Prediction of the Combustion Enthalpy of Municipal Solid Waste

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Abstract: It is important to discuss real-world problems when teaching a subject like thermodynamics in order to show the close relationship between classroom and laboratory work and chemistry as practiced. This manuscript describes the application of thermochemical concepts to the study of a real-world problem: the prediction of the combustion enthalpy of municipal solid waste. Two equations based on thermochemical concepts and two purely empirical formulas that are broadly used in combustion technology are compared with experimental data. Agreements and disagreements are analyzed. This problem is intended for the first physical chemistry course.

Introduction

Thermodynamics is one of the cathedrals of science [1]. As is well-known, its elegance is the result of only three fundamental laws, its treats an enormous body of experimental data, and there are absolutely no known exceptions. To the neophyte, ignorant of thermodynamics's rich history, this Euclidean perfection can be overwhelming seemingly reduces a student to only an onlooker. To involve the student in the study of thermodynamics, it is important to discuss real-world problems that show the current relevance of thermodynamics. The social problem concerning large quantities of municipal solid waste (MSW) and how to handle all of this waste is an important issue, and it provides a number of opportunities to apply thermodynamics.

Society faces an overwhelming problem that concerns the elimination (storage) and recovery (materials and energy) of MSW. An enormous amount of MSW is produced daily [2a, 3a], for instance, Mexico City produces ~12,000 tons per day of MSW [4]. Typical compositions of MSW for some countries are presented in Table 1. MSW composition is the term used to describe the individual components that make up MSW and their relative distribution. Notice in Table 1 that a higher percentage of food waste is associated with less-industrialized nations, undoubtedly because in these countries most food is not packaged for their sale; thus, paper and plastic consumption is smaller than in industrialized nations.

An interesting option in waste management and energy recovery is the combustion of MSW. Besides the liberated energy, this process also reduces MSW mass by up to 70% and MSW volume by up to 85%. This combustion usually occurs above 1,123 K in the presence of air to ensure the oxidation of organic compounds [6a]. In order to evaluate the resource-recovery and energy-generating alternatives, it is necessary to have an estimation of the heat released by MSW combustion; however, it is pertinent to point out that the term heat of reaction is rarely employed in MSW combustion technology. The two terms most frequently used in this field are: (i) the gross (or higher) heating value, HHV, and (ii) the net (or lower) heating value, LHV [3b, 7a]. The HHV represents the enthalpy change when a compound is stoichiometrically burnt at a reference temperature with the final products also at the reference temperature and any water present in the liquid state. In this manuscript, HHV and enthalpy of combustion will be used interchangeably. The LHV is similar to the gross heating value except that the water is in the vapor state, and so the difference (if any) between the two values represents the energy necessary to vaporize any water present. Most of the data currently available are given at a reference state of 289 K and 1 atm; moreover, there is only a small difference between this enthalpy change and that at the standard conditions, 298 K and 1 bar. Thus, it is generally considered that the values data are in reasonable agreement [7b, 8]. Typical HHV data (from calorimetric pump tests [9]) at standard conditions of the principal MSW constituents, their reduced chemical composition, and water content are given in Table 2. Some important observations concerning Table 2 are the following.

i) MSW can be thought of as a combination of semi-humid combustible and noncombustible materials. Indeed, the materials in the last three rows of Table 2 are largely inorganic in nature and resistant to combustion, while the other ones are primarily organic substances and consequently susceptible to oxidation.

ii) The enthalpy of combustion varies enormously for each kind of waste, and also a high water content decreases the recoverable energy; therefore, from the point of view of energy recovery, the combustion of food and yard wastes is less interesting than the combustion of paper, plastics, textiles, and wood.

iii) During combustion, the mineral waste fraction is essentially transformed into clinker, and consequently there is always a solid residue (ash) with a high metal concentration. In order to prevent other environmental problems, the residue from MSW combustion must be stored with utmost care [2b, 3b]. For this reason, the introduction of primarily inorganic wastes into a combustion chamber is not recommended because not only does it not contribute to energy liberation, but it also increases the final ash mass. Recovery and reuse of glass and metal waste is usually a good option [3c].

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Table 1. Examples of Typical MSW Composition (mass percentages as discarded) (Adapted from References [2a, 4, 5])

Waste	Colombia %	France %	Mexico %	USA %
Food	56	21	39	9
Paper	22	36	22	40
Plastics	5	7	6	8
Textiles	4	5	2	2
Wood	5	4	1	2
Yard	5	6	6	19
Glass	2	11	8	8
Metals	1	5	4	9
Ash, rock, and dirt	--	5	12	3

Table 2. Typical Water Content, Ultimate Analysis, Reduced Formula, and Combustion Enthalpy for the Principal MSW Components (Adapted from [2b, 3b])

Waste	(% H_2O)[a]	(%C)[b]	(%H)[b]	(%O)[b]	(%N)[b]	(%S)[b]	(% Ash)[b]	Reduced formula on dry basis	HHV (MJ kg^{-1})
Food	70.0	48.0	6.4	37.6	2.6	0.4	5.0	$C\,H_{1.6000}\,O_{0.5875}\,N_{0.0464}\,S_{0.0031}$	–5.5120
Paper	6.0	43.5	6.0	44.0	0.3	0.2	6.0	$C\,H_{1.6552}\,O_{0.7586}\,N_{0.0059}\,S_{0.0017}$	–15.8000
Plastics	2.0	60.0	7.2	22.8	0.0	0.0	10.0	$C\,H_{1.4400}\,O_{0.2850}\,N_{0.0000}\,S_{0.0000}$	–32.5640
Textiles	10.0	55.0	6.6	31.2	4.6	0.2	2.5	$C\,H_{1.4400}\,O_{0.4255}\,N_{0.0717}\,S_{0.0014}$	–17.2445
Wood	20.0	49.5	6.0	42.7	0.2	0.1	1.5	$C\,H_{1.4545}\,O_{0.6470}\,N_{0.0035}\,S_{0.0008}$	–18.6080
Yard	60.0	47.8	6.0	38.0	3.4	0.3	4.5	$C\,H_{1.5063}\,O_{0.5962}\,N_{0.0610}\,S_{0.0024}$	–6.5130
Glass[c]	2.0	0.5	0.1	0.4	0.1	0.0	98.9	$C\,H_{2.4002}\,O_{0.6001}\,N_{0.1714}\,S_{0.0000}$	–0.1400
Metals[c]	3.0	4.5	0.6	4.3	0.1	0.0	90.5	$C\,H_{1.6000}\,O_{0.7167}\,N_{0.0191}\,S_{0.0000}$	–0.6980
Ash, rock, dirt	8.0	26.3	3.0	2.0	0.5	0.2	68.0	$C\,H_{1.3688}\,O_{0.0570}\,N_{0.0170}\,S_{0.0029}$	–6.9780

[a] Mass percent on a wet basis.

[b] Mass percent on a dry basis.

[c] Organic content can come from coatings, labels and other attached materials

In practice, the enthalpy of combustion of a solid mixture is not usually determined by calorimetric pump tests. Instead, due to the actual availability of various fast and reliable instrument packages for ultimate analysis, HHV is usually obtained via entirely empirical relationships between reduced chemical composition and combustion enthalpy. This kind of relationship has been very useful in combustion technology; nevertheless, its pedagogic contribution to the teaching of thermodynamics is poor. This is why two more fundamental approaches will also be presented here. In the first one, the HHV is approximated as a function of the standard enthalpies of formation of CO_2, H_2O, NO_2, and SO_2. In the second one, the HHV is approximated through the mass and electronic balances of a hypothetical anaerobic fermentation reaction of the fuel to CH_4 and CO_2, followed by the combustion of the methane. The arguments for both frameworks will be introduced and discussed afterwards.

This manuscript presents the material as follows. First, two purely empirical formulations widely used in industrial work are discussed. Second, two formulations based on thermochemical concepts are presented. Third, for the different MSW components, the computed HHV results using both thermochemical and empirical equations are compared with experimental data. Also, the enthalpies of combustion of MSW with different compositions, those given in Table 1, are calculated via empirical and fundamental approaches. The differences among the HHV predictions of the diverse formulations are analyzed and discussed here. In such a way, this work presents an exercise about the application of thermochemical concepts to a real-world problem. All these procedures can be used in a first-year physical chemistry course.

Empirical Approach

Physical chemistry texts provide the necessary tools to calculate the enthalpy of combustion of pure substances (see, e.g., [10a]); however, this traditional framework is not truly appropriate for calculation of the combustion enthalpy of a complex mixture. Hence, in the absence of calorimetric data, the HHV of a combustion mixture may be estimated by using one of the several equations specifically developed previously for this purpose. In these treatments, the fuel chemical composition is usually given in terms of mass percent, on a dry basis, of carbon (% C), hydrogen (% H), oxygen (% O), nitrogen (% N), and sulfur (% S) (see Table 2). The HHV is then calculated through a linear combination of these quantities. For instance, Lloyd and Davenport [11] subjected 138 fossil fuels to a multiple regression analysis, a least-squares fit, of enthalpy of combustion as a function of elemental composition, forcing the fit through the origin. The resulting equation was:

$$\mathrm{HHV} = \left(1 - \frac{\%\mathrm{H_2O}}{100}\right) \begin{pmatrix} -0.3578(\%\mathrm{C}) - 1.1357(\%\mathrm{H}) + 0.0845(\%\mathrm{O}) \\ -0.0594(\%\mathrm{N}) - 0.1119(\%\mathrm{S}) \end{pmatrix} \tag{1}$$

Another mathematical correlation that is widely used in combustion technology was developed by Boie [12]; it has the form:

$$\mathrm{HHV} = \left(1 - \frac{\%H_2O}{100}\right) \qquad (2)$$
$$\begin{pmatrix} -0.3517(\%C) - 1.1625(\%H) + 0.1109(\%O) \\ -0.0628(\%N) - 0.1109(\%S) \end{pmatrix}$$

The units of all the HHV quantities in this manuscript are MJ kg^{-1}; and following [10a] the adopted sign convention is: work done by the system is taken to be a negative quantity.

As already discussed, empirical formulations are very useful to anticipate the system behavior, but they are not justified from a fundamental point of view, and so their educative significance is not really appropriate for the teaching of thermodynamics. More understandable and fundamental approaches will be introduced in the next section.

Formulas Based On Thermochemical Concepts

A formula based on thermochemical concepts for HHV prediction of organic wastes was developed by Wilson [13] as follows.

$$\mathrm{HHV} = \left(1 - \frac{\%H_2O}{100}\right) \qquad (3)$$
$$\begin{pmatrix} -0.3279(\%C) - 1.4292(\%H - \%O/8) - 0.0928(\%S) \\ +0.0242(\%N) - 0.1038(\%H - \%O/8) - 0.0248(\%O) \end{pmatrix}$$

The main thermochemical concepts assumed in this equation are

i) When oxygen is present, it is assumed that all this oxygen is associated with hydrogen to form water with excess hydrogen available for combustion. This quantity is estimated through the expression “%H – %O/8”. Note that the coefficient of the oxygen term is one-eighth that of the hydrogen term, that is, as the mass proportion of the water molecule.

ii) By definition, complete combustion of a fuel involves the conversion of carbon to CO_2, available hydrogen to H_2O, sulfur to SO_2, and nitrogen to NO_2. The standard enthalpy values –393.509, –142.915, –296.830, and +33.85 kJ mol^{-1} correspond, respectively, to the formation of one mole of CO_2(g) from graphite carbon, half a mole of H_2O(l) from available hydrogen, one mole of SO_2(g) from sulfur, and one mole of NO_2(g) from nitrogen and oxygen gases [10b]. This information is normalized to a kilogram of reactant and included in the coefficients of the four first terms on the right side of eq 3. Note that all the coefficients in all the equations included in this work are given in order to approximate the HHVs as a function of the mass percents shown in Table 2.

iii) The last two terms on the right side of eq 3 arise from the fact that in a MSW sample, hydrogen and oxygen are not present as gases, but are bonded to other elements. Assuming that all available hydrogen is bonded to carbon, the enthalpy associated with the formation of hydrogen gas is –20.7652 mJ kg^{-1} [13]. Because hydrogen in the reduced formula is H and not H_2, the available hydrogen concentration must be divided by two before multiplying by –20.7652 MJ kg^{-1}, that is, the corresponding factor is –10.3826 mJ kg^{-1}. Besides, the energy released during formation of oxygen gas is determined similarly as for hydrogen gas and the corresponding factor is found to be –2.4849 mJ kg^{-1} [13]. Notice the similarity among the coefficients of eqs 1, 2 and 3, making it logical to expect similar behaviors.

An alternative framework that is also based on thermochemical concepts will now be introduced. It is pertinent to remember that anaerobic digestion is a process to recover the energy contained in organic materials in the form of methane [14]. To start, let us establish a hypothetical transformation reaction from an electrically neutral organic reactant of reduced formula $CH_aO_bN_cS_d$ to methane and carbon dioxide, in the form

$$CH_aO_bN_cS_d\,(s) \rightarrow v\,NO_2(g) + w\,SO_2(g) + x\,CH_4(g) + y\,CO_2(g) + z\,H_2O(l) \qquad (4)$$

In this equation methane is the only reduced product, so the calculation of the stoichiometric coefficients in this equation leads to the derivation of the HHV of the organic reactant as the liberated energy due to the combustion of the methane produced. Obviously, any hydrocarbon-saturated compound could be chosen, but methane is the simplest saturated hydrocarbon and its standard enthalpy of combustion is well-known, –890.36 kJ mol^{-1} [10c]. It is important to keep in mind that hydrogen has an oxidation state of +1, oxygen has an oxidation state of –2, and the electric charge of the organic reactant $CH_aO_bN_cS_d$ is zero. Some assumptions concerning the initial oxidation degrees of nitrogen and sulfur are also necessary. As shown in Table 2, these elements are commonly present in relatively small amounts, but their initial oxidation states are unknown. In this respect, let us presume that: (i) the nitrogen initial oxidation state is –3, like in amine and amide compounds and (ii) the sulfur initial oxidation state is –2, like in a thiols. Using these assumptions, the average initial oxidation state of carbon is 2d + 3c + 2b – a.

From the definition of combustion, nitrogen and sulfur are oxidized to NO_2 and SO_2, respectively. So, through the hypothetical transformation represented by eq 4, the oxidation states of nitrogen and sulfur are changed from –3 to +4 and from –2 to +4, respectively. Consequently, the final average carbon oxidation state is –4d – 4c + 2b – a. In addition, within the products of eq 4, the carbon oxidation state is globally the same. This equality is established as

$$4(y - x) = -4d - 4c + 2b - a \qquad (5)$$

Therefore, methane’s yield by mole of gasified organic carbon, $x + y = 1$, is

$$x = \frac{4d + 4c - 2b + a + 4}{8} \qquad (6)$$

The HHV is finally obtained by multiplying methane’s yield by the standard methane combustion enthalpy. The resulting equation, normalized to one kg of reactant is:

$$\mathrm{HHV} = \left(1 - \frac{\%H_2O}{100}\right)(-0.0927)(\%C)(4d + 4c - 2b + a + 4) \qquad (7)$$

The values of a, b, c and d for the various MSW components are presented in Table 2. In the next section, the HHVs

Table 3. Enthalpy Combustion Values of Computed and Calorimetric MSW Components (MJ kg^{-1})

Waste	Eq 1	Eq 2	Eq 3	Eq 7	Experimental
Food	–6.4395	–6.1078	–5.7756	–6.1714	–5.5120
Paper	–17.5787	–16.3892	–15.1647	–15.8006	–15.8000
Plastics	–27.1641	–26.4046	–26.3698	–26.5452	–32.5640
Textiles	–22.3505	–21.4803	–20.5691	–22.3986	–17.2445
Wood	–16.7522	–14.6480	–15.7379	–15.3352	–18.6080
Yard	–8.3766	–7.9275	–7.3911	–8.0948	–6.5130
Glass	–0.2593	–0.2489	–0.2431	–0.2673	–0.1400
Metals	–1.8761	–1.7753	–1.6253	–1.7168	–0.6980
Ash, rock & dirt	–11.6843	–11.5635	–11.8639	–11.9580	–6.9780

Table 4. Computed (eq8) global combustion enthalpy of MSW in MJ kg^{-1}

From	Colombia	France	Mexico	U.S.A
Eq 1	–11.0060	–12.5789	–10.6236	–12.6979
Eq 2	–10.3569	–11.8610	–10.1022	–11.9731
Eq 3	–9.8894	–11.3207	–9.6913	–11.3474
Eq 7	-10.3493	–11.7745	–10.0877	–11.8276
Experiment	–10.1465	–11.5215	–9.3778	–11.6591

obtained from eqs 1, 2, 3, and 7 are compared with experimental calorimetric data.

Numerical application

In Table 3 the results obtained from the numerical application using data given in Table 2 of eqs 1, 2, 3, and 7 are compared with experimental values. In general, there is good agreement between calorimetric data and computed values. Indeed, all the equations follow the same qualitative behavior with respect to the path followed by experimental data. Note, however, that the HHVs of plastics and wood are underestimated by all the equations, and the HHVs of the other MSW components are generally overestimated. Also, the major differences between computed and calorimetric HHV data are detected for the case of primary inorganic materials, like glass, metals, and ash, rock, and dirt, with relative differences between the arithmetic mean of all four computed values and experimental data of 0.45, 0.60, and 0.41, respectively.

Certainly, a more precise chemical composition characterization should improve the prediction of the MSW component's combustion enthalpies. For instance, the single composition values given in Table 2 represent the entire category of plastics; more realistically, the composition of plastics ranges dramatically as a function of the plastic type [6b]. Moreover, because MSW components, especially ash, rock, and dirt often contain carbonate carbon, the computed values in Table 3 are overestimated. This error can be corrected with the inclusion in eq 3 of the endothermic decomposition of calcium carbonate, assuming that all carbonates in solid-waste samples are calcium carbonates [13] and introducing solely the organic carbon content into the other equations. This correction is not made here, because it includes the experimental determination of the inorganic carbon content. This determination is, however, not commonly made in combustion technology, and it means an additional manipulation of the reactant, which could be a real inconvenience in the case of a mixture so disagreeable to manipulate as MSW. Finally, it is pertinent to point out that in glass and metal wastes the organic content is made up of coatings, labels, and other attached materials; so, it is judicious to think that in these systems, combustion development during the HHVs calorimetric determination could be hindered due to poor organic content and heterogeneous repartition of organic matter.

With respect to the global MSW enthalpy combustion, experience suggests that this value can be approximated as

$$\mathrm{HHV} = \sum_i f_i \mathrm{HHV}_i \tag{8}$$

Where f_i and HHV_i represent the mass fraction and the enthalpy of combustion, respectively, of the ith MSW component. The HHV_i are given in Table 3, and the f_i can be easily derived from Table 1. For example, in the case of MSW from American cities, the calorimetric HHV data are regularly positioned in the range 11.600 to 12.100 MJ kg^{-1} [3d], and there is good agreement with the results predicted by eq 8. These results are presented in Table 4. The combustion enthalpy of MSW from industrialized countries is greater than the HHV of less-industrialized countries, fundamentally because of the larger paper content found in MSW from industrialized nations. Even so, from our evaluations, paper waste always represents a very important part of the combustion enthalpy of MSW, that is, about 60% of the total HHV. This is in agreement with the results presented by Khan and Abu-Ghararah [15].

Conclusions

The enthalpy of combustion is a measure of the energy available from a fuel. An appropriate knowledge of this value is essential for assessing the commercial worth of a refuse-derived fuel and for providing the basis of a commercial contract between producer and user. Physical chemistry texts provide the necessary tools needed to calculate the combustion enthalpy of pure substances; however, these tools are insufficient in the case of a solid complex mixture such as MSW. Due to the current availability of several fast and reliable instrument packages for ultimate analysis, the prediction of the combustion enthalpy of a fuel is commonly made under the assumption of purely empirical relationships, characterized by restricted applicability and poor significance in the teaching of thermodynamics, between chemical composition and combustion enthalpy. Nevertheless, there equations based on thermochemical concepts that give similar results to those obtained via empirical equations do exist, but with the fundamental advantage of providing a logical framework for chemistry students and more global applicability. By comparing the HHV values from empirical and fundamental equations with experimental calorimetric data, we have presented an example of the application of thermochemical concepts to contribute to the solution of a real-world problem. The study of real-world problems attracts the attention of neophytes by showing a close relationship between classroom and laboratory work and the solutions to real problems. This exercise can be used in first-year physical chemistry.

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