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AN ANALYSIS OF SOME PRACTICAL METHODS FOR ESTIMATING HEATS OF COMBUSTION IN FIRE SAFETY STUDIES

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ABSTRACT

The theoretical (net) heat of combustion of materials is a basic information important for fire safety studies. This paper is a review of existing methods ranging from use of tabulated data to calculations relying on more or less sophisticated engineering correlations based on the elemental compositions of materials and in some cases on their chemical structures. The presentation emphasises only those calculation methods that allow user-friendly estimations of the heats of combustion, that is to say when at most a simple datasheet processor is the only tool required.

Empirical correlations developed in early times of combustion science by *Dulong* (France), *Boie* (Germany) and some others are examined here in the context of fire engineering. More recently proposed predictive methods of heats of combustion in fire or chemical engineering background, taking account of structural effects of the molecules on their heats of combustion are then presented and compared.

Finally, consideration of the relevance and accuracy of the listed methods is provided and commented either by comparison of literature and calculated values, either by reference to measured data obtained by use of conventional oxygen bomb calorimetry.

INTRODUCTION

The theoretical heat of combustion of a given product is the maximum amount of heat that a product liberates in a fire as a result of complete combustion. Depending on the context of use, this parameter is also referred to as the enthalpy of combustion, the calorific or the heating value. In a fire, water as a product is present as a gas, the use of the net heat of combustion (lower heating value with water as gas) is more appropriate than the gross heat of combustion or calorific value (upper of higher heating value, water as liquid). However, the gross calorific value is most often the commonly reported value obtained from measurements in the oxygen bomb calorimeter and in a series of empirical correlations developed from actual measurements databases. In practice, heats of combustion may be reported in various units (kcal/kg, kJ/kg, MJ/kg, kJ/mol,...) and may vary in extreme cases for substances liable to sustain oxidative processes between a few MJ/kg to some 130 MJ/kg (hydrogen). Most net heating values for organics lie within a range of 20 MJ/kg to 45 MJ/kg.

The heat of combustion of materials and products in enclosures or storage commodities may easily be related to the fire load of a given premise or its fire load density, which may give a first valuable information in a preliminary risk assessment process. The fire load of an enclosure is generally defined as the total amount of energy that can be liberated by all combustible matter present in the enclosure. The fire load density is the same quantity normalised by the overall floor surface area.

Extensive analysis of fire load densities typical from various premises has been published by Rabash in the Fire Safety Journal¹ (1987).

In France, a value of 2500 kJ/kg is used as a limit value to consider inherent non-combustibility property of building products (Rating 'M0' of building materials²). French insurers also base a very rough classification of the fire hazard in terms of critical values of fire load densities³. 'Low' risk is admitted if the fire load remains below 25 kg/m² wood equivalent (425 MJ/m²), a value of 50 kg/m² wood equivalent (850 MJ/m²) is rated as a 'medium' fire risk, and a value of more than 100 kg/m² wood equivalent (1700 MJ/m²) is rated as 'high' fire risk.

Drastic limitation of fire load inherent to structural elements and to furnishing materials in rooms is also a basic safety measure implemented by law enforcement in French high-rise buildings⁴, whatever occupancy is housed in. In the same way, fire load is also a basic consideration to determine areas of special fire risks in hospitals and other healthcare premises⁵. Heats of combustion may also in turn be correlated to other safety parameters, for example as suggested by Suzuki⁶ to flammability limits.

The assessment of fire risk based on heat of combustion, naturally, has limitation. For example, two materials with same heat of combustion can have different heat release rates depending on the total exposed surface area burning, heat of gasification of the materials and flame heat transferred back to the burning materials. Moreover, fire dynamics may lead to significant changes in the course of a single fire process⁷. Measurement of actual heat release rate using fire calorimetry based on OC or CDG will then provide more detailed information when required to qualify materials fire behaviour^{8/9}.

Despite the limitations, it may be advantageous to use of a number of simple predictions rules for the theoretical heats of combustion. For practical reasons, the evaluation of the heat of combustion cannot systematically rely on conventional means of determination such as actual measurement, reference to tabulated data, or calculation derived from thermochemistry laws. The authors wish to comment on that in a first section. Then, for the benefit of the fire specialists, they present and comment on a selection of other simple predictive methods based on empirical correlations derived from measured data, and making use of information regarding elemental composition of the products.

TABULATED DATA AND SIMPLE CALCULATIONS BY USE OF THE THERMOCHEMISTRY LAWS

Finding the actual heat of combustion of the desired product in a universal table is probably the wish of every fire engineer. Indeed, extensive compilations have been done in the past in the context of combustion, chemical engineering and fire science that give numerous values for a variety of products^{3-10/13}. The accuracy of the data concerning common pure organics are commonly within 2-3% from one table to another, but may easily reach 5 to 10 % with less well defined products, in terms of technical grades, isomers and so on. The user will draw advantage of using a single reference database as far as possible to limit discrepancies.

However, further care may sometimes be required, when the selection of heating values for uncommon chemicals or chemicals departing significantly from hydrocarbons by their chemical composition is dealt with.

As an illustration of this, tables 1 and 2 have been plotted from previous literature review regarding non hydrocarbon chemicals, sulphur and carbon disulphide, for which printing mistakes is probably a better explanation of the abnormal values observed than uncertainties or heterogeneities on thermodynamic data with respect of the physical state or phase considered for reference.

| product : Sulphur (S) | ΔH (MJ/kg) | ref. | relative scatter ($\Delta\%$) |
|--------------------------|--------------------|---------------------------|---------------------------------|
| tabulated | 11.03 | after Weiss ¹⁴ | + 19.1% |
| (polysulfur) tabulated | 09.72 | (a) | + 5.0 % |
| tabulated | 04.64 | (b) | - 49.9 % |
| tabulated | 09.27 | (c) | + 0.1 % |
| tabulated | 09.28 | (d) | + 0.1 % |
| tabulated | 09.3 | (e) | - 15.7 |
| (Boie formula) predicted | 10.46 | (see next section) | + 12.9 % |
| calculated (Hess's law) | | this work (required | |
| S as a solid | 09.26 | data from ¹⁵⁾ | 0% |

(a) to (e) miscellaneous literature references

Table 1 : comparison of existing tabulated values for heat of combustion of sulphur

| product : CS ₂ | ΔH (MJ/kg) | ref. | relative scatter ($\Delta\%$) |
|---------------------------|--------------------|---------------------------|---------------------------------|
| tabulated | 13.52 | after Weiss ¹⁴ | - 4.3% |
| tabulated | 06.34 | (a) | -55.1 % |
| tabulated | 13.60 | (f) | +0.6 % |
| tabulated | 13.86 | (c) | - 1.9 % |
| (Boie formula) predicted | 14.37 | (see next section) | +1.7 % |
| calculated (Hess's law) | 14.13 | this work (required | 0 % |
| | | data from ¹⁵⁾ | |

(a) (c) (f) miscellaneous literature references in agreement with nomenclature of table1

Table 2 : comparison of existing tabulated values for heat of combustion of carbon disulphide

To check the most proper tabulated values for sulphur and carbon disulphide presented in the above tables, we have performed very well know calculations based on the thermochemistry laws including the Hess law of constant heat summation that relates in an easy way the heat of combustion of a product to the enthalpy change between the reactants and the products of combustion¹⁶. However this method remains simple only if the enthalpy of formation in standard conditions of temperature and pressure of the product is tabulated in some thermodynamic properties database such as given in Reference 15. Although a large number of organic products are listed in the tables, data for many products of interest such heavy weight molecules as agrochemicals or pharmaceutical drugs are not available.

SIMPLE CORRELATIONS DERIVED FROM FOSSIL FUELS COMBUSTION SCIENCE

The heats of combustion of any organic compound is associated with the bond energies between the atoms forming the chemical structure of the compound, and therefore with the character of the bonds. However, in spite of the absence of fundamental scientific validation, the possibility that the heat of combustion might be calculated for solid fuels (e.g. coals) with fair accuracy from elementary composition alone has led many researchers to establish empirical correlations from their commonly measured characteristics. Those correlations are often expressed in the form of linear combinations of the weight percentages of the atom elements C, H, O, sometimes expanded to S and N. The reason is that major elements in the chemical composition of fossil fuels is actually limited to C, H, O, N, and S in their organic part.

Table 3 shows a selection of such empirical correlations giving the gross heat of combustion ΔH_{gross} of the given fuel. The net heat of combustion ΔH_{net} may then easily be derived from the gross heat of combustion by deduction of the latent heat of vaporisation of water, e.g. by use of eq. (1) :

$$\Delta H_{net} = \Delta H_{gross} - 21.96 H \quad (MJ/kg) \quad (1)$$

where H is the mass fraction of hydrogen in the product.

| formula name | atoms | expression of ΔH_{gross} (in MJ/kg) |
|------------------------------------|---------------|---|
| | | (concentrations of designated elements as mass fractions) |
| Dulong ^{17,20} | C, H, O | $\Delta H = 33.8 C + 144.2 H - 18.03 O$ |
| Dulong (expanded) ^{18,22} | C, H, O, S | $\Delta H = 33.8 C + 144.153 H - 18.019 O + 9.412 S$ |
| Dulong&Petit ²¹ | | $\Delta H = 33.8 C + 144.0 H - 18.0 O + 10.46 S$ |
| D'Huart ²² | C, H, O, S | $\Delta H = 33.9 C + 143.4 H + 22.25 S - 30.4 O$ |
| Boie ^{18,19, 23} | C, H, O, N, S | $\Delta H = 35.160 C + 116.225 H - 11.090 O + 6.280 N + 10.465 S$ |
| Seyler ¹⁹ | C, H, O | $\Delta H = 51.87 C + 162.4 H - 17.87 + 10.46 (O)^2$ |
| Strache-Lant ²² | C, H, O, S | $\Delta H = 34.05 C + 143.23 H - 15.32 O + 10.46 S$ |
| Gumz ²² | C, H, O, N, S | $\Delta H = 34.03 C + 124.31 H - 9.836 O + 6.278 N + 19.09 S$ |
| Vondracek ^{21,22} | C, H, O, S | $\Delta H = (37.29 - 2.595 C)C + 113 H - 11.3 O + 10.46 S$ |
| Vondracek ²⁴ (a) | C, H, O, S | $\Delta H = (32.9 + 3.7 (1-C)^{0.25})C + 89.99 H - 9 O + 10.46 S$ |
| Mahler ²¹ | C, H, O, N | $\Delta H = 34.07 C + 144.4 H - 12.56 (O+N)$ |
| Patary (a) ²¹ | C, H, O, N | $\Delta H = 35.58 C + 113 H - 11.3 O + 10.46 S$ |
| Mott & Spooner ^{19,22} | C, H, O, S | $\Delta H = 33.61 C + 141.9 H - 14.52 O + 9.417 S$ (if $O_2 \leq 15\%$) else $Q = 33.61 C + 141.9 H - (15.32 - 7.20 O) O + 9.417 S$ |

(a) gives the net heating value contrary to the other correlations presented, (b) reported by Patary, author unknown

Table 3 : examples of early correlations developed to predict heats of combustion

As can be seen, most expressions are of the form of eq.2 :

$$\Delta H = \alpha C + \beta H + \gamma S - \sigma O + \delta N \quad (2)$$

where C, H, O, N, S are the weight fractions or weight percentages of the corresponding elements in the fuel, and $\alpha, \beta, \gamma, \sigma$ « calorimetric » coefficients the values of which are dependant on the units of expression of ΔH .

These correlations are the results of extensive experimental determinations of parallel sets of ultimate analyses of fuels and related measured heats of combustion by means of oxygen bomb calorimetry.

Dulong who pioneered the work at the end of XIXth century assumed, as can be seen in the earliest expression of his formula (see eq. 3, with original units)¹⁷, that oxygen was associated in the proper ratio with hydrogen as water, the excess hydrogen being available for combustion. The accuracy of the Dulong formula in its expanded form (see table 3) is reported to within 1.5 % of actual values determined by use of a oxygen-bomb calorimeter for coals²². All other correlations of table 3 with exception of the Boie formula may indeed be considered as inspired of the Dulong formula, with modified assumptions as regard the way oxygen is associated to the hydrocarbon frame.

$$\Delta H_{gross} = 8,080 C + 34,462 \left(H - \frac{O}{8} \right) \text{ (in kcal / kg)} \quad (3)$$

The extrapolation of such correlations to other types of combustible organic materials is feasible to some extent for more or less simple chemicals, when accuracy requirement is not severe.

Table 4 gives a comparison of predictive values of heats of combustion by use of formerly mentioned equations for a number of simple chemicals.

| formula name | carbon graphitic | n- heptane | xylene | acetone | aniline | carbon disulphide | sulphur (solid) |
|------------------------------------|---------------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|----------------------|--------------------|
| | C | C ₇ H ₁₆ | C ₈ H ₁₀ | C ₃ H ₆ O | C ₆ H ₇ N | CS ₂ | S |
| ref. Q _{gross} value | 32.80 | 48.07 | 42.89 | 30.83 | 36.44 | 14.13 | 9.26 |
| Dulong ^{17,20} | 33.8 | 51.6 | 44.3 | 31.0 | 37.1 | 5.3 | - (b) |
| Dulong (expanded) ^{18,22} | 33.8 | 51.6 | 44.3 | 31.0 | 37.1 | 13.3 | 9.4 |
| Dulong&Petit ²¹ | 33.8 | 51.5 | 44.3 | 31.0 | 37.1 | 14.1 | 10.5 |
| D'Huart ²² | 33.9 | 51.5 | 44.3 | 27.6 | 37.1 | 24.1 | 22.3 |
| Boie ^{18,19, 23} | 35.2 | 48.2 | 42.9 | 30.9 | 37.0 | 14.4 | 10.5 |
| Seyler ¹⁹ | 34.0 | 51.8 | 44.5 | 32 | 34.6 | -9.7 | - 17.9 |
| Strache-Lant ²² | 34.1 | 51.6 | 44.4 | 31.8 | 37.2 | 14.2 | 10.5 |
| Gumz ²² | 34.0 | 48.6 | 42.6 | 31.4 | 36.7 | 21.4 | 19.1 |
| Vondracek ^{21,22} | 34.7 | 47.65 | 42.3 | 30.8 | 35.9 | 14.6 | 10.5 |
| Mahler ²¹ | 34.6 | 51.8 | 44.6 | 32.7 | 35.4 | 5.4 | - (b) |
| Patary (a) ²¹ | 35.6 | 48.0 | 42.9 | 30.7 | 36.1 | 14.4 | 10.5 |
| Mott & Spooner ^{19,22} | 33.6 | 51 | 43.9 | 31.95 | 36.8 | 13.2 | 9.4 |

(a) unknown author, reported by Patary²¹ - (b) not relevant

Table 4 : gross heats of combustion (values in MJ/kg) as predicted by first generation of correlations for hydrocarbons and other chemicals departing from fossil fuels

It is worth noticing that the *Boie* formula is the only one of the series that was introduced to give heats of combustion of other products than coals, whereas the *Dulong* formula is perhaps the most well known correlation in the field of the combustion science. The formula of *Vondracek*, of a non linear type, seems also very good in terms of accuracy, as argued by Patary²¹ at the light of table 4. The initial database on which Boie established his correlation contained 149 solid and liquid products including biomass fuels, coal/coke/char fuels and oil fuels¹⁸. Further use of the equation for 300 new solid and liquid fossil fuels led to a maximum error of 3%²⁵

The French professional association *Infoplast*²³ in the 80's and Marlair²⁶ in the 90's first investigated capabilities of the *Boie* and *Dulong* formulae for fire safety purposes. Brief relevance of those correlations were shown for easy and fast running estimation of heats of combustion of plastics and agrochemicals, respectively.

Indeed, table 4 clearly outlines the fairly good predictive capacity of the *Dulong* (expanded) and *Boie* formulae, even for products bearing high N or S contents, when those elements are generally only present in minor quantities in coals. However, one may also notice that high concentrations of the quoted hetero-atoms in the sample molecules lead with other listed formulae to some erroneous or aberrant predictions for extreme cases.(products containing unusual high mass fractions of sulphur).

Surprisingly, even for products containing other hetero-atoms than those included in the initial products databases that were used to derive the aforementioned formulae, the predicted values derived from *Boie*, *Dulong* or *Vondracek* are still in reasonable agreement with 'actual' values (e.g. measured or tabulated in literature), with exception of a few cases, as shown hereafter. Table 5

focuses on examples of predicted values by the *Dulong*, *Boie* and *Vondracek* formulae for more complex molecules selected among pesticides and polymers, principally.

| | | ref. values (MJ/kg) | Predicted values of heats of combustion (MJ/kg) | | | |
|---------------------------|---|----------------------------|--|--------------|-------------------------|----------------------------|
| | | <i>Lit. or measure</i> | Boie value error | | Dulong (expanded) | Vondracek ²⁴ |
| | chemical formula | ΔH | ΔH_{net} | $\Delta(\%)$ | ΔH_{net} | ΔH_{net} |
| TDI (e) | $\text{C}_9\text{H}_6\text{O}_2\text{N}_2$ | 23.6 (d) | 24.1 | + 2.3 | 21.9 | 23.7 |
| Nylon | $(\text{C}_6\text{H}_{11}\text{NO})_n$ | 30.8 (b) | 30.8 | 0 | 31.0 | 30.3 |
| PVC | $(\text{C}_2\text{H}_3\text{Cl})_n$ | 16.9 (c) | 18.1 | + 07.1 | 18.9 | 18.3 |
| chlorobenzene | $\text{C}_6\text{H}_5\text{Cl}$ | 26.5 (g) | 26.7 | + 0.8 | 27.1 | 26.9 |
| fluorobenzene | $\text{C}_6\text{H}_5\text{F}$ | 30.9 (f) | 31.3 | 1.3 | 31.8 | 31.4 |
| isoproturon | $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}$ | 31.84 (a) | 32.8 | + 3.0 | 33.0 | 32.1 |
| atrazine | $\text{C}_8\text{H}_{14}\text{ClN}_5$ | 22.28 (a) | 23.9 | + 07.3 | 23.1 | 22.0 |
| aclonifen (91%) | $\text{C}_{12}\text{H}_9\text{ClN}_2\text{O}_3$ | 20.45 (a) | 18.8 | - 8.1 | 19.3 | 21.0 |
| phosalone (94%) | $\text{C}_{15}\text{H}_{15}\text{ClNO}_4\text{PS}_2$ | 20.32 (a) | 17.8 | - 12.4 | 16.8 | 18.1 |
| chlormephos (96%) | $\text{C}_5\text{H}_{12}\text{ClO}_2\text{PS}_2$ | 19.10 (a) | 15.2 | - 20.4 | 15.1 | 15.6 |
| mancozebe (85%) | $(\text{C}_4\text{H}_6\text{N}_2\text{S}_4\text{Mn})\text{ZnO}$.1 | 15.62 (a) | 13.9 | - 11.0 | 13.1 | 13.4 |
| Rigid polyurethane (b) | $\text{CH}_{1.2}\text{O}_{0.22}\text{N}_{0.1}n$ (b) | 25 (c) | 27.9 | - 11.6 | 27 | 27.9 |
| Tefzel ETFE (b) | $(\text{CHF})_n$ (b) | 12.6 (b/c) | 16.2 | + 28.5 | 16.5 | 16.4 |

(a) determined by INERIS (according to AFNOR M0 003), from oxygen bomb calorimetry, corrected for water as gas and for the residue ; (b) from ref.²⁷ ; (c) determined by FMRC, from oxygen bomb calorimetry, corrected for water as gas and for the residue ; (d) from ref.¹¹ ; (e) Toluene diisocyanate ; (f) from ref.¹² ; (g) from ref.¹⁰.

Table 5 : typical prediction of net heats of combustion derived from the *Dulong*, *Boie* formulae, or by use of the *Vondracek* formula²⁴

Predictions shown in table 5 present higher relative errors, in most cases than in those of table 4, likely due to the presence of 'new' hetero-atoms like halogens and phosphorus in the sample molecules.

It must be noticed however that part of the apparent deviation between predicted values and values quoted as reference data may be attributed to the technical grades of pesticides that were used for the measurements of 'actual' heats of combustion by use of an oxygen bomb-calorimeter, whereas predicted values are derived from elemental composition of pure molecules.

Since the beginning of the 50's, both following ideas have emerged to develop new prediction methods for the heats of combustion, starting once again from the combustion science, to further improve the scope and the accuracy of the correlations presented so far :

- take account of relevant structure effect of the products on their enthalpies of combustion
- expand first generation of correlations by use of chemical databases including other hetero-atoms in their elemental composition such as the halogen elements. Examples of R&D works bringing milestones in that way have been reported by Van Krevelen²².

MORE RECENT INPUTS FROM FIRE SCIENCE AND CHEMICAL ENGINEERING

In 1986, Carozo suggested a method based on the first order correspondence between the enthalpy of combustion and the total number of carbon, correction factors being introduced for functional groups and chain branching²⁸, but the application of his method requires again fastidious calculations.

Seaton et al¹² listed a series of other contributions of the kind not reported here.

More useful looks the correlation developed by FMRC giving the net heat of combustion of chemicals according to their generic group belonging, for reason that it is to our knowledge the only one specially built in the context of fire engineering²⁷.

Based on the correlations between the heat of combustion and molecular weight of materials within each generic group, the following equation (eq. 4) has been established :

$$\Delta H_T = h_T \pm (m_T/M) \quad (4)$$

where ΔH_T is the net heat of complete combustion (kJ/g), h_T is the mass coefficient for the heat of combustion (kJ/g), m_T is the molar coefficient for the heat of combustion, a function of the heat of formation of the bonds in the material (kJ/mole) and M is the molecular weight (g/mole).

| Chemical | h_T (kJ/g) | m_T (kJ/mole) |
|--|--------------|-----------------|
| Carbon-Hydrogen Atoms (Aliphatic) | | |
| Normal Alkanes | 43.6 | +104 |
| Branched Alkanes | 43.6 | +101 |
| Cyclic Alkanes | 41.3 | +209 |
| Alkenes | 43.3 | +131 |
| Alkynes | 43.7 | +107 |
| Dienes | 42.8 | +97 |
| Carbon-Hydrogen Atoms (Aromatic) | | |
| Arenes | 37.4 | +211 |
| Carbon-Hydrogen-Chlorine Atoms | | |
| Aromatic | 17.3 | +211 |
| Carbon-Hydrogen-Oxygen Atoms (Aliphatic) | | |
| Esters | 43.8 | -1750 |
| Alcohols | 45.4 | -813 |
| Ketones | 45.0 | -888 |
| Miscellaneous | 44.0 | -1550 |
| Carbon-Hydrogen-Oxygen Atoms (Aromatic) | | |
| Miscellaneous | 39.4 | -732 |
| Carbon-Hydrogen-Nitrogen Atoms (Aliphatic) | | |
| Monamines | 44.0 | -441 |
| Polyamines | 39.1 | -441 |
| Carbon-Hydrogen-Oxygen-Nitrogen Atoms (Aromatic) | | |
| Miscellaneous | 34.1 | -1750 |
| Carbon-Hydrogen-Sulfur Atoms | | |
| Aliphatic | 39.0 | -706 |
| Aromatic | 41.3 | -793 |

Table 6 : Expression of the mass coefficient h_T and the molar coefficient M_T of the predicted net heats of combustion, for various chemical groups, according to FMRC work

The values of h_T and m_T for a selection of chemical groups are listed in Table 6. The coefficients depend on the generic nature of the material. m_T is negative for materials with oxygen, nitrogen, sulphur and halogenated atoms in the chemical structure. For materials gasifying as high molecular weight products, $\Delta H_T \approx h_T$. Calculations based on Eq. 4 have been validated via direct measurements for materials with complex chemical structures.

Example of predictive values obtained by the use of this correlation are listed in table 7:

| | Lit values | predicted values | error (%) |
|-------------|------------|------------------|-----------|
| n heptane | 44.56 | 44.6 | ~ 0 |
| n-heptene | 44.3 | 44.6 | + 0.7 |
| xylene | 40.9 | 39.4 | - 3.7 |
| ethanol | 26.8 | 27.7 | + 3.3 |
| acetone | 28.6 | 29.7 | + 3.8 |
| TDI | 23.6 | 24.0 | + 1.7 |
| acetonifene | 20.4 | 19.7 | - 3.4 |

Table 7 : example of predicted net heats of combustion using the FMRC correlation

In the chemical engineering background, sometimes requiring more accuracy than in other scientific disciplines, the most recent contribution for the development of user-friendly correlations giving net heats of combustion leads to a two step procedure according to equation 5

The expression of the net heat of combustion according to Garvin²⁹ follows :

$$\Delta H_{net, Garvin} = \sum_i a_i w_i + \sum_j b_j (n_j / M) \quad (5)$$

where w_i is the weight fraction of element i in the fuel and the coefficients a_i are given in table 8, with equivalent a'_i coefficients for the Boie formula are given for comparison. The second term is a correction factor taking account of functional group contributions according to table 8, where b_j is the group contribution factor coefficient, n_j the number of occurrences of each group and M is the chemical's molecular weight (kg.kmol^{-1}).

| | | Garvin | Boie (a) |
|---|----------|---------------|----------------|
| i | element | a_i (MJ/kg) | a'_i (MJ/kg) |
| 1 | Carbon | 36.2 | 35.16 |
| 2 | Hydrogen | 90.0 | 94.26 |
| 3 | Oxygen | - 10.6 | - 11.09 |
| 4 | Nitrogen | 8.0 | 6.28 |
| 5 | Sulphur | 10.6 | 10.465 |
| 6 | Fluorine | -3.5 | -(b) |
| 7 | Chlorine | -2.05 | -(b) |
| 8 | Bromine | -0.16 | -(b) |
| 9 | Iodine | 0.26 | -(b) |

(a) coefficients relevant for the application of modified Boie formula, where, a_H has been corrected to obtain the net heat of combustion - (b) not developed in the Boie formula

Table 8 : a_i values for the prediction of the net heat of combustion using the Garvin formula, after²⁹, (by permission)

According to Garvin's method, the first step of the procedure consists in determining the main contributing factor of the enthalpy of combustion of the product (first term of equ.5), the role of which can be directly compared to formulae of the first generation. It may be noticed that the Garvin formula, so limited to the first contribution factor behaves in a similar fashion that the Boie formula and other 'good' formulae of the first generation : these correlations all overpredict slightly the heat of combustion of pure graphitic carbon.

Table 9 gives the b_i coefficients obtained by multiregression analysis that minimises the absolute error from actual values of the products included in the database used by Garvin (458 compounds from C1 to C20, including halogenated products of all types, and satisfying the conditions of a minimum heating value of 5,000 kJ/kg. and of enough hydrogen for the conversion of Cl in HCl, F in HF, and O into water vapour.

From errors calculations quoted by the author between predicted and referenced values included in the original database (average absolute error of 1.7 % and maximum error of 16%), first step of Garvin's procedure is expected to provide estimation of the net heat of combustion good enough in most practical cases interesting the fire safety engineer.

| Functional group | b_j , (MJ/kgmol) |
|-----------------------|--------------------|
| C-C double bond | 70 |
| C-C triple bond | 190 |
| Nitrile CN | 0 |
| Carbonyl CO | 0 |
| Acid COOH | -55 |
| Ester COO | -30 |
| Amide CON | -85 |
| Nitro NO ₂ | 200 |
| Alcohol OH | 20 |
| Amine N | -30 |
| Aldehyde CHO | 60 |
| Ether O | 50 |
| Anhydride CO-O-CO | -60 |
| Benzene Ring | -15 |
| 3- Member Ring (*) | 105 |
| 4- Member Ring (*) | 90 |
| 5- Member Ring (*) | 0 |
| 6- Member Ring (*) | -40 |
| 7- Member Ring (*) | -40 |
| 9- Member Ring (*) | - 160 |

(*) not to be applied to aromatic compounds or to their aromatic substitution derivatives

Table 9 : Group contribution b_j , for eq. 5, (by permission)

Refinements of the data obtained by application of second step of the procedure will probably satisfy all fire scientists (comparisons of predicted values and actual values listed in the original database lead to average absolute error and maximum error to 0.53 and 2.7%, respectively) owing to final limitations of any other more complex calculation procedures requiring more sophisticated tools to take account of detailed energy bonds contributions, as stressed by Seaton et al.

Calculation of the predicted values of heats of combustion for most products listed in table 5 by use of the Garvin method (first step only) are summarised in table 10.

| | (without correction) | error (%) |
|---------------|-----------------------|-----------|
| TDI | 24.9 | + 5.5 |
| Nylon | 31.3 | + 1.6 |
| PVC | 17.1 | ~ 0 |
| chlorobenzene | 26.5 | ~ 0 |
| fluorobenzene | 31.1 | + 1.2 |
| isoproturon | 33.4 | + 5 |
| atrazine | 24.2 | +8.5 |
| acetonifene | 21.5 | + 4.9 |
| phosalone | 19.1 | - 6.0 |
| chloromephos | 15.0 | - 20.4 |
| mancozeb | 15.3 | - 1.9 |
| TEFZEL | 14.3 | + 13.5 |

Table 10 : predicted values of net heats of combustion for complex molecules according to Garvin²⁹

As guessed, there is a majority of cases (compounds containing high mass fractions of halogens) where predictions have been improved by comparison of performance achieved by use of the *Boie* formula. However, the heat of combustion of the organophosphorous compound is as badly predicted by both correlations, as P was not included in the databases used for the regression analysis.

Although developed in different contexts, similarities appear clearly in the two methods presented in this section. They are both taking account of structural effects, although the calculation of the massic heat of combustion and the molar heat of combustion (correction factor) are not calculated in the same way. Both may be expected to lead to the better compromise 'accuracy versus simplicity' but do not put an end to any interest of formerly developed methods in the context of fire safety studies.

CONCLUSION

The heat of combustion is often the very first thermal characteristic of materials that the fire safety engineer may wish to estimate. Although this parameter does not reveal how far and how fast this potential energy would be liberated in a fire, this data is often required in practice for various purposes, e.g. : preliminary safety studies based on the analysis of fire load, fire load densities, or more scientific purposes such as the determination of combustion efficiency of chemicals in fire conditions.

Gross or net heats of combustion may be derived from conventional experimental measurements, using oxygen bomb calorimetry or by referring to thermochemistry laws, the latter method rapidly meaning fastidious calculations or requiring specialised computational softwares.

Hopefully, in a number of cases, one may refer to tabulated values that have been compiled by previous scientists in various backgrounds (combustion science, chemical engineering, fire science). Some scatter may however be expected between values of a single product from one table to another and even -though not frequent- some erroneous values may be faced. More technical limitation regards the lack of quoted values for chemicals having complex structures including several hetero-atoms, or for technical grades of products.

Alternatively, our review has led to the selection of a number of user-friendly ways to get reasonable up to fairly accurate values of heats of combustion by simple calculations derived from regression analysis of actual measurements data or other very simple assumptions. Those methods are generally applicable provided either elemental composition, or chemical nature is known.

Our analysis finally leads to the following statement:

- Among very simple correlations of the first generation, developed from end of last century to the 50's, the *Boie* formula, validated on an extensive number of C-H-O-N-S compounds is probably the more appropriate for a reasonable accuracy in the context of fire engineering, while the *Dulong* formula (same kind of compounds) remains the best known in the combustion science. The use of *Voudracek* formulae, although of slightly more complex configuration, is also a good compromise of similar performance ;
- Increased relevance or better accuracy may yet be expected, if required, by use and further development of a new generation of correlations, such as the formula reported by Garvin taking account a large number of atoms, including the halogens, and taking account of the structure of chemicals, in terms of correcting factors. Good examples of those have been recently reported by FMRC (1995) or Garvin (1998).

It would be a valuable work to go on collecting measured data on molecules of the fine chemistry to extend predictive capabilities of both last methods presented in this section (for instance data referring to organophosphorous and organometallic compounds). Among the metallic elements, Si would also be worth being taken into consideration due to commercially-important applications of silicones based materials and their related fire problems³⁰.

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