 100%	B 50	B 30	B 20	B 10
% of Straw		100	0	50	30	20	10
ITR, T (°C)		206.9	228.4	213.05	224.8	233.6	218.9
PT, T (°C)	PT1	77.8	81.8	77.6	77.9	83.1	83.7
	PT2	300.7	290.1	297.6	295.7	295	288.8
	PT3	401.5	438	404.1	–	431.6	412
BT, T (°C)		565.6	708.9	619.6	513.7	585	546

Table 10. Characteristic Temperature for a Heating Rate of 200°C/min

Characteristic Teperature	Straw 100%	Sewage Sludge 100%	B 50	B 30	B 20	B 10
ITR, T (°C)	252.9	265.2	267.5	261.9	260.1	247.5
PT, T (°C)	344	334.4	346.8	338.5	336.3	346.9
BT, T (°C)	671	648.9	648.8	687.2	677.3	683.9

8. Comparison of Temperatures and Derivatives

Figures 7 and 8 present a comparison of the DTG of all the samples used in the experiment at a heating rate of 10°C/min and 200°C/min, respectively.

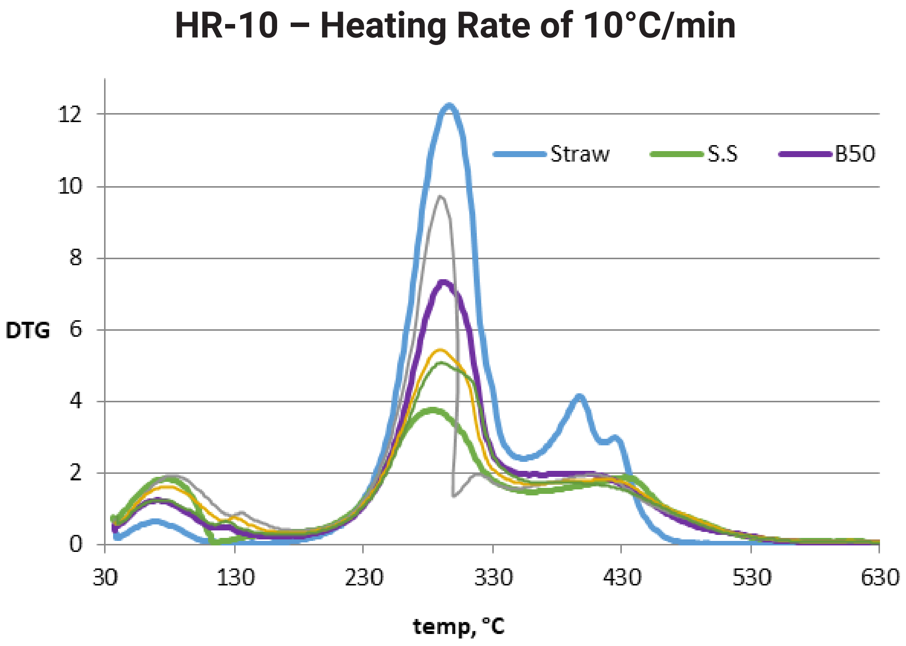

Fig. 7. DTG Comparison of a Heating Rate of 10°C/min

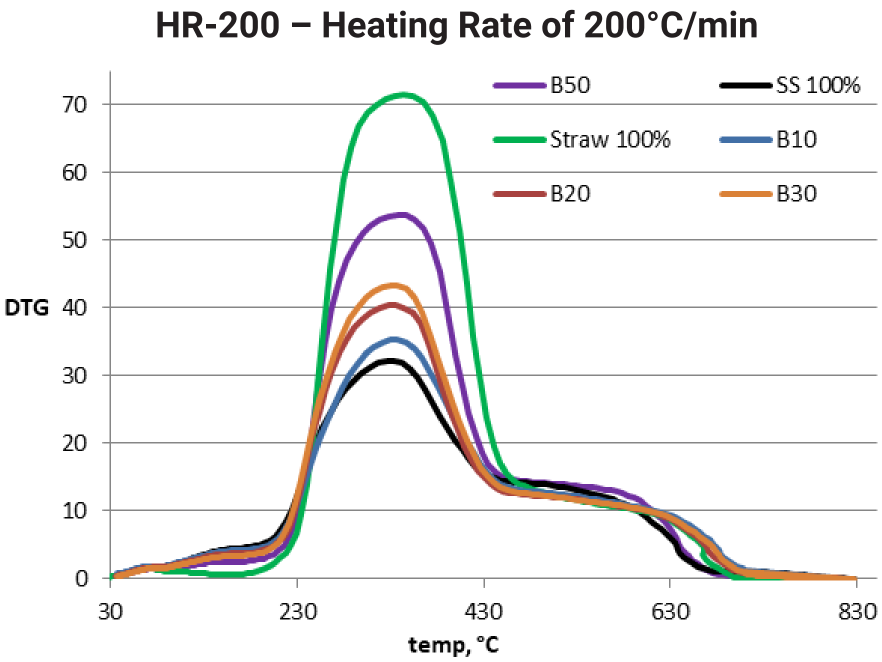

Fig. 8. DTG Comparison of a Heating Rate of 200°C/min

As shown in the figures, the derivative weight loss of straw was very quick when compared to that of the other mixtures because of its lightweight particles and high calorific value. The sewage sludge gradually decreased in weight loss because of the presence of heavy particles within it. Similar to the TGA, the DTG of the mixture with 50% of each sample decreased at an average rate between those of straw and sewage sludge, yielding a perfect curve in comparison to the other curves.

9. Experimental Ash Analysis for Ash Content

To analyse the ash content of the raw straw, raw sewage sludge and 50% straw/50% sewage sludge samples, furnace firing was used. The specimens were heated up to 850°C for one hour in an electric furnace and allowed to cool for 30 minutes. Table 11 shows the weight measured during the various stages of the experiment and the percentage of ash.

Table 11. Weight Measured for the Experimental Ash Analysis

	Straw	Sewage Sludge	B50
Tray Weight (g)	30.9	29.2	27.6
Tray with Sample (g)	32.5	32.9	28.9
After Test (g)	31	30.4	27.8
Raw Sample (g)	1.60	3.68	1.31
Mass of ash (g)	0.08	1.15	0.24
Mass involved in combustion (g)	1.52	2.53	1.07
% of Ash content (%)	4.9	31.2	18.4

The percentage of ash content was measured by the formula:

$$\% \; of \; Ash \; Content = \left(\frac{Ash \; Content}{Sample \; Weight}\right) \times 100 \qquad (1)$$

% of Ash content = (0.5 × % of ash content in Straw) + (0.5 × % of ash content in Sewage sludge) = (0.5 × 4.9) + (0.5 × 31.2) = 18.45%.

The above calculation proves that the percentage of ash content in straw and in sewage sludge can provide the exact percentage of ash content in the mixture of 50% of each fuel, as performed in the TGA experiments. Figure 9 shows the initial weight and the weight of ash content measured during the experiment.

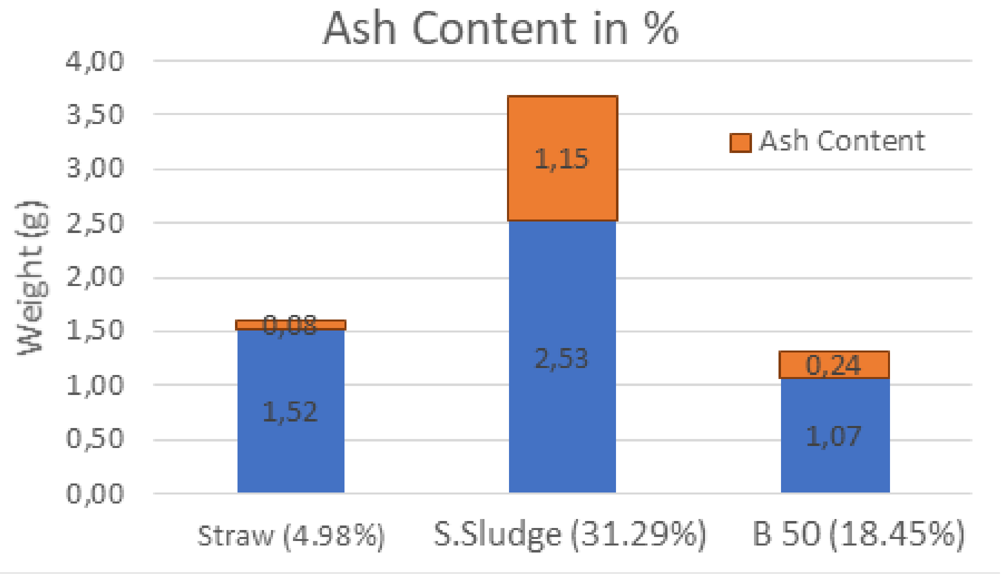

Fig. 9. Mass Involved in the Combustion and the Mass of Ash

10. Conclusions

The kinetic analysis for straw, sewage sludge and both fuels in different proportions were analysed using thermogravimetric analysis and the results were described. From these results, the ash content and activation energy were calculated and the thermal decomposition estimated. The moisture removal in all the experiments occurred at an average temperature of 105°C and 96°C for a heating rate of 10°C/min and 200°C/min, respectively. The combustion began above 240°C for all the specimens. The straw displayed a sudden drop in derivative and the burnout timing seems to be very short in comparison to that of other fuels, due to its volatile nature. The sewage sludge when combusted alone demonstrated very similar results to straw, but with a high ash content. This shows that the thermal behaviour of sewage sludge is adequate for use in various thermal technologies, such as gasification and pyrolysis.

The ash analysis of straw and sewage sludge (Table 7) varied: the straw consisted of 4.9% ash content, while the sewage sludge had 31.2% ash content. When mixed with straw at a certain proportion, sewage sludge had a lower ash content than raw sewage sludge, but still with good thermal behaviour. It is notable that the 50% mixture of straw and sewage sludge had very average ash content, between the other fuel mixtures. The TGA of the 50% mixture of fuels (B50) yielded significant TG and DTG curves at both heating rates, with a good characteristic temperature and an average contribution of a low amount of ash (18.4%).

The peak temperature of the 50% mixture was found to be high at both heating rates, illustrating that the fuel can be combusted with an average rate of mass loss. At some points the characteristic temperature of the 50% mixture demonstrated better thermal behaviour when fired rapidly, at a heating rate of 200°C/min. When comparing the two heating rates (10°C/min and 200°C/min), the faster rate had a higher initial temperature of reaction, peak temperature and burnout temperature than the slower rate, which suggests that the fuel has a good thermal stability and a low rate of mass loss. This is due to the thermal characteristics of straw and sewage sludge present in this exact proportion. In terms of the other samples, the B30, B20 and B10 had almost the same temperature and ash content as the raw sewage sludge. The thermal characteristics of sewage sludge were comparable to most of the biomass mixtures, apart from the high ash content. Even when it comes to ash accumulation issues, most of the fly-ash from power plants is used for various purposes, such as cement manufacturing and brick-making. The sewage sludge can be co-fired with other biomass for electricity generation, thereby extracting maximum efficiency from the fuel.

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