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HOW TO OBTAIN RELIABLE LOWER HEATING VALUES FROM DTA AND DSC ANALYSIS DATA

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ABSTRACT

The standard method widely used to determinate correctly higher heating values (HHV) is bomb calorimetry. However, a bomb calorimeter is not always available for the analysis, doing the heating value determination a little more limited. On the other hand, some thermal analysis techniques can be part of the solution for this problem as it is possible to estimate heating values from their analysis data. The most used and reliable techniques for this purpose are Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA), but the heating values obtained from their data cannot be directly compared to those obtained from bomb calorimetry. Besides to the fact that bomb calorimetry measures HHV and from DTA or DSC, the measured combustion peak areas are respectively, indirectly or directly related to the lower heating value (LHV), the reason, as shown in the present article, is related to the fact that, during solid fuel analysis, only part of the combustion heat can be measured. Therefore, this work proposes a new method to obtain reliable lower heating values from DSC and/or DTA data, minimizing the dependence on a bomb calorimeter for routine tests afterwards. For this purpose, two typical cases of renewable and fossil solid energy sources were analyzed: Brazilian rice husk and coal.

Keywords: eating Value, Thermal Analysis, Bomb Calorimeter, Rice Husk, Coal.

INTRODUCTION

The Brazilian energy matrix is strongly dependent on hydroelectric power generation. In 2016, the country faced a dramatic scenario owing to water reservoirs low level. This has given to the thermoelectric plants an even greater significance. Despite its adverse environmental impact, coal plays a fundamental role in the world as an effective energy source. This is due to the wide availability of geographically favorable reserves and the technological advancement of clean coal technologies. In this sense, environmental awareness about global energy supply has motivated new researches to enable a sustainable power generation.

The surveys are increasingly focused not only on economic benefits, but also on the renewable sources that promise results to the environmental mitigation. Therewith, several solid wastes have been exploited in scientific research to provide alternative sources of energy. Rice husk (RH) is a major agroindustry waste as it accounts for approximately 20% of the bulk grain weight [1]. In addition, it is well known that RH produces value-added byproducts such as its ashes [2].

The heating value is an important parameter to design thermal exchange equipment in combustion plants. In order to estimate thermal plants power generation, as the combustion gases leave the furnaces at high temperatures without condensing, an analysis of the fuels using lower heating value (LHV) is more useful. Thus, in general, furnaces operate as open systems, in which the fuel combustion generates water vapor, which remains in the flue gases.

The standard method, which is widely used to determinate correctly fuel higher heating values (HHV), is by bomb calorimetry [3]. However, when a bomb calorimeter is not available for the analysis, DSC and/or DTA have being used alternatively to estimate the heating values of many kind of fuels [4 –5].

The DSC technique gives the enthalpy changes of the transformations that occur to the sample, directly from respective DSC peak area, while the corresponding DTA peak area is proportional to the energy consumed or generated during the same transformation.

As further shown in this work, during solid fuel heating value determinations from direct DSC and/or DTA analysis, it was realized that the total combustion of the sample may not occur in the sample crucible. Consequently, respective measuring devices cannot actually register the total heat generated during combustion, as occurs in a bomb calorimeter, but only a fraction of the specific fuel LHV.

It must also be noted that, from bomb calorimetry, HHV is measured because the water vapor generated during combustion is condensed. Besides that, from DTA or DSC, the measured combustion peak areas are related indirectly or directly to the lower heating value (LHV) of the sample, because the water vapors generated by combustion do not condense during respective measurements and are carried, as other combustion products, by the purge gases.

Therefore, the purpose of this work about heating values of two kinds of solid fuel, Brazilian RH and coal, is to describe a method of LHV estimation from DSC and DTA analysis data, after obtaining a conversion factor from comparison with standard bomb calorimetry data.

This way, respective conversion factors are obtained for each kind of solid fuel, which consider the fraction of respective LHV that was effectively measured and thus, they can be applied to DSC or DTA data afterwards, to obtain reliable LHV data of new studied fuel lots from same origin.

MATERIALS AND METHODS

2.1. Samples

A Brazilian rice processing industry provided the RH used in this study. A Coal Mining Company supplied the run-of-mine coal. Those industries are located in Rio Grande do Sul State, Brazil. Both kind of samples have not received any chemical pretreatment before their thermal analysis.

RH and coal samples were first subjected to ultimate analysis, which were performed in a CHN Elemental Analyzer equipment, model Flash EA 1112 series, from Thermo Scientific. The results are presented in **Tables 1 and 2** respectively.

Table 1. Ultimate analysis of RH samples.

Elements	Test 1	Test 2	Test 3	Mean	Standard deviation
Nitrogen (%)	0	0	0	0	0
Carbon (%)	36.43	36.34	36.53	36.43	0.10
Hydrogen (%)	5.04	4.74	5.19	4.99	0.23

Table 2. Ultimate analysis of coal samples.

Elements	Test 1	Test 2	Test 3	Mean	Standard deviation
Nitrogen (%)	0	0	0	0	0
Carbon (%)	31.16	31.21	31.03	31.13	0.09
Hydrogen (%)	2.56	2.63	2.44	2.54	0.10

The thermal analyses were performed in a simultaneous TG-DTA equipment SDT Q600 model, from TA Instruments. As purge gases, 100 mL.min⁻¹ of synthetic air or nitrogen from Linde Gases Ltda. were used. The samples were heated in 90 µL alumina open crucibles.

In this work, ASTM D2015-77 standard method [6] was used for determining the respective HHV values, by using a bomb calorimeter model C 200, from IKA. Oxygen gas from Alta Pressão Rio Company was employed (99.95% purity).

The experimental conditions of thermal analysis for immediate analysis of the samples in alumina crucibles were: heating at 20°C.min⁻¹ from room temperature to 600°C in inert gas (N₂), followed by a 60 min isotherm at this temperature and then, at the same heating ratio (20°C.min⁻¹), the residual pyrolyzed material was heated up to 1000°C in air atmosphere. All samples were analyzed in triplicate. The weight loss until 200°C was attributed to moisture, from 200°C to 600°C to volatiles and, from 600°C to 1000°C to fixed carbon. The residual mass at 1000°C refers to the ash content.

The thermal analyses applied for the study of RH and coal combustion were performed in triplicate, according to the following procedure: about 10 mg of each sample was heated in alumina crucibles from ambient temperature (~25°C) to 1000°C, at 20°C.min⁻¹ heating rate.

The present paper discusses and compares both HHV values provided by bomb calorimetry (standard method) and by DSC and DTA. It is noteworthy that thermal analysis in air atmosphere has been used for several studies to obtain biomass thermal properties [7–11], but not as a direct method for estimation of LHV compatible to bomb calorimeter results, as it is in the present one.

2.2. Theoretical Background

LHV can be defined by the thermal energy released in the combustion of a mass unit of a solid or liquid fuel, with the resulting water staying in the vapor phase after formation [6]. Thermal analysis allows one to calculate the thermal energy released due to the combustion of organic compounds. This value actually corresponds to the LHV, since the water produced by the combustion of organic products does not condense during the analysis, as occurs in industrial furnace. From DTA curves, it is possible to correlate the peak area values with the LHV. From DSC, the LHV can be determined directly by time integration of the DSC peak area.

However, as when using a bomb calorimeter the water produced by combustion condenses, this measures the HHV, because it measures the water condensation and the fuel combustion enthalpies, which can be related to the LHV and the hydrogen content obtained from ultimate analysis.

It is worth remembering that the total mass content of hydrogen from ultimate analysis refers to the sum of the sample moisture content (obtained from immediate analysis) and the water produced by the combustion of organic products (combustion water) according the equation:

$$H^t = (W_m^t + W_c^t) \cdot \frac{2}{18} \quad (1)$$

where H^t is the total hydrogen content, W_m^t the sample moisture content, W_c^t the combustion water content.

Once known those variables, the combustion water content can be calculated as follows:

$$W_c^t = H^t \cdot \frac{18}{2} - W_m^t \quad (2)$$

On the other hand, the condensation enthalpy of the combustion water can be calculated as follows (MJ.kg⁻¹):

$$\Delta H_c = \lambda \cdot W_c^t \quad (3)$$

where ΔH_c is the condensation enthalpy of combustion water, λ the water condensation enthalpy at 298K, which is equal to 2.44 MJ.kg⁻¹ [12].

Thus, it is possible to calculate the LHV from HHV determined by bomb calorimetry taking into account the condensation enthalpy value of the combustion water (ΔH_c):

$$LHV = HHV - \Delta H_c \quad (4)$$

From the thermal analysis results, it was noticed that, for reasons that will be discussed with the experimental data, not necessarily all the energy released from the sample complete combustion can be quantified by the DSC or DTA equipment measuring devices under the conditions of the analyses. Therefore, it was established a conversion factor (F) to relate mathematically the values of the HHV given by the bomb calorimeter (standard method) with the LHV estimated from DSC combustion enthalpy and/or from DTA combustion peak area. It should be noted that such corrections to properly estimate the LHV from respective DSC or DTA data are novel contributions.

RESULTS AND DISCUSSION

3.1. Bomb Calorimeter

The HHV estimated by the bomb calorimeter standard method for RH and coal in triplicate are presented in **Table 3**.

Table 3. HHV determined by bomb calorimeter.

Variable	Test 1	Test 2	Test 3	Mean	Standard deviation
HHV _{RH} (MJ.kg ⁻¹)	14.69	14.35	14.43	14.49	0.18
HHV _{coal} (MJ.kg ⁻¹)	12.55	12.07	11.96	12.19	0.31

In a bomb calorimeter pure oxygen at high pressure is used to burnout the samples, to assure a significant oxygen excess to complete the combustion in a closed and adiabatic vessel. In the case of DSC or quantitative DTA determinations, as they are open systems, through which air or oxygen gas flows usually at ambient pressure, it may not be enough oxygen to complete the combustion within the temperature range near the thermocouple measuring the exothermic effect.

Another important fact is that combustion of organic products first produces carbon monoxide (CO), which the formation enthalpy is -110.48 J.mol⁻¹ [6]. Afterwards CO is oxidized in gas phase to carbon dioxide (CO₂) releasing a complementary and higher amount of heat, -282.72 J.mol⁻¹ [6]. In a bomb calorimeter, as there is a significant oxygen excess and it is a closed system, all thermal effects are recorded. In DSC and DTA heating and measuring cells, not necessarily those two steps occur completely in a region in which the temperature or heat flux sensors can correctly register the respective thermal effects.

Besides these facts there is also the purge gas dragging effect, which may cause gas phase combustion to end far from the heat effect measuring device(s), or may drag very small solid particles ejected during intense combustion of solid wastes, as will be further shown.

3.2. Thermal analysis

In general, combustion is a complex process that consists of consecutive reactions. As temperature increases, the main steps are moisture evolution, dehydration, oxidation, combustion and/or other reactions in the gas phase. Physicochemical properties and chemical composition are crucial for the occurrence and duration of each step [13]. **Figure 1** shows the TG and DTG curves of RH samples in triplicate.

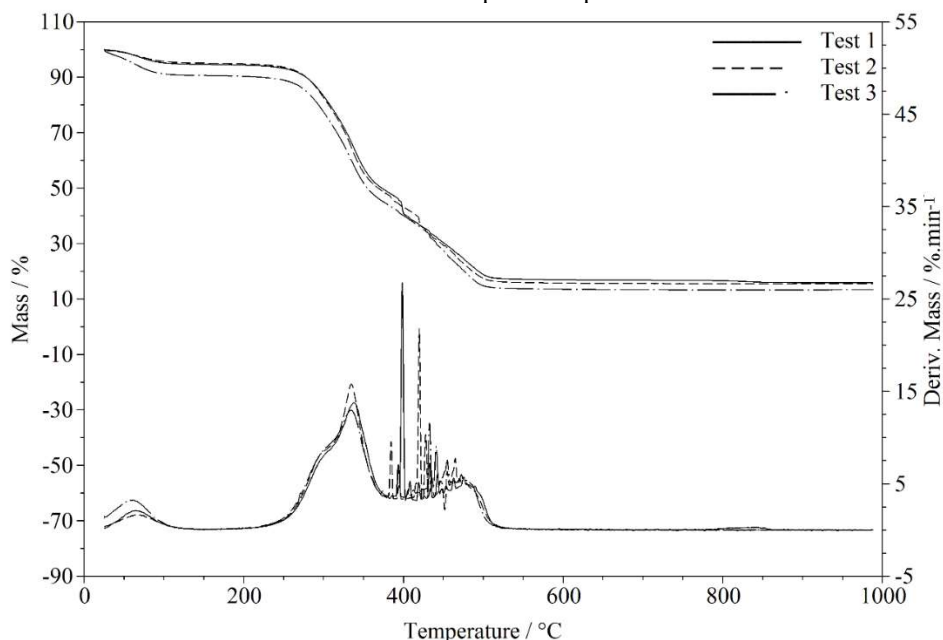


Figure 1. TG and DTG curves of rice husk samples in air.

According to the TG curves, and more precisely from DTG curves, it can be seen that there are three major weight loss steps: first of moisture release, and two subsequent steps of two main combustion stages. These burning stages refer, respectively, to the combustion of light and heavy organic compounds present in the RH. Previous studies about biomass pyrolysis revealed that, during thermal degradation, the mass loss events occur in this order: moisture evolution, hemicellulose degradation, cellulose degradation and finally lignin degradation [14]. Thus, TG and DTG curves exhibit the first combustion stage related to lighter organic compounds (hemicellulose and cellulose) and the second, owing mainly to lignin combustion.

DTG curves in **Figure 1** show, between 350°C and 500°C, many sharp narrow peaks, which means that there was a thermal instability during the decomposition and combustion of the RH. As long as those are natural fibrous structured materials (which are mostly bonded with lignin), after hemicellulose and cellulose burnout, the temperature range provides enough energy to decompose the structure, burning lignin at a very high rate. Consequently, the combustion gases may drag part of the fibrous solid material, which generates this unsuitable behavior. Thus, as the balance immediately detects and records the mass changes, the several peaks shown in the DTG curves indicate that there is an ejection of material during combustion. As it will be discussed, this fact contributes as one of the reasons that the energy released in the combustion was not accurately measured. In other words, the energy released (recorded by thermal analysis) is only a part of the real one. **Figure 2** shows the TG and DTG curves of coal samples in triplicate.

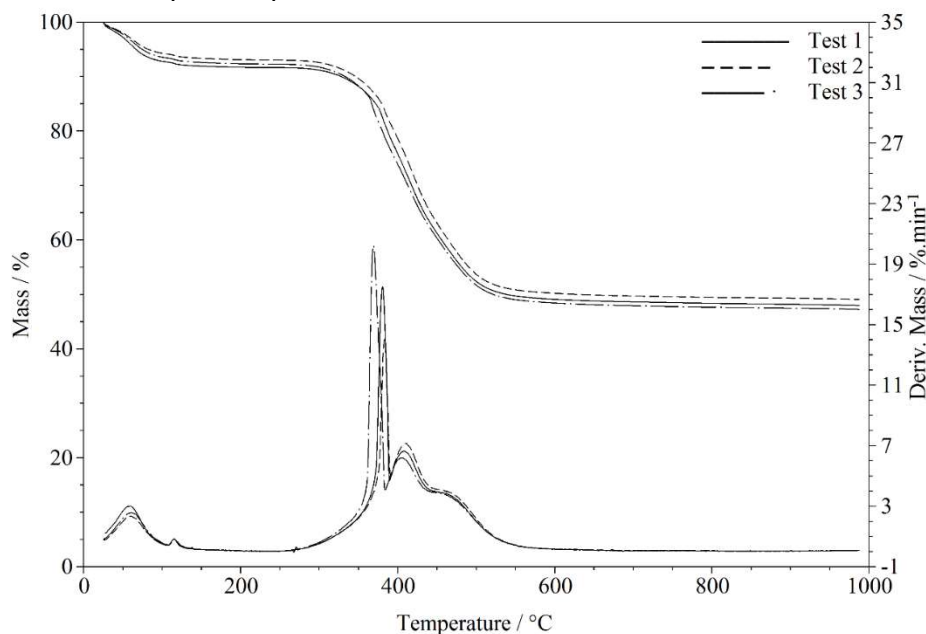


Figure 2. TG and DTG curves of coal samples in air

It is possible to observe, in **Figure 2**, five main steps of mass loss. The first concerns the volatilization of free water absorbed in the pores, followed by the loss of the coordination water of the free cations (up to 200°C) of the clays constituting the studied coal [15]. Three stages of mass loss are verified between 200°C and 700°C, during coal combustion, referred to the three possible main organic groups burnout: light (loss of mass up to 390°C), intermediate (loss of mass between 390°C and 450°C) and the heavier residual carbonaceous products (loss of mass between 450°C and 700°C). It should be noted that during the combustion stages, the dehydroxylation of the present clays also occurs, as well as the pyrite decomposition and combustion [15].

Figures 3 and 4 show DTA and DSC curves of the RH samples and **Figures 5 and 6** show DSC and DTA curves of the coal samples, all curves obtained in triplicate. The endothermic peaks up to 200°C refer to the moisture mass loss in both cases. The following exothermic peaks show and confirm the multistage combustion seen in respective TG and DTG curves.

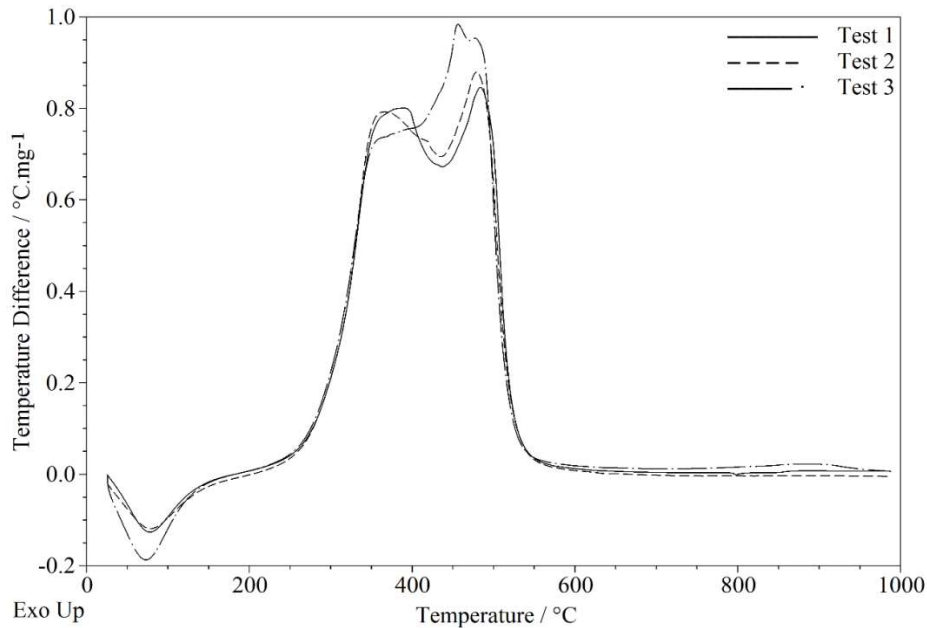


Figure 3. DTA curves of rice husk samples in air

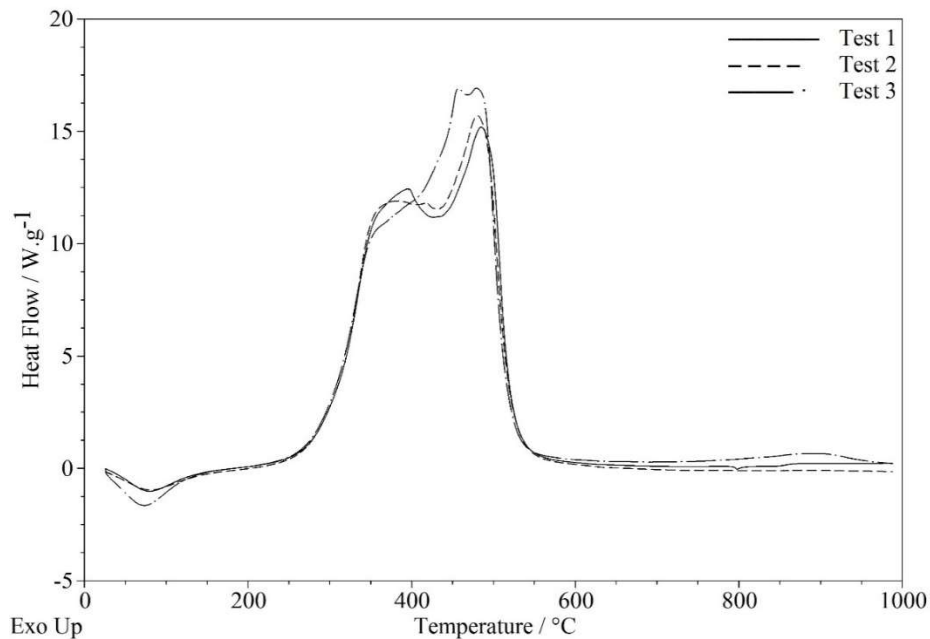


Figure 4. DSC curves of rice husk samples in air

It can be noticed that, in all cases, the thermal effects of the mass oscillating steps during combustion cannot be accounted by respective DTA or DSC analysis data. That is because the measured thermal effects actually represent temperature changes of the measuring sensors in which temperature does not change as fast as the oscillating mass changes occur. This probably also occurs owing to a little lag time between those mass changes occurrences and possible temperature changes of the sensors, which in turn are also “softened” due to the many heat transfer steps between the burning gases and the sensors themselves.

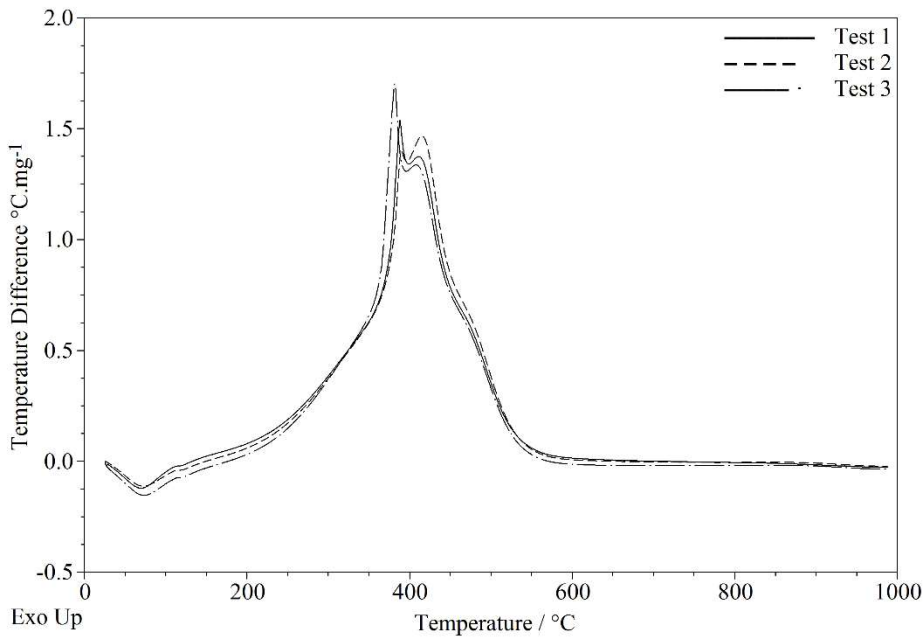


Figure 5. DTA curves of coal samples in air

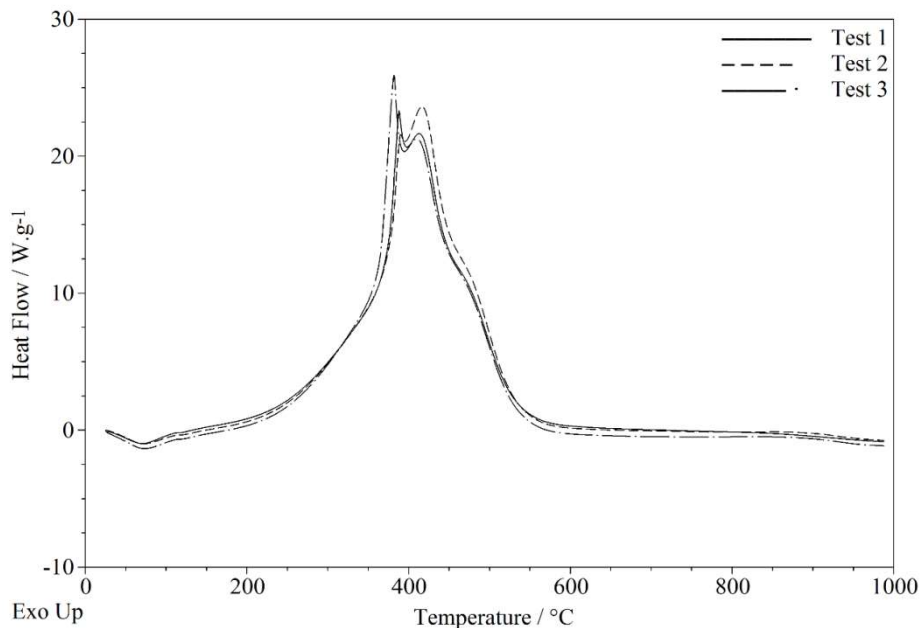


Figure 6. DSC curves of coal samples in air

Due to the different calibration methods used for DTA and DSC curves in the used equipment, the respective DTA peak shapes and respective areas, as well as the loss of endothermic water and exothermic combustion are little different and are obtained in different units. Besides that, the integration of the peak areas estimated different LHVs for each analysis of a same sample, because of the natural origin of the studied materials. **Tables 4 and 5** present the data obtained for RH and coal by DTA and DSC respectively.

Table 4. RH and coal combustion data obtained from DTA curves.

Peak area (°C.min.mg ⁻¹)	Test 1	Test 2	Test 3	Mean	Standard deviation
<i>RH</i>					
Water loss (up to 200°C)	0.37	0.31	0.52	0.40	0.11
Combustion	-7.90	-8.10	-8.20	-8.07	0.15

<i>Coal</i>					
Water loss (up to 200°C)	0.22	0.21	0.26	0.23	0.03
Combustion	-10.28	-10.63	-10.86	-10.59	0.29

Table 5. RH and coal combustion data obtained from DSC curves.

Peak area (kJ.kg ⁻¹)	Test 1	Test 2	Test 3	Mean	Standard deviation
<i>RH</i>					
Water loss / up to 200°C	0.18	0.15	0.27	0.20	0.06
Combustion	-7.52	-7.67	-7.80	-7.66	0.14
<i>Coal</i>					
Water loss / up to 200°C	0.32	0.29	0.29	0.30	0.02
Combustion	-8.32	-9.28	-9.62	-9.07	0.67

Table 6 presents the mean of the LHV estimated by using bomb calorimeter results for HHV according to the method described in the subsection 2.2.

Table 6. Mean LHV estimated for RH and coal

Sample	Mean Values						HHV	
	H ^t	W ^t	H _m ^t	W _c ^t	ΔH _c	by bomb	LHV	
	(m%)	(m%)	(m%)	(m%)	(MJ.kg ⁻¹)	calorimeter	(MJ.kg ⁻¹)	
RH	4.99	6.57	0.73	38.34	0.87	14.49	13.62	
Coal	2.54	7.61	0.85	15.28	0.34	12.19	11.85	

According to the methodology presented in this work, it is possible to correlate **Tables 4 and 5** data with those of estimated LHV values in **Table 6**. For this purpose, the respective estimated conversion factor (F) was calculated as shown in **Table 7**.

Table 7. DTA and DSC LHV conversion factors of RH and coal.

Sample	F _{DTA}	F _{DSC}
RH	1.69	1.78
Coal	1.12	1.31

As can be seen, the mean values of DSC peak area were generally lower than the corresponding mean LHV estimated by using bomb calorimetry results. For the RH, it was observed from respective TG curves that the volatilization of light compounds retained within the RH induces ejection of the neighboring material away from the detection area of thermocouples. The energy released in the combustion of the dragged material cannot be totally registered by the equipment. Hence, the results differ because only partial combustion has occurred in the detection zone of the sample thermocouple.

Therefore, it is not always possible to ensure that the total thermal burning effect of solid biomasses or coal particles can be measured correctly if only the DTA or DSC peak data are used for this purpose. In other words, the solid fuel combustion in thermal analysis instrument may not be completed due to the available amount of oxygen and other discussed factors. It seems that the combustion, which occurs within the equipment, is partial. Besides that, the energy released near to the detection zone of thermocouple is due initially to the formation of carbon monoxide and then, to the carbon dioxide formation in the gaseous phase.

Depending on the operating conditions, as discussed in the introduction, the reaction of CO₂ formation may be occurring far from the thermocouple or another sensor detection zone. This is why the total energy released in this

combustion process cannot be accounted for. As was already discussed, this problem does not occur in a bomb calorimeter due to the excess of pure oxygen for the complete combustion, besides it provides an adiabatic and closed environment, where the total combustion occurs.

But, as was seen in the triplicate analyses, when all thermal analysis operating conditions and variables are repeated, respective experimental occurrences are also repeated, independently of the equipment has been previously calibrated. Thus, the proposed method is a practical way to use DTA and DSC data to estimate reliable LHV values for routine analysis, after obtaining the conversion factor for each kind of solid fuel. It also includes the correction of different experimental unavoidable facts that may happen during combustion, which lead to partial measurement of heating values, even when the equipment are well calibrated.

CONCLUSIONS

DSC and/or DTA are useful tools to estimate heating values comparable to bomb calorimeter standard results. The proposed method solves the unavoidable combustion experimental problems that may occur during thermal analyses, by previously obtaining a conversion factor from corresponding standard bomb calorimetry data.

This procedure allows one to estimate accurately the LHV from DTA and/or DSC data, for each specific solid fuel for further routine analysis, when a bomb calorimeter is not available. This methodology does not replace any conventional method for determining the HHV or LHV, but it is a valuable and practical method that mostly depends on a DSC and/or DTA equipment.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper

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