

Energy Evaluation of Materials by Bomb Calorimetry

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1. Introducción

The aim of this chapter is to introduce the user in the field of combustion bomb calorimetry.

This technique is one of the oldest and most precisely studied in the field of modern physical chemistry and is the complement to some others calorimetric techniques.

2. Historical background

Early studies related to combustion calorimetry are reported in the latter part of the XVIII century. Lavoisier and Laplace described, in 1784, an ice calorimeter from which heats of combustion could be determined. They studied the heat release from animal respiration.

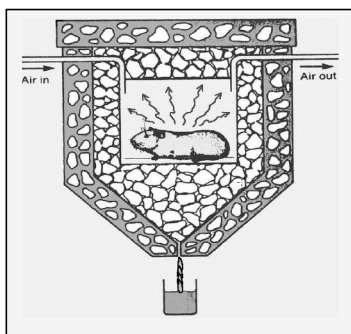


Figure 1. Lavoisier and Laplace ice calorimeter

In 1788 Crawford used a similar experimental procedure by which he concluded the key role of oxygen during the combustion of organic matter in animals, and that part of the energy generated during this process is used at different levels for the animal metabolism.

It was Thompson who, years later, transformed the calorimetric research by starting to study the heats of formation of different daily used materials such as wood, oils and/or spirits. This is the moment that should be considered as the beginning of the applied calorimetry.

The brake of nearly 50 years suffered by Thermochemistry, as a consequence of the theories presented by Lavoisier helped to scientists to realize that heat was a form of energy. However this concept was not firmly established until 1840 by G. H. Hess.

The probable first calorimetric bomb was used in 1848 by Andrews to determine the heats of combustion of a variety of solid, liquid and gas substances. Gases were burned in a 580 cm³ volume thin-walled copper cylinder while solid and liquid samples were placed in a platinum crucible introduced in a 4 dm³ copper cylinder which was them filled with oxygen. Ignition of the sample was achieved by passing through a platinum wire the electric current generated by a battery.

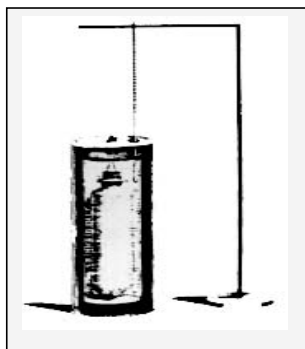


Figure 2. First calorimetric bomb designed by Andrews

Favre and Silbermann introduced the term “calorie” for the unit of heat into the thermochemical publications. They studied a variety of organic compounds and published their results in 1852. They constructed their own thermometers that detected temperature differences of 0.001 °C to 0.002 °C.

Thomsen conducted thermochemical research at Copenhagen in the period from 1851 to 1885. His studies were collected in a work entitled “Thermochemische Untersuchungen”, published from 1882 to 1888. M. P. E. Berthelot began, in 1864, his studies in thermochemistry in Paris. His studies were published in 1878 in a series of papers in which a glass flame calorimeter was described. Together with Ogier reported a technique for burning liquids in glass ampoules. In 1885, Berthelot and Vielle developed a combustion bomb technique, which was very useful for solid and low volatility liquid samples. This new method used 25 atm of oxygen.

Owing to the technological progress experienced at the beginning of the XX century, it was necessary to introduce some innovations in the design and development of calorimeters trying to optimize their performance in specific studies. Kroeker, Parr and some other investigators were able to make changes such as: the use of nickel chromium alloy with suitable acid-resistant properties, the substitution of a rubber gasket for one of lead, etc.

In 1915, Dickinson published an article in which procedures, apparatus and calculations in combustion calorimetry together with values for the heats of combustion of some substances were reported. Also, he stressed on the advantage of using a platinum resistance thermometer instead of a mercury in glass thermometer.

W. A. Roth introduced some improvements in the calibration of his isothermal-jacket bomb calorimeter. The heats of combustion of benzoic acid, naphthalene and

sucrose as well as electrical measurements were used to obtain the water equivalent. Temperature changes were observed with a Beckmann thermometer which could be read to 0.0005 °C. He also introduced corrections for the formation of aqueous nitric acid and carbon residues. At the Third Meeting of the I.U.P.A.C. in 1922 at Lyon (France) the benzoic acid was selected as the chemical standard. The value adopted was 6324 cal (15 °C) g⁻¹ (air).

E. W. Washburn recommended that in conjunction with certifying a value for standard benzoic acid to be used to calibrate bomb calorimeter a series of corrections known as Washburn corrections should be done.

In the 1950's, the developing of electronics allowed the design of new calorimeters with technological improvements mainly in the field of temperature detection systems.

Since that, the calorimetric technique has very much improved and enlarged its application in different scientific fields such as: the search for alternative energy sources, evaluation of soils potential activity, design of pharmaceuticals, environmental studies, design of new industrial materials, etc.

3. Calorimetry

Calorimetry is a technique by which heat exchange is measured either directly or indirectly, Combustion calorimetry is a technique that measure the heat exchanged. Combustion calorimetry refers to the measurement of heat (at constant pressure) or energy (at constant volume) of a reaction in which the carbon skeleton of a compound is totally broken when the compound is burnt under a gaseous oxygen atmosphere. The term reaction calorimetry applies to the measurement of the energy or heat of any reaction other than combustion.

Every calorimetric experiment consists of three well defined stages:

- *The calorimetric part which concerns the accurate determination of the energy generated in the reaction.*
- *The chemical part which concerns the characterization of the initial and final states.*
- *The transformation of the results obtained in the calorimetric experiment to a standard-state combustion energy at 298.15 K, from which a standard enthalpy of formation can be calculated.*

4. Calorimeters

All calorimeters are based on variations of the same basic principle: the process to be studied takes place inside the boundaries of a more or less closed area known as the actual calorimeter in controlled thermal contact with its surroundings, the jacket. The calorimeter and jacket are supplied with different auxiliary devices such as:

- A thermometer that controls and measures the temperature changes resulting from a experiment.
- Stirring devices that homogenize the temperature at any place time in the calorimeter.
- Ignition system, to start the reaction.
- Temperature controller to conduct the heat exchange between the proper calorimeter and its jacket.

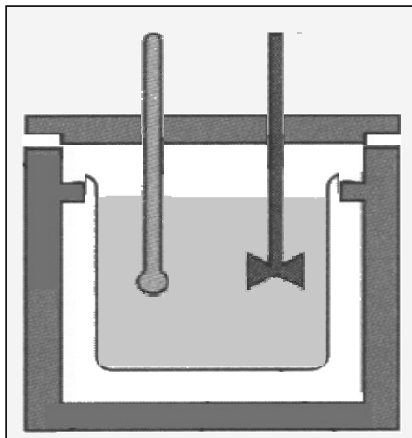


Figure 3. Basic calorimeter sketch

The calorimeters can be classified following different criteria. The arrangement of calorimeters in a classification system should be based on a simple structure suitable for practical application. There are different classification criteria, but it must not be attempted to classify every calorimeter in every detail because it leads to unclarity and insignificance in practice. Moreover, many calorimeters can be operated in diverse modes so that a calorimeter can be classified in different ways, depending on the mode of operation. For this reason we adopt different primary and secondary criteria. According to the mode of operation (temperature) the calorimeters can be classified as:

- Adiabatic calorimeters. There is no heat exchange between proper calorimeter and: jacket because calorimeter and jacket temperatures are identical during the experiment.
- Isoperibol calorimeters in which the jacket temperature remains practically constant during the experiment heat exchanging calorimeters.
- Isothermal, in which the temperature of the proper calorimeter remains constant.
- Bomb calorimeters. In this type of apparatus the reaction chamber consists of a heavy-wall container hermetically closed. The reaction is carried out under an oxygen or fluorine atmosphere and the reaction vessel can be either static or moving, thus differentiating between static or rotating bomb calorimeters.
- Flame calorimeters, in which the reaction between the sample and an oxidizing agent is started by a flame.



Figure 4. Calorimetric bomb



Figure 5. Bomb calorimeter assembly used by the Research Group TERBIPROMAT

5. Theory of an isothermal experiment

In a calorimetric experiment the difference in energy between two well defined states the initial and final of a combustion reaction, is determined.

The process is assumed to take place inside an enclosure that is totally isolated from the surroundings, thus adiabatically ($\Delta Q = 0$), and at constant volume ($\Delta V = 0$). According to the first law of thermodynamics, $\Delta U = 0$, what means that $U(\text{state}_1, T_1) = U(\text{state}_2, T_2)$, (see Fig. 6).

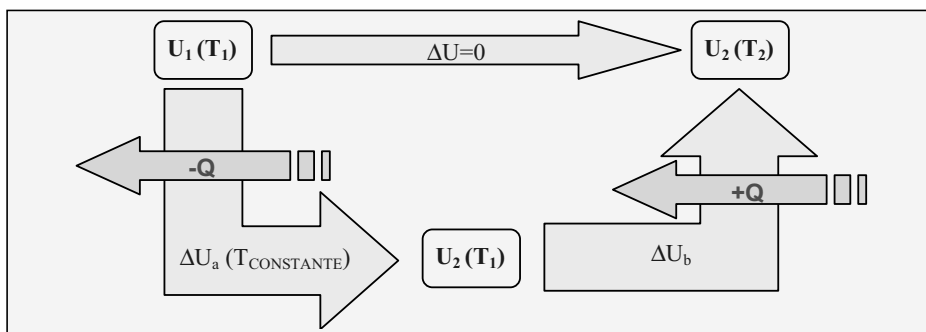


Figure 6. Theory of a calorimetric experiment I

This process can be modified and the system heated from T_1 to T_2 and then the reaction takes place isothermally at temperature T_2 . (see Fig. 7).

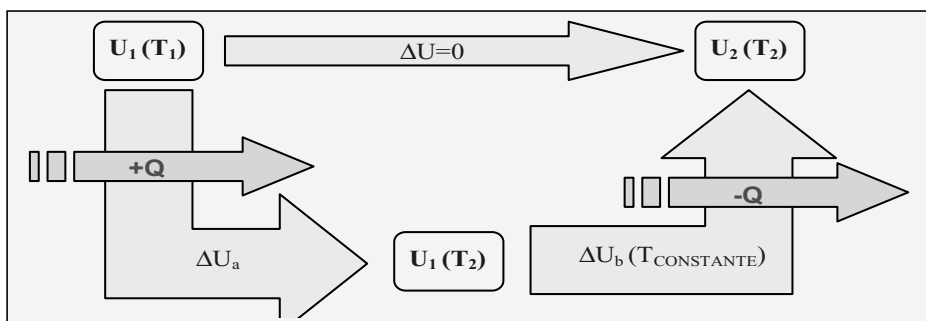


Figure 7. Theory of a calorimetric experiment II

6. Temperature vs. Time plot

Throughout a combustion calorimetric experiment, measurements of temperature at fixed time intervals, say 15 seconds, are made. The calorimetric experiment is ordinarily divided into three periods as it is shown in Figure 8:

- Initial period in which the temperature change of the calorimeter is due completely to heat exchange between calorimeter and surrounding (thermal leakage) and heat of stirring.
- Main period in which the most part of the temperature rise takes place as a consequence of the combustion originated in the bomb.
- Final period in which the temperature change of the calorimeter is again due totally to thermal leakage and heat of stirring.

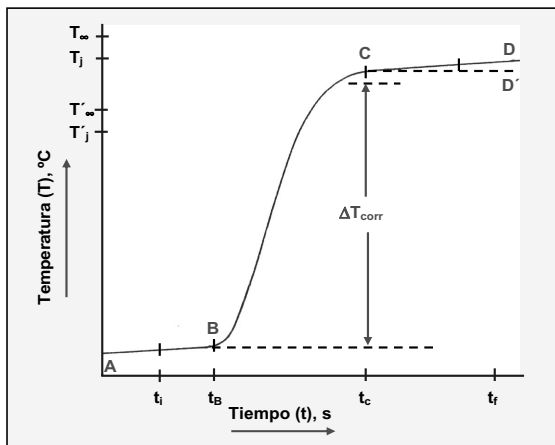


Figure 8. T - t plot corresponding to a calorimetric bomb experiment

7. Calorific value

The calorific value of a fuel sample is the heat generated by complete combustion of one mass unit of sample in a oxygen atmosphere.

According to the standards by the International Standards Organization (ISO) two calorific values must be considered depending on the conditions in which the combustion takes place:

- The higher heating value (HHV), at constant volume, is defined as the quantify of heat generated by complete combustion of a mass unit of sample, in an oxygen atmosphere, under standard conditions. Final products after combustion are: oxygen, carbon dioxide, sulphur dioxide, nitrogen all of them in gas phase, together with water in liquid phase in equilibrium with its vapour and saturated of carbon dioxide, and a solid phase formed by ashes.
- The lower heating value (LHV), at constant value, is the heat generated by complete combustion of one mass unit of sample, assuming that the water in the final products remains in the form of vapor.

8. Use of the bomb combustion calorimetry as a complement to thermal analysis in the field of R+D

Bomb calorimetry is used in the field of R+S to determine calorific values of different materials. A brief summary of the research developed by our research group TERBIPROMAT in the University of Santiago de Compostela, is given:

1. *Search for alternative energy sources from residue materials* mainly Municipal Solid Waste (MSW) and forest waste originated from different forestry tasks carried out in Galicia (N. W. Spain). Table I shows data for the different zones of MSW originated in Vigo (Galicia). These studies were complemented by thermogravimetric analysis to study the degradation of these materials trying the possible control of their polluting elements.

Table 1

Zone characteristic	HHV (kJ kg ⁻¹)	LHV (kJ kg ⁻¹)	MOISTURE (%)	ASH (%)
RESIDENTIAL- COMMERCIAL	20400	12060	30	19
COUNTRY AREA	13600	7300	27	28
COUNTRY-INDUSTRIAL	20700	11500	31	21
RESIDENTIAL- INDUSTRIAL	27000	16100	30	19
RESIDENTIAL	20600	12500	29	19
R.D.F.	19700	10500	30	22

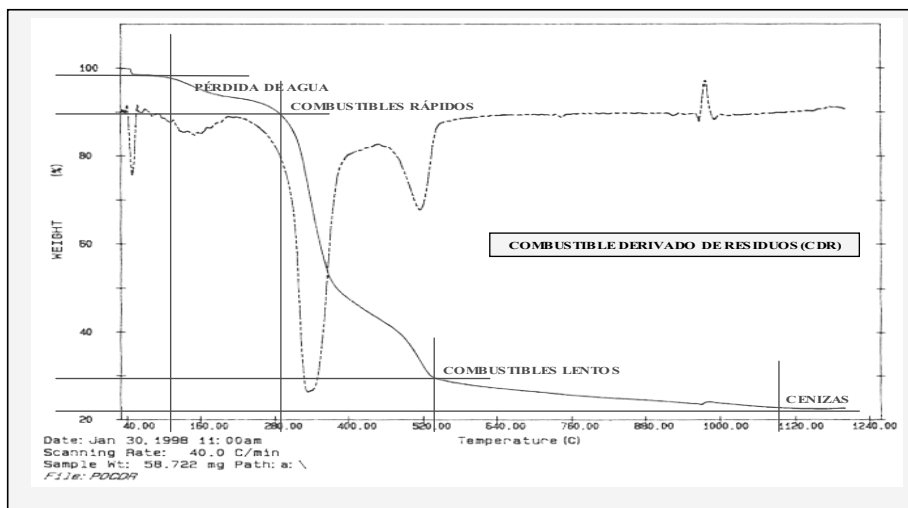


Figure 9. Degradation of a Residue Derived Fuel (RDF)

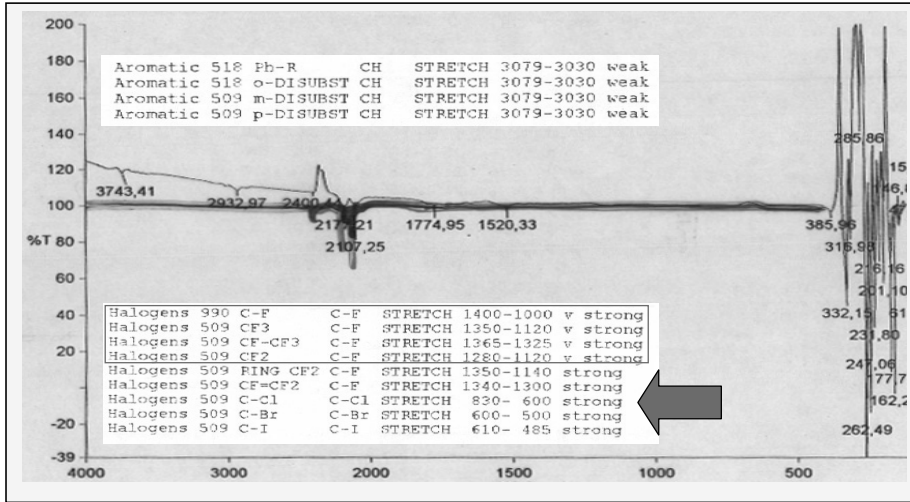


Figure 10. Use of FT-IR to detect pollutants

2. Design of risk indices to prevent and fight forest fires. This research line was used to make combined analysis of different physical, chemical, biological, and environmental parameters with the aim to obtained a numerical value capable of helping in the prevention and fight against forest fires. These numerical values are represented in the form of risk index maps.

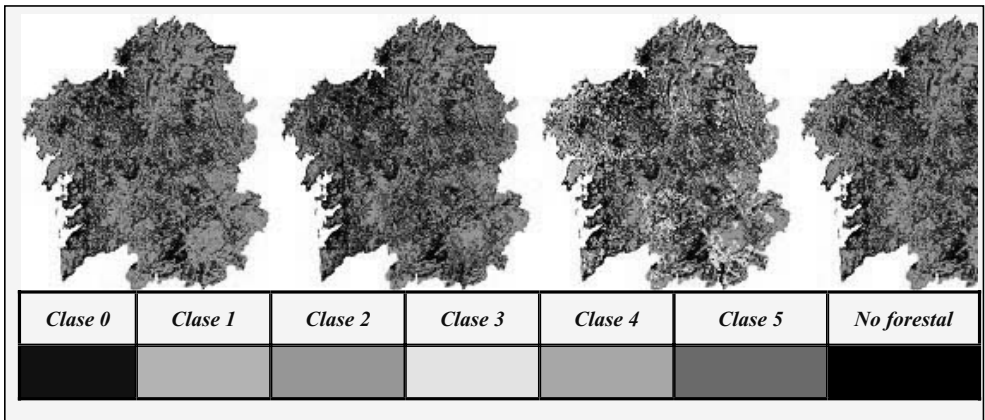


Figure 11. Risk index maps of the conifer species existing in Galicia

3. Study of the behaviour of different materials, with the aim of considering their possible recycling. The example refers to an epoxy resin.

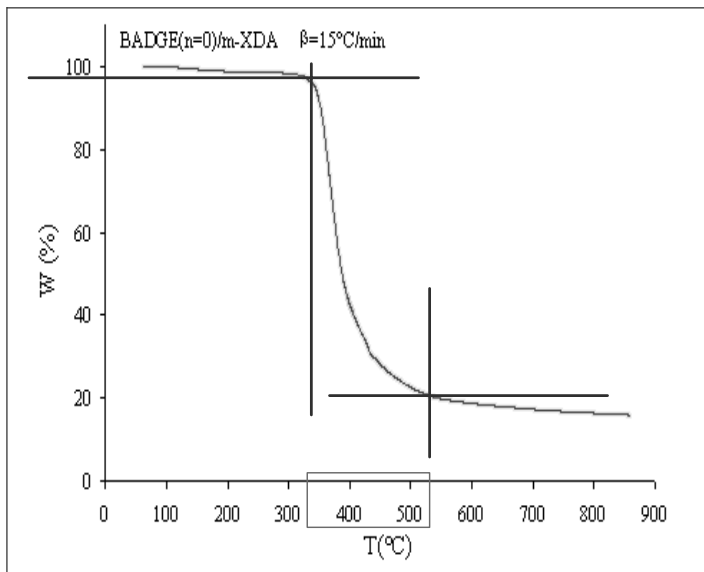


Figure 12. Thermogravimetric study of an epoxy resin

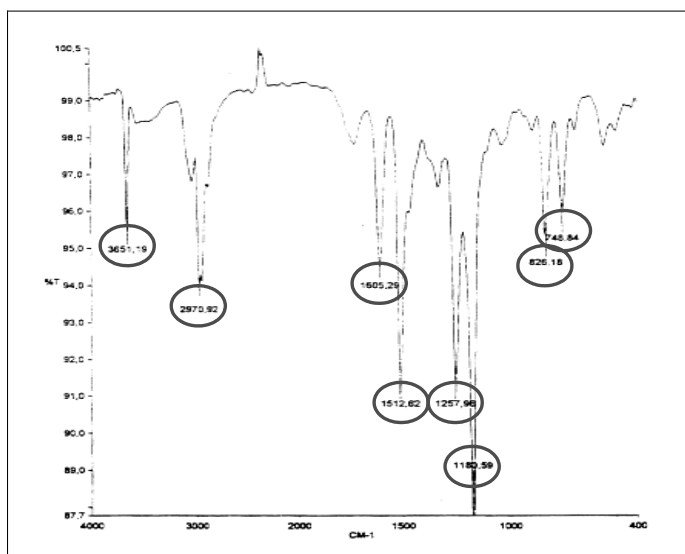


Figure 13. FT-IR spectrum

Table 2

	HHV (kJ kg ⁻¹)	LHV (kJ kg ⁻¹)	MOISTURE (%)	ASH (%)
POLYMER	32100	20200	28	7
PAPER-CARBOARD	16000	10800	21	12
TEXTILE	23200	11800	42	9
ORGANIC MATTER	13800	6100	43	39

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