Effect of sewage sludge composition on the susceptibility to spontaneous combustion

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ABSTRACT

The different technologies applied to the sewage sludge management have in common a first step devoted to the storage. In the case of dried sludges, this storage leads to important safety concerns because of the explosive character of the resulting dusts. In order to ensure safety in the storage step, it is necessary to evaluate the spontaneous combustion trends on terms of measurable chemical and physical properties of the dried sludges.

In order to accomplish this scope, twelve samples from different wastewater treatment plants were characterized, correlating the susceptibility to spontaneous combustion with both the sludge composition and the heating value. Equations traditionally used for coals were used to determine the higher heating value from the chemical composition, finding as main source of error the high oxygen content of the sludge samples. Concerning the thermal susceptibility, different parameters were obtained (Maciejasz Index, induction temperature, maximum weight loss temperature, characteristic temperature and activation energy), being in all cases the spontaneous combustions favored by high H/C and low O/C ratios. Likewise, the presence of sulphur in the dried sludge was found to increase the thermal susceptibility of the material. This effect is tentatively explained with the formation of pyrophoric iron sulfides.

Keywords: self-ignition risk, sewage sludge, chemical analysis, explosion hazard

1. **INTRODUCTION**

Due to the urbanisation and industrialisation, the installed treatment capacity of wastewater is closer to 70 % of the generated wastewater in high income countries [1]. Empirical records suggest that globally more than 330 km^3 $year^{-1}$ of (mostly) municipal wastewater are produced. Thus, the management of sewage sludge from wastewater treatment facilities is becoming into a major environmental problem, as well a new sustainable source of renewable carbon to be considered. Must of the alternatives for the treatment or upgrading of these sludges deal with the management of dried sludges and its further storage step, with the subsequent problem of dusts formation. The formation of this dust leads to important safety concerns, since in presence of oxygen and one or multiple ignition sources, the risk of explosion is important.

The dust explosions are known in the industry of grain and flour milling and coal mining over two centuries ago [2-5], but it is scarcely studied for the case of dried sewage sludge. In a pioneering work, Fernandez-Anez and coworkers [6] determined the explosion severity, flammability and thermal susceptibility analysis of several dried sewage sludge samples, and correlated these features and the chemical composition. Likewise, these authors evaluated the thermal susceptibility of sludge by activation energy and the characteristic oxidation temperature, observing a higher self-ignition trend with the H content [7]. This work was afterwards extended to different biomass samples from agriculture and forestry, cokes, solid recovered fuels, and sewage sludge, remarking the differences among the biomass materials and coals, attributing to the heat transmission mechanism the reported differences [8-10].

Thus, the aim of this work is to correlate the ignition properties of dried sludges with chemical and heating features of these sludges. This information would allow forecasting safety constraints of the storage and handling of dried sludge on terms of chemical information easy to obtain. In order to fulfil this scope, the thermal susceptibility of different samples of sewage sludge received in a Spanish facility for the management of sewage sludges (COGERSA, Asturian Region, North of Spain) was measured. For each sludge sample, both chemical and thermal analysis of the dried samples were carried out, in order to correlate the chemical composition (both proximate and ultimate analysis) or volatile content in the drying process with the potential flammability properties.

2. EXPERIMENTAL

2.1. Sampling and materials

Twelve samples of sewage sludge were collected by COGERSA, the waste management company in Asturias (1 million habitants region in the North of Spain). The samples, collected in the first semester of 2017, proceed from the main urban wastewater treatment plants from the region. Thus, wastewaters treated in these plants are mainly domestic wastewater, with minor contribution of industrial wastewater and stormwater runoff. The industrial wastewaters discharged into this collection network must be assimilable to domestic wastewaters. Specifically, from nine different plants, since samples SLU-8, SLU-9 and SLU-10 proceed from the same WWTP (samples taken in different weeks), as well as SLU-11 and SLU-12. For all samples, proximate analysis (moisture and ash), elemental analysis, as well as the heating value was determined.

The moisture of the samples was obtained after drying treatment in an oven at 105 ºC until constant weight. The ash content was determined by introduction of portions of about 1.5 g in a muffle furnace at 550 ºC in air, and volatile matter was calculated by difference, that is, subtracting the weight of the ashes from the weight of the dried solid. The subsequent analyses were carried out on the dry sample, after milling and sieving taking a fraction of crush, mill and sieve the materials, taking a sample of 50-100 μm for performing the test. This approach avoids the effect of the particle diameter of the studied properties, focusing the study on the effect of the intrinsic chemical properties of the material. The ultimate analysis (C, H, N, S contents) was measured in an elemental analyzer (Elemental Vario EL) device, where the complete oxidation of the sample took place at 1000 ºC, whereas a helium stream carried the flue gas to a Thermal Conductivity Detector (TCD) for quantifying. The determination of oxygen content was calculated by difference, that is, sample excluding the ash, hydrogen, carbon, nitrogen and sulphur (wt%) content. Iron content was analyzed using an Agilent 7975c inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion in a microwave digester of a 0.25 g sample with 50 mL of HNO_3.

Determination of the Higher Heating Value (HHV) of the sludge samples was conducted using an adiabatic calorimeter (IKA C4000) device. All analyses were done by duplicate, and periodic calibrations with benzoic acid (GCV= 26460 kJ/kg) were performed. The Lower Heating Value (LHV), which considers that all the water of the sample is present as vapor after the combustion, is obtained from the HHV according to the following expression:

$$LHV_{wet}=\left[HHV_{dry}-2442\left(\frac{W}{100}+9\frac{H_{dry}}{100}\right)\right]\left(1-\frac{W}{100}\right) \qquad (1)$$

where LHV_{wet} and HHV_{dry} are the Low Heating Value in wet basis and the Higher Heating Value in dry basis for each sample, expressed in kJ/kg; 2442 kJ/kg is the heat of vaporization of water; H_{dry} is the percentage of hydrogen in dry basis and the nine (9) refers to the water produced in the combustion in relation to the initial content of hydrogen, which is nine times this amount of water produced; W is the moisture content (in percentage) in each sample.

These methods are standardized for solid biomass according to the European Standards (Table 1).

2.2. Thermal susceptibility

Thermal susceptibility referred to the parameters that allow studying the thermal behavior of solids and to determine the possibility of spontaneous combustion [11]. Among this group of parameters, the most widely known is the Maciejasz Index (MI) [9], which is a measurement of the reactivity and avidity of a sample for oxygen, after treating it with hydrogen peroxide. In the case of present reactivity to oxygen, and exothermic reaction will occur and its temperature will rise. The MI is determined as:

$$MI=100/t$$

Where t is the time (minutes) needed to rise the temperature of the sample in 65 ºC from the initial ambient temperature measured. The risk of self-ignition exists for $MI > 10$.

Thermogravimetric test measures the amount of weight change of a material as a function of increasing temperature, from ambient temperature to 600 ºC, with a heating rate of 5 ºC/min, and in an air flow of 20 mL/min. These parameters are useful since they provide a measurement of the tendency to self-ignition, as it was observed from comparison with flammability and explosivity parameters [9]. Plots of the weight loss versus the temperature (thermograms) are the typical representation of the experimental data. From this data plotting, different parameters can be obtained, among them: the induction temperature (IT), temperature at which the oxidation reaction boost; and the maximum weight loss temperature (MLT), temperature at which the minimum of the derivative curve (dTG) is obtained. Likewise, the susceptibility to start exothermic oxidation process can be represented by two parameters: the activation energy (Ea), calculated by the mathematical approach proposed by Cumming, at the maximum weight loss, from the slope of the least-squares straight line fitted to the chosen test data; and the characteristic oxidation temperature (Tc), that is, the temperature at which oxidation occurs when the stream is just oxygen.

3. RESULTS AND DISCUSSION

3.1. Chemical analyses

The modification of the external aspect of the samples is observed in Fig. S1. In all cases the initial sludge is a viscous-pasty liquid, whereas after drying is transformed into a dried solid. The most remarkable difference is the red color of the SLU-7 sample, as well as the resulting powered material obtained upon drying. These differences are explained by the use of $FeCl_3$ as coagulant in the primary settling of the treatment plant. The other samples present colorations among the brown and black, which could be influenced not only by the nature of the sludge but also by the aerobic or anaerobic fermentation processes which will change the product during storage. Thus, add to the nature of the sludge, other aspects as the water content, the days of the sludge keeping could influence both the rheological properties and drying behavior.

Ultimate and proximate analyses of the dried samples are summarized in Table 2. From data it is observed a clear positive relationship between the carbon, hydrogen and oxygen content of the sludge and the volatiles of the samples. In this way, it is remarkable the low ash ratio (high volatiles and C content) of samples SLU-8, SLU-9 and SLU-10, the three samples with the same origin and different temporality, both in comparison with the other samples considered in this work, but also in comparison with sewage sludge from other wastewater treatment plants [6]. The pasty appearance of these samples could give an idea about the high organic content of the original material, which is transformed in volatile matter in the drying process. Likewise, SLU-2, SLU-3 and SLU-6, also with a pasty aspect, present values of volatile matter higher than 76 %. Contrary, the SLU-7 sample, with a different coloration and a mineral aspect, showed the largest ash concentration (50 %). Other samples, SLU-1, SLU-11 and SLU-12 exhibit a more granulated aspect, in good agreement with its intermediate ash content among the studied samples (31-33 %). Finally, SLU-4 and SLU-5 show also a granulated and even porous appearance although the ash content (21-24 %) is similar to samples with a pasty morphology.

Also from the ultimate analysis, the atomic H/C and O/C ratios are obtained (Table 2). The H/C ratio varies between 1.22 and 2.04, whereas the O/C, between 0.34 and 0.53. Both parameters, plotted in Figure 1 in a van Krevelen diagram, are considerable higher than coals [12], but similar than other sewage sludge [9]. If these values are compared to other biomass resources, such as grass, straw, wood or waste wood, the H/C and O/C ratios vary around 1.5 and 0.7, respectively [13].

The H/C atomic ratio is a measure of saturation degree, which could have a higher variability for the different sludge samples than for other biomass materials. Thus, this gives an idea about the lack of homogeneity in sludges. The O/C ratio indicates the presence of less oxygenated species than biomass. Two different causes justify this difference: on the one hand sewage sludge present significant lipid content (lipids present O/C and H/C ration largely lower than cellulosic materials. On the other hand, biological transformations of the sewage (both aerobic and anaerobic) lead to the loss of oxygenated functionalities of the organic fraction.

Likewise, from Fig. 1 two separated areas can be observed. The upper one, the highest H/C ratio samples, match with those with the highest ash content –due to the inverse relationship between ash and carbon content-; whereas those sludges with the lowest values of both H/C ratio and ash weight are under the above-mentioned line. Two cases are considered as singular. On one hand, SLU-2, SLU-4 and SLU-6 samples are in the area upper the curve although the ash content between 22 and 25 % could be considered as average. These samples present the highest H/C ratio (> 5.79 %), add to O/C values among the more elevated. Thus, these samples could present a lower degradation degree that the other essayed samples, that is, they have carried out dehydration and decarboxylation reactions at lower extent. That is, dehydration reaction implies the loss of a water molecule, so a decrease in the O/C ratio is observed after this reaction. In the case of decarboxylation reaction, a CO_2 molecule is lost, so a decrease in O/C ratio and a slight increment in H/C ratio is observed. On the other hand, SLU-3 sample, with an average ash content, but the lowest H value (3.89 %) is situated at the bottom of the plot, and this sludge sample is the closest to that of a ligno-cellulosic biomass.

3.2. Enthalpy of combustion

Table 3 shows the higher and lower heating values (combustion enthalpy) expressed on dry and wet basis, respectively, for each sample. The use of sewage sludge material as fuel could contribute to cost savings of raw materials and even, economical benefits. COGERSA facilities received 53000 tons of wet sludge (in 2017), with an average HHV (Table 3) of 18.63 MJ/kg (average LHV of 3.91 MJ/kg). Thus, the combustion of the received sludge will generate $1.9 \cdot 10^8$ MJ/year. Table 4 shows three empirical models used for describing HHV as function of the elemental composition [14]. These models were satisfactory used both to predict the heating content of coals and municipal solid wastes [15] but, to the best of our knowledge, not for sewage sludge. As can be observed, both the C and H content implies is directly related to the heating value, whereas the O content means a subtraction in the HHV. The negative contribution of the O coefficient in the overall models decrease in the order Scheurer-Kestner, Dulong and Steuer, respectively. Fig. 2 shows a comparison of the HHV predicted with the experimental values, whose data could be analyzed jointly with the sum of squares of the residuals (SSR) and the R^2 values for the three models studied. From the plotted data, the Scheurer-Kestner model provided the best fit, followed by Dulong and Steuer. Thus, since the contribution of both C and H are equivalent for the three equations, and the main difference consists on the O one, which means that the model with the lowest subtraction due to the oxygen obtained the best fitting. Since these equations were developed for coals, and coals present O/C ratios typically among 0.1 and 0.3, this difference could justify the dispersion in the predicted data.

3.3. Thermal susceptibility

Table 5 shows the results obtained by thermogravimetry for the thermal susceptibility of the sludge samples. The Maciejasz Index varies between 0 and 44, the SLU-7 sample exhibiting the maximum value, followed by SLU-12, SLU-11, SLU-3 and SLU-1, with MI of 19, 13, 11 and 8, respectively. This decreasing order is coincident with the diminution is ash content (Table 2), from 50.1 to 35.51 %, for SLU-7 and SLU-1, respectively, with the exception of SLU-3. It should be noted, that the ashes could be enriched into metals or other inorganic matter catalyzing oxidation reactions, since the radicalary reaction can be initiated even on inert particles. From Fig. 1, it can be observed that, add to the ash content (upper part of the plot), high H/C ratio, as well as low O/C one, increase the MI, thus the scarce oxygen content could increment the easiness for the reactivity in presence of the hydrogen peroxide. The lower oxidation temperatures, that is, higher easiness for combustion, was already described for samples, of different origins, providing high H/C ratios and low O/C ratios [9]. Furthermore, the H/C ratio presents larger influence on the MI than O/C, since samples with both high ash content and high H/C ratio are those with largest MI, with the exception of SLU2, SLU-4 and SLU-6 –probably due to the different degradation degree-, and SLU-3 –with the largest dehydration extent-.

The induction temperature (IT) and the maximum weight loss temperature (MLT), are situated in the range 199-285 and 264-413 ºC, respectively. In both cases, the results are comparable to other sewage sludge samples, and even similar to other organic wastes from different origins, such as straw [9]. Both parameters are related to the initial oxidation temperature, so it is easily justified as those samples with a higher volatiles content exhibit lower IT and MLT, Fig. 3. Likewise, this evidence is congruent with the habitual practice to avoid explosion risk consisting on the addition of inert dust to combustible materials, since the volatiles content is inversely proportional to the ash content. These temperatures can also be related to the H and O content. As in the case of the Maciejasz Index, the easiness of oxidation (high MI) would be correlated to low IT and MLT, and it is obvious that these trend is not followed by the studied samples (Table 4). This fact is a good agreement with the reported by García Torrent et al. [9], in the case of sewage sludge samples, finding more confident results from the Ea and Tc parameters. In this way, Fig. 4 shows the ignition parameters Ea and Tc on a characteristic risk plot. The maximum Tc reached corresponds to SLU-5 (282 ºC), whereas the Ea varies between 21.7 and 54.5 kJ/mol. The two differenced areas in the plot correspond to areas of very high risk and high risk of self-ignition, being the 250 ºC the border between both areas [16].That is, five samples are in the zone of very high risk, another six samples in the zone of high risk and another one in the borderline. Comparing the self-ignition risk of these sewage sludge samples with other of biomass nature or even from fossil fuels [9], it is remarkable the higher dangerousness of these samples. Likewise, the location of the sludge samples in the very high and high risk areas, was already described for sludge of different origins [7].

From a thorough analysis of this plot, several conclusions must be outlined. Samples SLU-11 and SLU-12, from the same WWTP, show in both cases a very high risk, that could be related both to the partial contribution to the water to be treated of industrial effluents, and to the high H/C and low O/C ratio. In fact, it was previously mentioned that samples with these characteristics have a larger trend to spontaneous combustion. Sample SLU-7, with the lowest O/C ratio and the highest H/C ratio, is however, in the area that corresponds to lower ignition risk, being remarkable in this sample, the high ash content. Thus, as it was mentioned for the IT and MLT parameters, the presence of volatiles is key in the determination of the ignition risk. In agreement with this argument, SLU-9 and SLU-10 samples, with H/C ratio in the low area of Fig. 1, but with the highest volatiles content, are also in the zone with the highest ignition risk. Even a difference should be pointed out with respect to SLU-8 sample, with very similar characteristics to the previous mentioned, and this difference is the lower H content. Considering that in most cases, for sewage sludge, the highest H/C and the lowest O/C is synonym of a higher risk of ignition, so the ignition temperature decreased with increasing H/C ratio [17], an incongruence is noted at first insight. What is more, SLU-4 sample, in the area of very high risk, present one of the highest O/C ratio. This fact suggests that add to the H/C and O/C ratios, another parameter could influence the self-ignition risk, whereas no clear influence of both HHV and LHV can be inferred. In this way, from Table 2, it can be inferred a positive effect of the sulphur content in the explosion risk increment. Thus, in order to relate more easily all the parameters involved, Fig. 5 plots the sulphur content versus the O / H ratio. Considering that the explosion risk increases with the H and S content, whereas the oxygen could partially hinder this process, it is clear that the upper left corner of the plot would represent the area of maximum risk. In fact, SLU-12, SLU-4, SLU-9, SLU-10 and SLU-11 are in this area, and close to these samples, SLU-2. Considering that in the Fig. 4, SLU-2 sample was situated in the border very high/high risk, whereas SLU-8 was situated in the high risk are, the same could be reproduced in the Fig. 5. In this way, sulphur content higher than 2.5 and O/H ratio lower than 5.5 would be the conditions to maximize the explosion risk. By parallelism with Fig. 4, SLU-1, SLU-3, SLU-7 and SLU-8 are out this area. From comparison of Fig. 4 and Fig. 5, just SLU5 and SLU-6 are not located in the same zone, which could be attributed to the high volatiles content of both samples in comparison with the less danger sludges. In order to contrast this hypothesis, blue points correspond to sludges from the literature [7]: one of them situated in the area of maximum risk, as in Fig. 5, and the second one, located in an area of medium risk, hence the dotted line indicates that the zone of high risk comprises from 1 to 2.5 % of sulphur. Sulphur effect can be tentatively explained by the presence of pyrophoric sulphur species, such as iron sulphides which could be formed during the drying process [18], in fact, from the ICP-MS analysis, the presence of iron content is confirmed (varying from 18 g/kg for SLU-11 and SLU-12, on dry basis, to 50 g/kg for SLU-7). At this point, Dewil, et al. [19] observed that sulphates were the predominant compounds in secondary sludge. Downstream, during thickening, the sulphates are gradually transformed into sulphides. What is more, the process continues when thickened sludge is stored in the sludge storage tanks due to the anaerobic conditions, so inorganic sulphur is mainly transformed into sulphides.

CONCLUSIONS

Results obtained in the study of the thermal susceptibility of twelve different samples of sewage sludge are presented, relating these parameters with the results of elemental analysis and calorific value.

The higher heating value (HHV) was fitted to predicted values obtained from Scheurer-Kestner, Dulong and Steuer equations. The goodness of the fitting of these models is conditioned by the weight of the oxygen composition in the equation.

Concerning the thermal susceptibility, from the Maciejasz Index, induction temperature (IT) and the maximum weight loss temperature (MLT), it could be inferred that the high H/C ratio (van Krevelem diagram) as synonym of the highest reactivity, was not enough in this case. In fact, both the presence of volatiles, ash and oxygen could influence the spontaneous combustion risk. Even the sulphur content were found critical in the assignment of explosion risk according to the Ea and Tc parameters. In this way, the highest H/C ratio in the sewage sludge samples, derived from the highest portion of carbohydrates, the lowest O/C ratio, and maximum S content, makes maximum the ignition risk.

So, it can be concluded that S content higher than 2.5 % and O/H ratio lower than 5.5 is an important insight for expecting high self-ignition risk in dried sewage sludges.

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Table 1. European Standards of solid biofuels followed for the parameters determination. Specific standards for sludge are also included in brackets.

Measured parameter	**European Standard**
Determination of moisture content.	EN 18134-3:2016 (ISO 12880:2001)
Determination of ash content.	EN 18122:2016
Determination of content in volatile matter.	EN 18123:2016
Determination of the total content of carbon, hydrogen and nitrogen.	EN 16948:2015
Determination of the total sulphur and chlorine content.	EN 16994:2017
Determination of calorific value	EN 14918:2011 (EN 15170:2009)

Table 2. Proximate and ultimate analysis of the sewage samples.

Sample	Proximate analysis (wt%)			Ultimate analysis (wt%)					H/C	O/C
	Moisture	Ash[a]	Volatiles[a]	C	H	N	S	O		
SLU-1	84.04	31.51	68.49	33.83	5.18	5.63	1.69	22.16	1.84	0.49
SLU-2	83.07	20.18	79.82	37.84	6.32	6.55	2.41	26.71	2.00	0.53
SLU-3	79.73	23.18	76.82	38.38	3.89	4.72	2.67	27.16	1.22	0.53
SLU-4	83.15	24.68	75.32	35.5	5.79	6.35	3.90	23.78	1.96	0.50
SLU-5	76.63	21.16	78.84	40.97	5.59	4.79	2.60	24.89	1.64	0.46
SLU-6	76.72	23.10	76.90	38.81	6.17	4.38	3.47	24.07	1.91	0.47
SLU-7	77.68	50.10	49.90	27.86	4.73	3.62	1.18	12.51	2.04	0.34
SLU-8	78.76	16.38	83.62	44.07	4.57	5.05	3.83	26.10	1.24	0.44
SLU-9	78.06	17.63	82.37	45.06	5.78	4.50	2.64	24.39	1.54	0.41
SLU-10	79.44	17.59	82.41	44.25	5.45	4.38	2.77	25.57	1.48	0.43
SLU-11	74.56	32.97	67.03	37.46	5.25	3.03	3.47	17.83	1.68	0.36
SLU-12	77.77	32.67	67.33	36.31	5.56	3.31	4.12	18.03	1.84	0.37

[a] Dry basis.

Table 3 . HHV and LHV values of all the sample studied in this work.

Sample	**HHV (kcal/kg)**	**LHV (kcal/kg)**
SLU-1	3919	582
SLU-2	4776	753
SLU-3	4626	896
SLU-4	4183	654
SLU-5	5058	1114
SLU-6	4665	1011
SLU-7	3199	659
SLU-8	5318	1079
SLU-9	5391	1117
SLU-10	5665	1107
SLU-11	4659	1116
SLU-12	4598	958

Table 4. Higher heating value: empirical models and comparison between experimental and predicted values

Model name	Equation	SSR	R^2
Dulong	$\mathrm{HHV}=81\mathrm{C}+342.5\left(\mathrm{H}-\frac{\mathrm{O}}{8}\right)+22.5\mathrm{S}-6(9\mathrm{H}-\mathrm{W})$	4,967,107	0.61
Scheurer-Kestner	$\mathrm{HHV}=81\left(\mathrm{C}-\frac{3}{4}\mathrm{O}\right)+342.5\mathrm{H}+22.5\mathrm{S}+57\left(\frac{3}{4}\right)\mathrm{O}-6(9\mathrm{H}-\mathrm{W})$	2,011,553	0.70
Steuer	$\mathrm{HHV}=81\left(\mathrm{C}-\frac{3}{8}\mathrm{O}\right)+57\left(\frac{3}{8}\right)\mathrm{O}+345\left(\mathrm{H}-\frac{0}{10}\right)+25\mathrm{S}-6(9\mathrm{H}-\mathrm{W})$	5,425,464	0.30

C,H,O,S,W, and N: carbon, hydrogen, oxygen, sulfur, moisture and nitrogen content (wt %)

SSR: Sum of the squares of the residuals

Table 5. Thermal susceptibility parameters determined for the different samples considered in this work

Sample	Maciejasz Index	MLT (ºC)	IT (ºC)	Tc (ºC)	Ea (kJ/mol)
SLU-1	8.1	264	207	256	28.8
SLU-2	0.0	260	209	249	26.8
SLU-3	11	348	199	276	38.9
SLU-4	3.7	264	200	226	24.5
SLU-5	2.7	342	217	282	54.5
SLU-6	5.4	350	208	259	50.8
SLU-7	44	413	285	264	27.7
SLU-8	2.6	346	224	269	51.0
SLU-9	2.4	347	224	232	40.8
SLU-10	2.1	348	225	234	43.6
SLU-11	13	325	246	224	38.7
SLU-12	19	325	241	222	21.7

FIGURE CAPTIONS:

Figure 1. H/C vs O/C ratios for the sludge samples. The dotted line split the samples in two areas according ash content higher (upper the line) or lower (under the line) than the average of the samples. In the small diagram the sludge samples of the manuscript are compared with other fuels, as coals and biomass.

Figure 2. Comparison of the predicted higher heating values from Dulong, $R^2 = 0.61$ (●), Scheurer-Kestner, $R^2 = 0.70$ (◆) and Steuer, $R^2 = 0.30$ (□) equations and experimental HHV.

Figure 3. Influence of volatiles content on the induction temperature, IT (▲), and the maximum weight loss temperature, MLT (◆)

Figure 4. Plot of self-ignition risk according to Ea and Tc parameters. Risk characterisation according to reference [16]

Figure 5. Influence of sulphur content on O/H ratio. Areas of very high risk and high risk of self-ignition are indicated. Data of this work (◆) and from the literature [7], for comparison purposes, (◆) are included.

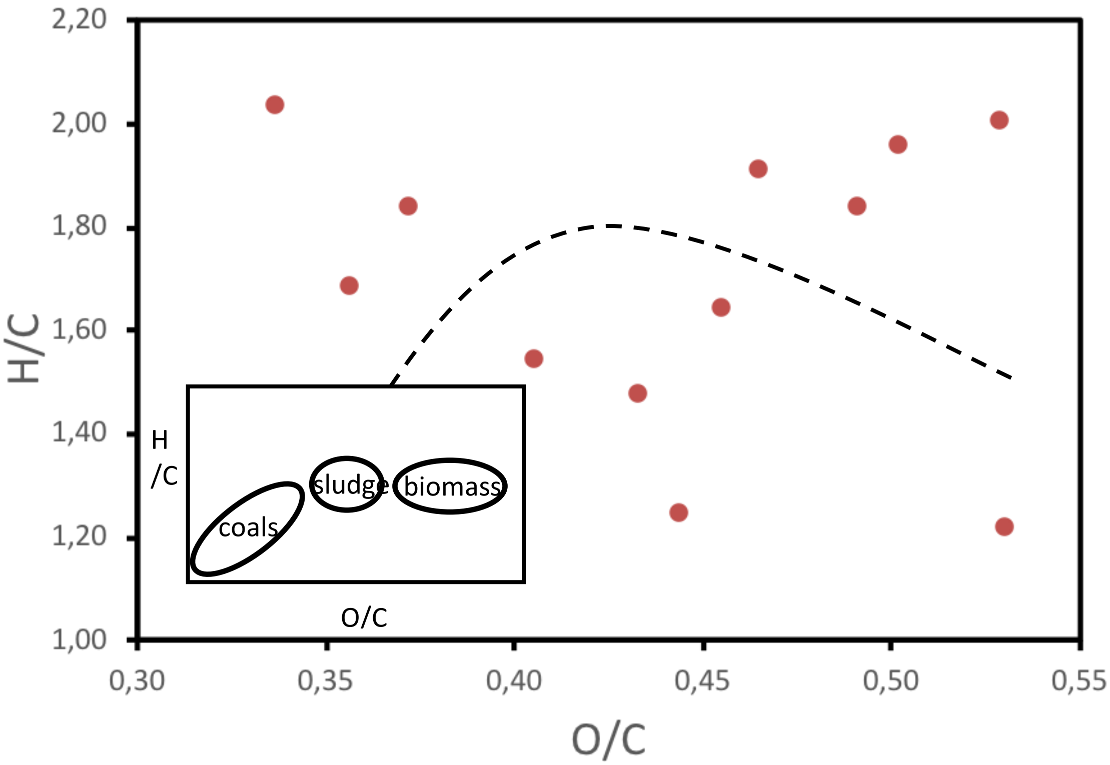
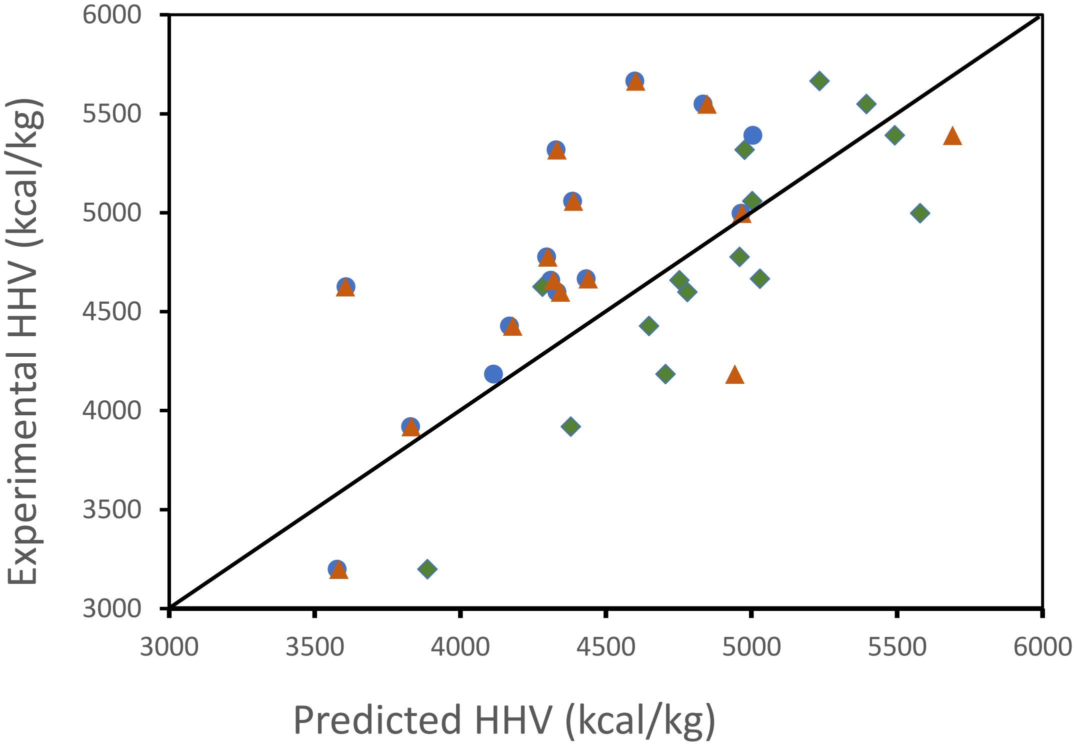

2,20
2,00
1,80
1,60
1,40
1,20
1,00
H/C
0,30
0,35
0,40
0,45
0,50
0,55
O/C
H
/C
coals
sludge
biomass
O/C

Fig. 1



6000
5500
5000
4500
4000
3500
3000
3000
3500
4000
4500
5000
5500
6000
Experimental HHV (kcal/kg)
Predicted HHV (kcal/kg)

Fig. 2

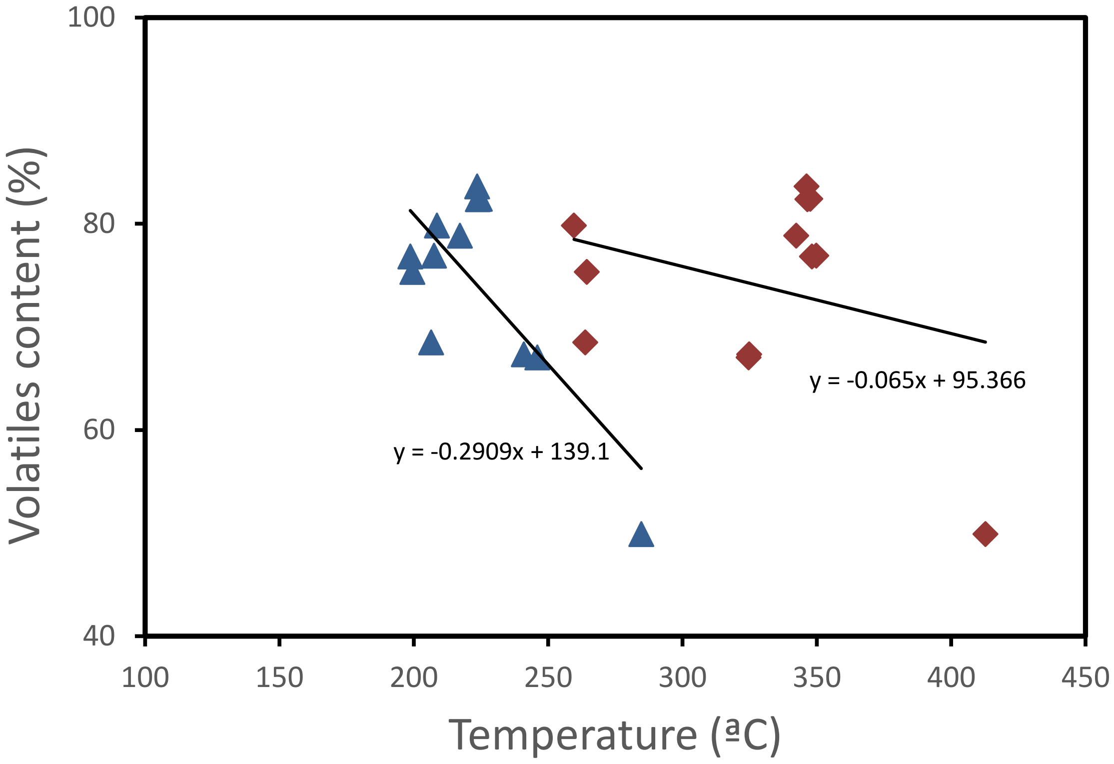

100
80
60
40
Volatiles content (%)
100
150
200
250
300
350
400
450
Temperature (ªC)
y = -0.2909x + 139.1
y = -0.065x + 95.366

Fig. 3

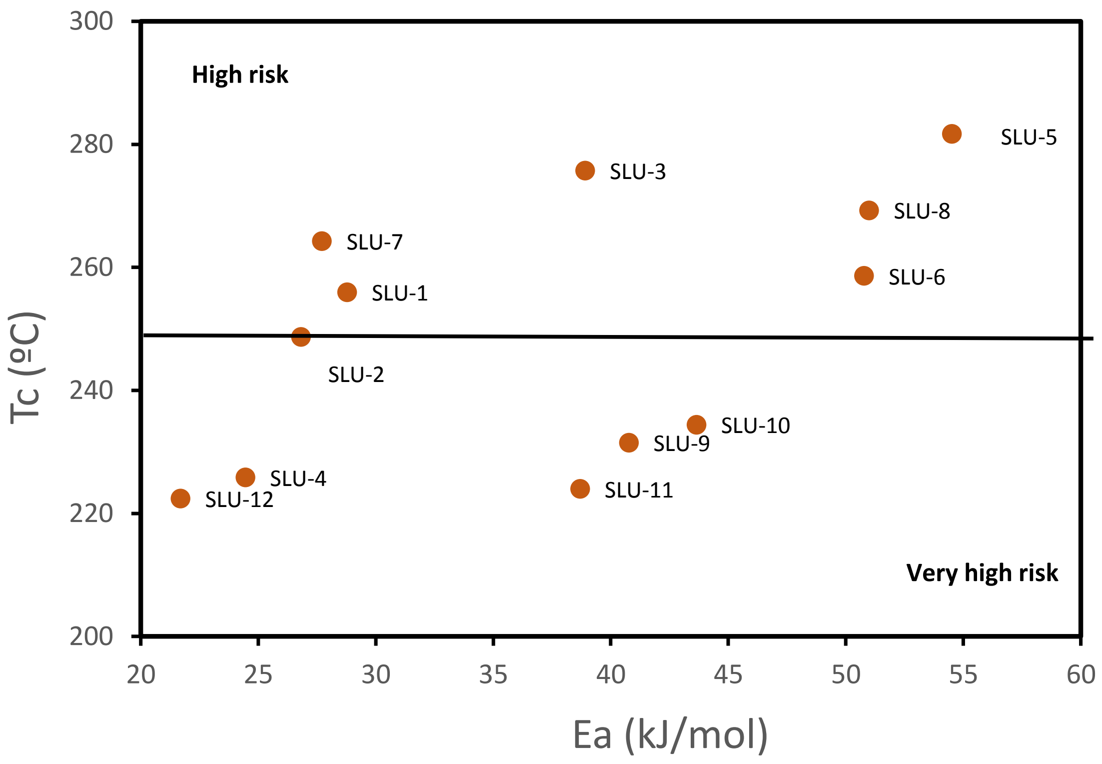

High risk
Very high risk
SLU-1
SLU-2
SLU-3
SLU-4
SLU-5
SLU-6
SLU-7
SLU-8
SLU-9
SLU-10
SLU-11
SLU-12
Tc (ºC)
300
280
260
240
220
200
Ea (kJ/mol)
20
25
30
35
40
45
50
55
60

Fig. 4

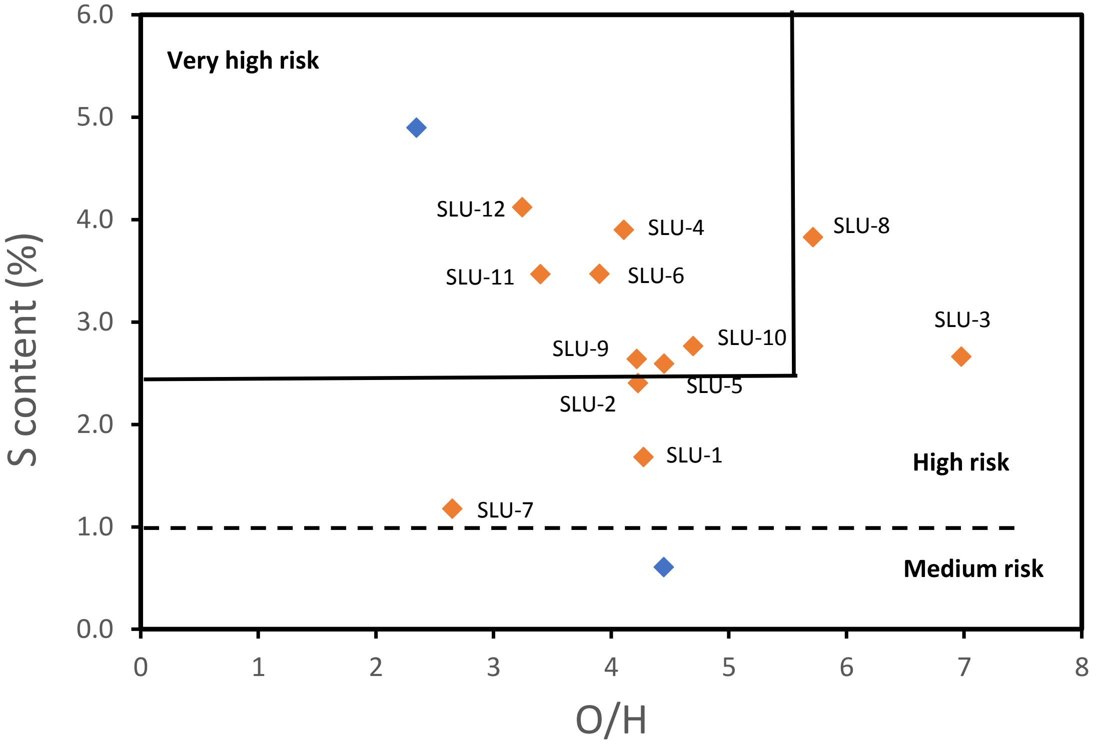

Very high risk
High risk
Medium risk
SLU-12
SLU-4
SLU-8
SLU-11
SLU-6
SLU-3
SLU-9
SLU-10
SLU-5
SLU-2
SLU-1
SLU-7
S content (%)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
1
2
3
4
5
6
7
8
O/H

Fig. 5