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Suitability of thermo-chemical corrections for determining gross calorific value in biomass

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Abstract

The objective of this paper is to study the suitability of several laboratory methods for calculating the thermo-chemical corrections (TCCs) of acid formation, which generate extra heating during the combustion of biomass in a calorimetric bomb. Three methods for calculating TCCs are considered in this paper: two of them are based on the titration of acidity, and the third one is based on analysing anion (nitrate, sulphate and chloride) content. This work compares the three TCCs with the composition of one coal and eight biomass samples. TCCs based on titration are not recommended because of the neutralisation of the nitric and sulphuric acids produced during the combustion of the biomass. The compounds contained in the biomass ash, such as $CaCO_3$, are probably the cause of this neutralisation. The measurement of nitrate content in order to calculate the TCC of the formation of nitric acid was found to be the most suitable and accurate. The formation of aqueous hydrochloric acid is improbable in the biofuels considered.

Keywords: Biomass; Combustion; Calorific value; Thermo-chemical corrections

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1. Introduction

Biomass is considered a renewable and CO_2 neutral energy resource, with high potential for future utilisation for the generation of heat and electricity. In Europe, an important energy increase is expected to come from energy crops and agro-industrial residues [1]. Another kind of biomass is sewage sludge. It is becoming a problem due to increases in the number of urban wastewater treatment plants. The utilisation of sewage sludge as fuel for producing heat and electricity is a possibility.

Calorific value is the amount of energy per unit mass released upon complete combustion. The precise determination of the calorific value is of great importance for trading biomass due to the fact that the calorific value is the most important parameter for determining the price of the biofuel to be paid the supplier by the user of the biomass.

The gross calorific value (GCV) is measured in a bomb calorimeter for solid fuels. The definition of the gross calorific value at constant volume given in different standards or technical specifications is practically the same; there varies only the kind of fuel utilised in the standards. According to the technical specification CEN/TS 14918 [2], which is considered the future European norm for determining the calorific value of solid biofuels, GCV is defined as: “the absolute value of the specific energy of combustion, in joules, for unit mass of a solid biofuel burned in oxygen in a calorimetric bomb under the conditions specified. The products of combustion are assumed to consist of gaseous oxygen, nitrogen, carbon dioxide and sulphur dioxide, of liquid water (in equilibrium with its vapour) saturated with carbon dioxide under the conditions of the bomb reaction, and of solid ash, all at the reference temperature”. The gross calorific value is calculated from the corrected temperature rise and the effective heat capacity, with corrections made for the contributions from the ignition energy, the combustion of the fuse and the thermo-chemical reactions of formation of acids, mainly nitric and sulphuric acids.

Thermo-chemical corrections are carried out in biomass samples [2] taking into account the TCCs applied to the coal and other fuels [3–5]. However, several discrepancies in the measurement of TCCs can occur due to the different compositions of

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the fuels. So, for example, coal contains three main forms of sulphur, i.e., pyritic, organic and sulphate sulphur [6], whereas, for example, lignocellulosic biomass contains two forms: organic sulphur and inorganic sulphur as sulphate [7]. Moreover, the amount of sulphur is considerably higher in coal than in biomass. The nitrogen content varies widely in biomass depending on the kind of biomass or the part of the plant. High nitrogen values could influence the formation of nitric acid. In addition to coal, other new TCCs may need to be applied to biomass. For example, it might be necessary to correct for the formation of aqueous hydrochloric acid because of chlorine contained in the biomass. However, according to the new technical specification for determination of the calorific value in solid biofuels [2], this TCC can be neglected because most biofuels have low chlorine content, typically below 0.5 wt% (d.b.).

In contrast to the minerals composing coal, which are mainly based on silica (SiO_2) and silicates such as kaolinite ($Al_2Si_2O_5(OH)_4$) [7], the principal minerals composing lignocellulosic biomass are, in addition to silica, calcium compounds such as calcite ($CaCO_3$) and alkaline compounds such as sylvite (KCl), anhydrite (K_2SO_4) and fairchildite ($K_2Ca(CO_3)_2$) [8,9]. These different mineral compositions could influence the reactions of acid formation in the combustion of the sample in a calorimeter bomb.

This paper compares three different TCCs with the composition of one coal and eight biomasses, which include woody, herbaceous, agro-industrial, and waste biomasses. The biomasses assayed in this work together with their different and varied compositions in nitrogen, sulphur and chlorine provide new information about the studied laboratory methods for correcting the formation of nitric, sulphuric, and hydrochloric acids.

2. Experimental

2.1. Biomass and coal tested

Eight biomass samples were considered in this work and compared with one coal, which was a certified reference material (SRM 1632c) from National Institute of Standards and Technology (USA). The biomasses selected were seven solid biofuels and one sewage sludge from the urban wastewater treatment plant of Soria (Spain). The solid biofuels were one woody biomass (vineyard pruning), three agro-industrial biomasses (grape pips, almond shells, and orujillo), and three herbaceous biomasses (two were thistle and one was brassica).

Orujillo, this is the Spanish name of the final residue produced in olive oil extraction. The “orujillo” biomass utilised in this work is a de-oiled and dried residue obtained after the extraction of the olive oil from the “orujo”, a by-product of the olive oil three-phase extraction process [10].

Thistle *Cynara cardunculus*, the entire aerial part of the thistle plant was considered. This species shows significant potential as an energy crop in the semiarid conditions of the southern EU countries [11].

Brassica *Brassica carinata*, this is a species next to rape and one of the most important sources of vegetable oil in the world. Recently, Spain, Greece and Italy, countries in which semi-arid climatic condition prevail, show an interest in developing this species as a new source of solid biomass [12].

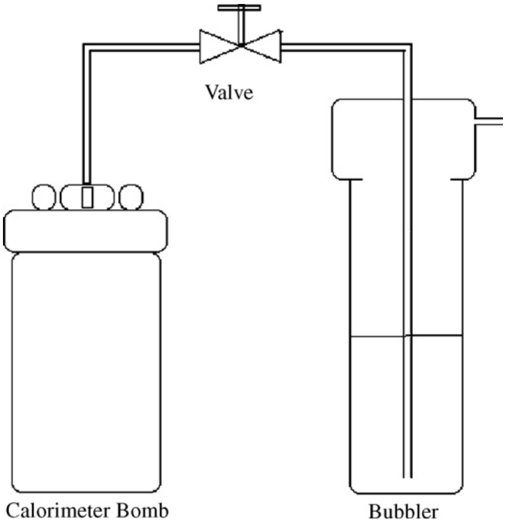

Fig. 1. System utilised for scrubbing the combustion gas from the calorimeter bomb.

2.2. Methods for determining the thermo-chemical corrections

The preparation procedure was common to the three methods for determining TCCs considered in this work. It is as follows: the gases of combustion of the calorimeter bomb were passed through a bubbler containing 75 ml of distilled water by means of a venting valve connected to the combustion bomb (Fig. 1). After this process, the inside of the bomb, specifically its walls, electrodes, crucible and internal bomb head, was washed with 75 ml ultrapure water recovered from the previous gas scrubbing. The washing of the calorimeter bomb was repeated with another 75 ml of ultrapure water. All of the rinse solution was transferred to a flask. Three laboratory methods for calculating the formation of nitric and sulphuric acids were carried out.

2.2.1. Thermo-chemical corrections of “single titration”

“Single titration” with Na(OH) of the bomb washings and theoretical correction for sulphur, following the principles given in the technical specification CEN/TS 14918 [2] or in the standard ASTM E711 [3].

The basis of this first method called in this paper “single titration” is to titrate the total acidity of the washing solution. The procedure was as follows: an aliquot of 75 ml was boiled to expel the carbon dioxide and the solution was titrated with sodium hydroxide using phenolphthalein solution as indicator. The overall correction (nitric and sulphuric acid—$Q_{N,S}$) is given below, but taking into account only the heat of reaction of formation of nitric acid [2,3].

$$Q_{N,S}\,(J) = 6.0 V_{NaOH}$$

where V_{NaOH} is the volume, in millilitres, of NaOH (0.1N) titrated.

A theoretical and thermo-chemical correction for sulphur (Q_{Sc}) was performed taking into account only the heat of reaction of formation of sulphuric acid but decreasing its heat of reaction by an amount included previously in $Q_{N,S}$. The final formula is given below [2,3]:

$$Q_{Sc}\,(\mathrm{J}) = 57SM$$

where M is the sample mass (in grams) and S is the sample sulphur (as a percentage in weight).

2.2.2. Thermo-chemical corrections of "double titration"

"Double titration" with $Ba(OH)_2$ and HCl of the bomb washings according to CEN/TS 14918 [2] or the standard ISO 1928 [4].

The basis of the second method, referred to in this paper as "double titration", was to titrate the total acidity of the washing solution, but with $Ba(OH)_2$ instead of Na(OH), where barium sulphate was precipitated and separated from the solution by filtration. The nitrate from nitric acid formation was measured by means of a back titration utilising sodium carbonate in the first step and hydrochloric acid in the second step. Finally, the sulphate content was determined by the difference between the chemical equivalents of $Ba(OH)_2$ used and the chemical equivalents calculated by the back titration. The procedure was as follows: an aliquot of 75 ml was boiled to expel the carbon dioxide and the solution, while it was still hot, was titrated with barium hydroxide using phenolphthalein solution as indicator. A volume of 20 ml of sodium carbonate was added to the warm solution, which was filtered and the precipitate was washed with ultrapure water. When it was cold, the filtrate was titrated with hydrochloric acid using screened methyl orange solution as indicator. The corrections for formation of nitric acid (Q_N) and sulphuric acid (Q_S) are given below taking into account their corresponding reaction heats of formation of nitric acid and sulphuric acid, respectively [4]:

$$Q_N\,(\mathrm{J}) = 6.0\,[V_2 - V_3]$$

$$Q_S\,(\mathrm{J}) = 15.1\,[V_1 - (V_2 - V_3)]$$

where V_1 is the volume used, in millilitres, of $Ba(OH)_2$ (0.1N), V_2 is the volume added, in millilitres, of Na_2CO_3 (0.1N), and V_3 is the volume used, in millilitres, of HCl (0.1N).

2.2.3. Thermo-chemical corrections of "anion analysis"

The third method, called "anion analysis" in this paper, was based on the measure by analytical techniques of the contents of nitrate and sulphate ions contained in the bomb washings. In this study, ionic chromatography was performed using Methrom equipment, although other analytical techniques can be used, e.g., capillary electrophoresis. The corrections for formation of nitric acid (Q_N) and sulphuric acid (Q_S) are given below taking into account their corresponding reaction heats of formation of nitric acid and sulphuric acid, respectively [2]:

$$Q_N\,(\mathrm{J}) = 0.97M_{NO_3}$$

$$Q_S\,(\mathrm{J}) = 3.14M_{SO_4}$$

where M_{NO_3} and M_{SO_4} are the nitrate content and the sulphate content, both in milligrams, found in the solution, respectively.

2.3. Physical and chemical characterisation

In order to study the formation of nitric, sulphuric and hydrochloric acids, physical and chemical characterisations were carried out, including analyses of elements by atomic emission spectrometer (ICP) and analyses of inorganic compounds by X-ray diffraction. The biomass sample was dried until moisture equilibrium with the laboratory atmosphere and ground to pass a 2-mm sieve. Next, the homogenized sample was divided into several fractions by means of the Jones divider, and one fraction was again ground to pass a 0.5-mm sieve to obtain the analytical sample. The calorific value was measured using an IKA bomb calorimeter (C5000) following the technical specification CEN/TS 14918 [2]. Around 1 g of biomass was pelletised and introduced in the bomb, which had a volume of 210 ml and was charged slowly with pure oxygen ($>$ 99.99 vol.%) to a pressure of 3.0 ± 0.2 MPa without displacing the original air. The net calorific value was calculated according to the procedure described in that document.

Ash obtained at 550 °C and elemental analysis (C, H and N) measurement were carried out for biomass and coal samples by internal procedures, which are mainly based on ASTM standards for wood, refuse derived fuels and coal. The elemental analyser FISONS CHNS-1108 (CARLO ERBA equipment) was used to determine C, H and N. This instrument contains a tube furnace where the sample is burned, and a chromatographic column and a thermal conductivity detector where the gases are separated and measured, respectively. Chlorine and sulphur contained in the biomass and coal were determined by ionic chromatography after the combustion of the sample in an IKA bomb calorimeter and lixiviation of the gases and ashes with ultrapure water utilising the same procedure as was described previously in Section 2.2.3.

Ash samples obtained at 550 °C were digested in a closed vessel using HCl, H_2O_2, HNO_3 and HF in a first step, and H_3BO_3 in a second step. After digestion of the samples, chemical analyses of the elements Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Si, Sr, Ti and Zn were carried out by atomic emission spectrometry (ICP) using a THERMO JARRELL ASH simultaneous spectrometer (IRIS AP). Chlorine analysis was carried out in the ash obtained at 550 °C following the standard ASTM D-2361-66 "Test for chlorine in coal" by means of the dry ashing of the ash of biomass or coal sample with Eschka mixing (sodium carbonate and magnesium oxide).

The dry ashing method at 550 °C was found to be suitable for obtaining ashes without organic carbon, i.e. less than 1 wt% [13], consequently, the analysis of carbon in ash at 550 °C, by means of the elemental analyser FISONS CHNS-1108, results in inorganic carbon from the carbonates.

Dust X-ray diffraction was utilised to determine the inorganic compounds in the ashes, using a PHILIPS X'PERT-MPD diffractometer. Identification of compounds was made using the diffractometer software with the JCPDS database as the source of reference data.

Table 1
Characterisation of the fuels (wt% dry basis)

	Coal NIST	Vineyard pruning	Grape pips	Almond shells	Orujillo	Thistle I	Thistle II	Brassica	Sewage sludge
Ash	7.3	3.8	4.0	0.94	11.0	14.1	11.4	10.1	33.8
Carbon	77.7	38.9	48.0	49.7	48.6	40.5	43.9	45.0	38.4
Hydrogen	5.3	6.0	6.4	6.3	5.9	5.4	6.0	6.1	5.9
Nitrogen	1.55	0.72	1.70	0.26	1.45	1.15	0.87	1.40	5.24
Sulphur	1.52	0.06	0.12	0.01	0.14	0.15	0.53	0.63	0.83
Chlorine	0.10	0.03	0.01	<0.01	0.25	2.25	0.97	0.37	0.08
GCV	31.7	19.3	22.8	20.0	19.3	16.3	16.9	17.8	16.9
NCV	30.6	18.0	21.5	18.7	18..1	15.2	15.7	16.5	15.7

Calorific values are given in MJ/kg d.b. GCV: gross calorific value; NCV: net calorific value.

All data presented in this paper were rounded off to significant figures according to their expanded and combined uncertainties, which were obtained following the ISO guide “Guide to the Expression of Uncertainty in Measurement” (1993), and the EURACHEM guide “Quantifying Uncertainty in Analytical Measurement” (1995).

3. Results and discussion

3.1. Fuel characterisation

The results of analysing the ash, C, H, N, S and Cl contents together with the gross and net calorific values are shown in Table 1. The gross calorific value (GCV) and net calorific value (NCV) mainly depend on the carbon content and the ash content, i.e., calorific values are directly proportional to the carbon content and inversely proportional to the ash content.

The ash and nitrogen contents are very high in sewage sludge by comparing with the contents found in coal and solid biofuels. The concentration of sulphur is often higher in coal than in biomass, however some herbaceous biofuels such as thistle II and brassica or sewage sludge can reach important values higher than 0.5 wt%. In contrast, chlorine contents usually are higher in herbaceous biofuels than in coal. In this work, thistle samples, especially thistle I, have a very high chlorine content (2.25 wt%) compared with other solid biofuels. In general, woody biofuels never reach chlorine concentrations of 0.1 wt%.

3.2. Comparison of the overall and nitrogen thermo-chemical corrections in the fuels

The results of the TCCs for each method utilised in this work (Section 2.2) are shown in Table 2. It is important to note that the TCCs of anion analysis method (Q_{N} and Q_{S}) are the same ones as the TCCs mentioned in the double titration and both, are different from the TCCs shown in single titration ($Q_{\mathrm{N,S}}$ and Q_{Sc}).

One of the main results from Table 2 is that the total sum of the TCCs in the anion analysis method is higher than the total sum of the TCCs in the single titration and double titration methods. It is also important to notice that the nitrogen contents determined in anion analysis method (Fig. 2) by ionic chromatography are similar for all the biomasses, including the sewage sludge, and in general, lower than the nitrogen contents determined by the elemental analyser, which are also shown in Fig. 2. The explanation for this is that the formation of nitric acid in the calorimeter bomb is mainly due to the oxidation of nitrogen from the air introduced in the bomb when it is closed.

As can be observed in Fig. 2, the profile of the curve for nitrogen determined by ionic chromatography resembles the profile

Table 2
Thermo-chemical corrections of formation of nitric and sulphuric acids for the three methods

	Coal NIST	Vineyard pruning	Grape pips	Almond shells	Orujillo	Thistle I	Thistle II	Brassica	Sewage sludge
Single titration									
$Q_{\mathrm{N,S}}$ (J/g d.b.)	90	14	20	17	5	6	28	24	20
Q_{Sc} (J/g d.b.)	87	3	7	1	8	9	30	36	47
Total correction (J/g d.b.)	176	17	27	18	13	15	58	60	67
Double titration									
Q_{N} (J/g d.b.)	43	7	18	14	5	5	9	7	14
Q_{S} (J/g d.b.)	118	17	5	5	−2	2	47	43	14
Total correction (J/g d.b.)	161	24	23	19	3	7	56	50	28
Anion analysis									
Q_{N} (J/g d.b.)	46	25	32	24	21	18	18	21	11
Q_{S} (J/g d.b.)	143	6	11	1	13	14	50	59	78
Total correction (J/g d.b.)	189	31	43	25	34	32	68	80	89

d.b.: dry basis.

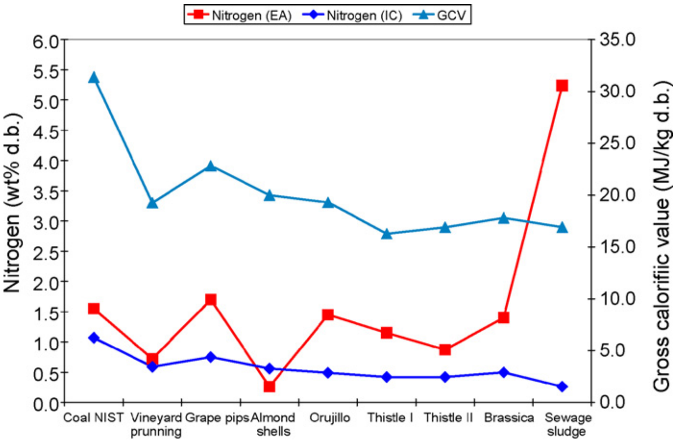

Fig. 2. Comparison of nitrogen in the fuels determined by elemental analyser (EA) on the fuel and by ionic chromatography (IC) on the bomb washings, and gross calorific value.

of the curve of the gross calorific value. This correspondence can be explained by the higher concentrations of nitrogen oxides (and finally of nitrates) formed as a consequence of the higher temperatures achieved in the bomb with the higher calorific values. Thus, the higher the calorific value, the higher the nitrogen content from the bomb washings.

According to Table 2, the TCC for the nitric acid formation (Q_N) in the anion analysis method is always higher than the Q_N in double titration for all biomasses, except for sewage sludge, and even higher than in single titration for most of the biomasses in the first correction (nitric and sulphuric acids—$Q_{N,S}$). So it could be deduced that the biomass ashes neutralise the acidity. For sewage sludge, the TCC for the nitric acid formation (Q_N) in double titration is a little higher than in the anion analysis, which suggests that a very small part of its initial and elevated nitrogen content (5.24 wt%, Fig. 2) could have been converted into nitric acid. Under both methods coal NIST exhibits a similar correction of formation of nitric acid, which validates the TCC of formation of nitric acid for the double titration and anion analysis methods for coal samples.

To verify the hypothesis of the neutralisation of the acidity by mineral matter contained in the ashes of the biomasses, analyses of the elements and crystalline compounds were carried out and the results are shown in Table 3. Crystalline phases of $CaCO_3$ and SiO_2 are always detected by X-ray diffraction as major compounds in the ashes of the biomasses studied, except for thistle I, whose phase of calcite is a minor crystalline compound. Calcite can neutralise the acidity by forming bicarbonate and even carbonic acid, according to the following sequence:

$$CaCO_3 + H^+ \Rightarrow CaHCO_3^- + H^+ \Rightarrow CO_2 + H_2O + Ca^{2+}$$

Alkaline compounds vary from one biofuel to another. Thistle biomass has in its ashes high chlorine and sodium concentrations forming compounds such as sylvite (KCl) and halite (NaCl), whilst anhydrite (K_2SO_4) is a major alkaline compound in orujillo and brassica; fairchildite ($K_2Ca(CO_3)_2$) is a major alkaline compound in vineyard pruning, almond shell and orujillo; and potassium carbonate (K_2CO_3) in orujillo. Alkaline chlorides do not decrease the acidity, however the other alkaline com-

Table 3
Results of the crystalline compounds and inorganic elements (wt% d.b.)

	Coal NIST	Vineyard pruning	Grape pips	Almond shells	Orujillo	Thistle I	Thistle II	Brassica	Sewage sludge
Major	SiO_2; Fe_2O_3	$CaCO_3$; $K_2Ca(CO_3)_2$; SiO_2	SiO_2; $CaCO_3$	$K_2Ca(CO_3)_2$; $CaCO_3$; $KHCO_3$; SiO_2	$K_2Ca(CO_3)_2$; K_2SO_4; SiO_2; K_2CO_3; $CaCO_3$	SiO_2; KCl; NaCl	$CaCO_3$; $Ca(OH)_2$; KCl; SiO_2; NaCl	$CaCO_3$; $Ca_5(PO_4)_3OH$; K_2SO_4; $K_2Ca_2(SO_4)_3$; SiO_2	SiO_2; $CaSO_4$; $CaCO_3$
Minor	$CaSO_4$; $KAl_2Si_3AlO_{10}(OH)_2$; $(Ca,Na)(Si,Al)_4O_8$; $Mg_x(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2{\cdot}4H_2O$	MgO; $CaSO_4$; K_2SO_4; $Ca_5(PO_4)_3OH$	$Ca_5(PO_4)_3OH$; $Ca_3(PO_4)_2$; K_2SO_4; $KAl_2Si_3AlO_{10}(OH)_2$; Na_2SO_4	$NaAlSi_3O_8$; $MgSO_4$; $K_2Mg(CO_3)_2{\cdot}4H_2O$; $Mg_2CO_3(OH)_2{\cdot}3H_2O$	$KAl_2Si_3AlO_{10}(OH)_2$; $Ca_5(PO_4)_3OH$; MgO	MgO; $Na_2Mg(CO_3)_2$; $(Na_{0{\cdot}82}K_{0{\cdot}18})_2$ $Ca(CO_3)_2$; $Ca_5(PO_4)_3OH$	CaO; $CaSO_4$; $K_2Ca(CO_3)_2$; $K_3Na(SO_4)_2$; MgO; Na_2SO_4	KCl; $K_2Ca(CO_3)_2$; MgO	TiO_2; Fe_2O_3; $KAl_2Si_3AlO_{10}$ $(OH)_2$; $Ca(Al_2Si_2O_8)$
Al_2O_3	23	2.2	1.5	1.4	4.6	1.7	2.6	1.0	12
CaO	2.5	33	27	20	22	14	26	27	11
Fe_2O_3	14	0.88	1.5	1.0	2.4	0.69	1.0	0.42	3.4
K_2O	2.1	11	5.6	24	19	15	9	16	2.2
MgO	0.75	7.7	3.3	3.4	6.1	2.5	3.4	3.1	1.5
Na_2O	0.59	0.75	0.22	0.98	0.55	9.2	7.3	0.71	0.44
P_2O_5	0.50	4.2	11	2.2	3.6	1.5	1.2	4.7	12
SO_3	3.0	3.1	3.9	1.6	2.2	2.4	7.8	16	3.1
SiO_2	45	10	31	14	23	14	15	9.0	41
Cl	0.34	0.02	0.06	0.28	1.5	14	6.6	3.2	0.07
CO_2	1	24	14	28	12	17	12	15	14
Sum	92	96	99	96	97	92	91	96	100

pounds can neutralise the acidity by forming bisulphate and bicarbonate. Another example is the basic calcium phosphate ($Ca_5(PO_4)_3OH$), one of the principal compounds contained in brassica, which could also generate neutral and acid phosphates. In contrast to biomass samples, NIST coal contains SiO_2 and Fe_2O_3 as major compounds, which do not reduce the acidity.

Therefore among the TCCs studied in this work in relation to the determination of the gross calorific value of solid biofuels, the measurement of the nitrate content for calculating the TCC by the formation of nitric acid should be regarded as the most suitable and accurate method. Depending on the level of accuracy required for the calorific values a correction of the heat released by the formation of nitric acid could be carried out in all biomass samples, or it could also be omitted due to its low value (around 20 J/g, Table 2) compared with gross calorific value (more than 16,000 J/g, Table 1).

Because of the neutralisations of the acidity by the biomass ash salts, which generate a heat of reaction, new thermo-chemical corrections can be taken into account, although these neutralisation heats could be extremely low compared with the gross calorific value. In addition to these phenomena, other thermo-chemical corrections could be considered as consequences of reactions or changes of the mineral phases such as the known endothermic reaction of decarbonation of calcite. These new TCCs would require specific and detailed studies.

3.3. *Comparison of the sulphur thermo-chemical corrections in the fuels*

The TCCs of single titration and anion analysis due to the formation of sulphuric acid are theoretical and based on the content of sulphur measured in the biomass. These corrections are based on the assumption that all acid titrated is H_2SO_4 formed by the following reaction:

$$SO_2(g) + 0.5O_2(g) + H_2O(l) \Rightarrow H_2SO_4(l)$$

The sulphur obtained from dry ashing at 550 °C (Table 3) is considered inorganic sulphur [9,13]. These data are recalculated to a biomass basis and represented in Fig. 3. The total sulphur analysed in the fuel (Table 1) is also represented in Fig. 3. As can be seen in Fig. 3, biomass contains a high percentage of inorganic sulphur in the form of salts, which could not be transformed to SO_2 and, consequently, do not generate sulphuric acid. Therefore, the theoretical values of Q_{Sc} (single titration) and Q_S (anion analysis) could be higher than the true values for the biomass.

In the case of coal, as a consequence of the higher proportion of pyritic and organic sulphur, the proportion of inorganic sulphur is much lower than it is for biomasses. Pyrite (FeS) undergoes intensive oxidation in the temperature range between 100 °C and 500 °C with the formation of hematite (Fe_2O_3) and liberation of sulphur oxides [14]. This means that the theoretical TCCs (single titration and anion analysis) of formation of sulphuric acid in coal are more similar to the experimental TCC (double titration) than for biomass samples. The percentage of sulphur that is converted to SO_2 and this to SO_3 to form sulphuric acid will require further research in the case of biomass because of the complex reactions involved in the combustion of the sample within the calorimeter bomb such as disintegrations of sulphur salts, reactions among different salts, side reactions with gases including water vapour, etc.

Moreover, the neutralisation of the acidity by formation of sulphuric acid can also occur as was mentioned in Section 3.2. Nevertheless, the TCCs for the formation of sulphuric acid can be omitted because of their low values in most of the biomasses, such as woody biofuels and agro-industrial biofuels analysed in this study, which have sulphur contents below 0.2 wt%.

3.4. *Comparison of the chlorine thermo-chemical corrections in the fuels*

The differences between inorganic and total chlorine presented in Fig. 4 were obtained by applying the same criterion previously applied for sulphur (Section 3.3). According to Fig. 4, the total chlorine is always higher than the inorganic chlorine obtained from ashing the fuel at 550 °C. An explanation of this fact is due to the release of chlorine as ionic species or as radicals during the dry ashing at temperatures as low as 200 °C [15].

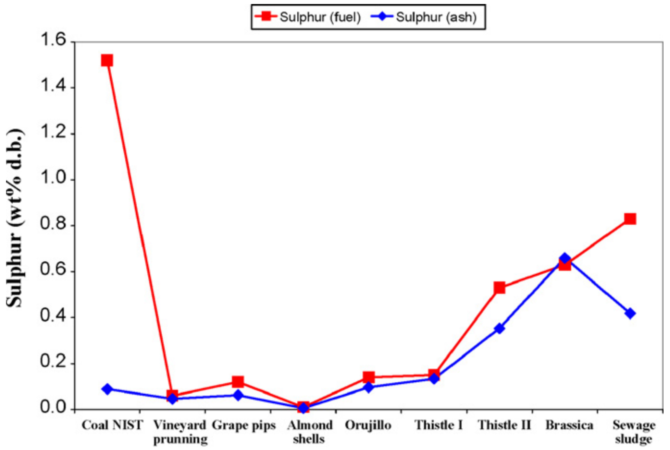

Fig. 3. Comparison of sulphur in the fuels determined on the fuel and on the fuel ash.

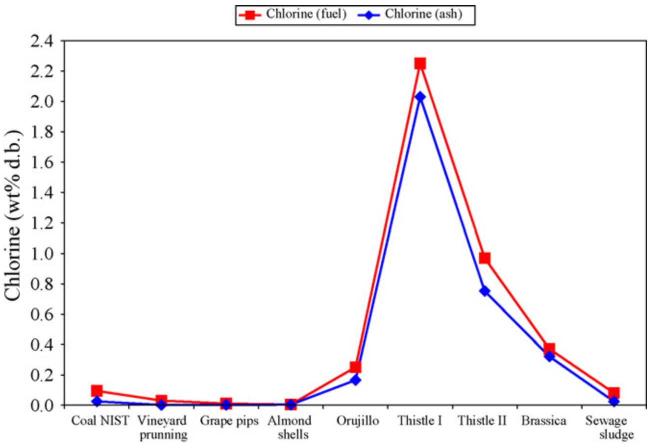

Fig. 4. Comparison of chlorine in the fuels determined on the fuel and on the fuel ash.

It is important to note that the TCCs based on double titration are similar for thistle II and brassica (Table 2). Thistle II and brassica have similar concentrations of sulphur but thistle II has a higher chlorine content (0.97 wt%). This means that TCC (double titration) would be higher in thistle II than in brassica if aqueous HCl were formed. However, this does not occur. It is possible that a stronger neutralisation could have been produced in thistle II than in brassica due to $Ca(OH)_2$, which is found as a major compound (Table 3) in thistle II. However, thistle I has a chlorine content (2.3 wt%) higher than thistle II (0.97 wt%), and thistle I does not posses either $Ca(OH)_2$ or $CaCO_3$, only KCl, NaCl and SiO_2 as major compounds. Moreover, the experimental TCCs based on double titration are considerably lower for thistle I than for thistle II. Therefore, it is extremely improbable that the formation of HCl in biofuels occurs, at least in significant proportion. This firm conclusion can be made despite the remarks of the new CEN technical specification for determination of calorific value in solid biofuels [2]. This technical specification establishes that TCC by HCl formation can be neglected because most biofuels have low chlorine contents, typically below 0.5 wt% d.b. and according to the obtained results in this work the formation of HCl is questionable.

4. Conclusions

- The measurement of nitrate content in order to calculate the TCC of the formation of nitric acid was found to be the most suitable and accurate of all TCCs studied in this work. As a consequence of its low value compared with the gross calorific value, and depending on the accuracy of the heating values required, the TCC of the formation of nitric acid could be omitted.
- The theoretical thermo-chemical corrections by the formation of sulphuric acid require further investigation, probably because only a part of the total sulphur can be converted to SO_2 for the generation of sulphuric acid. Nevertheless, the TCC by the formation of sulphuric acid could be omitted due to its low values for most biomasses.
- The formation of aqueous hydrochloric acid in a significant amount in the calorimetric bomb is not reliable for the biomasses studied in this paper.
- Thermo-chemical corrections based on titration are not recommended because of the neutralisation of the nitric and sulphuric acids produced during the combustion of the biomass. The compounds contained in the biomass ash, such as $CaCO_3$, probably cause this neutralisation. These neutralisations and other chemical reactions of the mineral matter of the biomass could generate new thermo-chemical corrections, which need further investigation, although these reaction heats could be extremely low compared with the gross calorific value, and consequently they could be neglected.

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