Oxygen consumption as the definitive factor in predicting heat of combustion

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Highlights

• The role of bond energies in combustion is analysed.

• Oxygen bond energy is a major contributor towards HHV of fuels.

• The proposed correlation is valid for a wide range of gaseous, liquid and solid fuels.

• The correlation is only a function of mass fraction of oxygen required for combustion.

• The correlation is simple, yet accurate, leading to useful insights in fuel development.

Abstract

An accurate correlation for estimating higher heating value (HHV) as a function of the mass fraction of oxygen consumed by combustion is presented. In its derivation, a theoretical and quantitative approach based on the reduction/oxidation half-reactions of the combustion reaction is used. The derivation relates HHV to changes in bond dissociation enthalpies with respect to the oxygen species and fuel elements. HHV is found to be a strong proportional function of changes in bond enthalpies with respect to the oxygen species compared to the other fuel elements, and may be described simply as $\Delta_c h°|_{\text{HHV}} = -13.87\, m_{O_2} - \Delta h_{\text{vap}}$ (MJ kg^{-1}), where m_{O_2} is the mass of oxygen required for combustion per $1\,\text{kg}$ of fuel. The constant is a simplification of a modifier function $\mu_{D_H} = -13.87\, e^{-0.092\, x_{O_2}}$ (MJ kg^{-1}) (being a function of the mass fraction of oxygen consumption only) that is used to reduce the complexity of the theoretical equation describing the heat of combustion. This yields a correlation for the heat of combustion $\Delta_c h°|_{\text{HHV}} = \mu_{D_H} m_{O_2} - \Delta h_{\text{vap}}$ (MJ kg^{-1}), which may also be expressed as $\Delta_c h°|_{\text{HHV}} = \frac{x_{O_2}}{1 - x_{O_2}} \mu_{D_H} - \Delta h_{\text{vap}}$ (MJ kg^{-1}). Using 1087 fuel combustion data of wide chemical composition based on the chemical formula of $C_{v_C} H_{v_H} O_{v_O} N_{v_N} S_{v_S} P_{v_P}$, the resulting correlation is shown to perform well statistically, with $R^2 = 0.98$, RMSE = 1.5 MJ kg^{-1}, and MBE = 0.0 %. Applying the proposed correlation, HHV was found to be much more sensitive to changes in oxygen content in the fuel than for similar changes in carbon and hydrogen content. Energy quality of fuels, especially in the production of biofuels that make use of highly oxygenated feedstock, should therefore rely on reducing oxygen content in the fuel via deoxygenation pathways such as decarboxylation and decarbonylation while avoiding routes that sacrifice hydrogen (such as hydrodeoxygenation and dehydrogenation).

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1. Introduction

Energy resources have been an indispensable part of our existence since their earliest discovery. With the onset of the industrial revolution in England during the 1800s, which subsequently spread to other coal-rich continental European countries (mainly Germany and France) and the United States, energy technologies and products saw vast improvements [1]. It was also in the United States where the modern-day inception of the global "oil age" occurred, beginning around 1859 and lasting up until now [2]. More recently the finite abundance of fossil fuel reserves has posed a serious risk to global energy security and has consequently encouraged the progression towards more renewable sources of energy that in turn rely on similarly renewable feedstocks such as biomass – the dominant energy form of antiquity [3]. Although often cited as non-renewable, fossil fuels nevertheless found their genesis in the incomplete degradation of renewable biomass via reductive reaction pathways [4]. Associated with this is the oxidative pathway of combustion applied to biomass- and fossil fuel-related entities by which their energy potential is redeemed via the reaction with atmospheric oxygen. Combustion reactions are exothermic reduction-oxidation (redox) reactions [5], and it is via these pathways of oxidation and reduction that we harness the energy from the energy stores that are fossil fuels, biomass, electrochemical fuel cells, and the like. Combustion of fossil fuels however also results in the release and accumulation of CO_2 in the atmosphere, which exacerbates and has become synonymous with climate change, and is yet another reason for the need to adopt more sustainable energy practices.
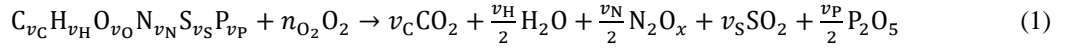
Adoption of biomass-based energy technologies is not without its challenges. Realizing the same degree of technological advancement as achieved with fossil fuels in the past is crucial for successful implementation of these technologies [3,6,7]. Most notable is the high oxygen content present in terrestrial biomass feedstock, as cellulose, hemicellulose and lignin all comprise an abundance of oxygenated substituents (as carboxylic acids, hydroxyls, ethers, and ketones) [8]. The adverse effects of oxygenates present in biofuels derived from woody biomass is well documented. The presence of carboxylic acids in pyrolysis oils for example (such as from the liberation of acetyl groups of xylan during thermochemical processing) increases their corrosivity and instability [9,10,11], and is quantified by either the total acid number (TAN) or acid number (AN) of the fuel [12,13]. Oxygenates in biofuels likewise impacts negatively on their heating value by reducing the oxidation potential. Measurement and estimation of the higher heating value (HHV) of fuels are crucial during the first stages of fuel utilization and valorization, in the design, analysis and control of energy systems, and in the efficient generation of heat and power on an industrial scale. Although experimental methods are the most reliable means of determining HHV, this is not always possible, and often requires indirect methods of approximation [13].

There have been many past attempts at correlating the heat of combustion of fuels with either the physical properties and composition of the fuel and/or the oxygen required for combustion, with most applicable to coal combustion. Dulong's correlation of 1880 (first published by Mott & Spooner [14] in 1940) was perhaps one of the first empirical correlations available for estimating the HHV of coal [14], and correlates HHV with the mass percentages of carbon, hydrogen, oxygen and sulfur in coal by means of correlation coefficients. Modified versions of this correlation were proposed (Strache & Lant, 1924 [15]; D'Haurt *et al.*, 1930 [16]) where the association of oxygen with carbon and hydrogen is considered (Steuer, 1926, [16]; Sumegi, 1940 [17]), and the effect of nitrogen is introduced (Dulong-Berthelot [16]). Several more empirically-derived correlations are available in the literature that make use of elemental analyses, which include nitrogen effects for coal (Gumz, 1938 [18]), assume specific associations of oxygen with carbon and hydrogen in coal (Mott & Spooner, 1940 [14]), and have more general applications such as for hydrocarbons (Boie, 1953 [19]), solid municipal waste (Khan & Abu-Gharah, 1991 [20]), waste water sludges (Niessen, 1995 [21]) and pure organic compounds (Chang, 1979 [22]). Grabosky & Bain assumed that all elements constituting fuels are responsible for the HHV and came up with a correlation based on elemental composition of C, H, S, and N [14]. Demirbaş *et al.* [23] similarly proposed a correlation for use with lignocellulosic materials and makes use of correlation coefficients close to the HHV for carbon and hydrogen, as well as the average bond dissociation enthalpy of oxygen (although it is unclear whether this was intended) and includes nitrogen, while the correlation by Beckman *et al.* is intended for use with biomass-derived oils [16]. Further correlations exist that include thermodynamic considerations and heating values for elements (Wilson, 1972 [24]) and bond dissociation enthalpies with respect to carbon (Vondrecek, 1927 [25]). Channiwala & Parikh offer a more general correlation applicable over a wide range of gaseous, liquid and solid fuels, and provides an in-depth background on the development of most correlations discussed here [16]. A less popular approach is to correlate HHV proportional to oxygen consumed with combustion while also taking into account the oxygen content of the fuel and few correlations are based on this approach are available in the literature (Schuster, 1931; Grummel & Davis, 1933 [16]; Schmidt-Rohr, 2015 [26]).

The commonality of the afore-mentioned correlations, being mostly empirical, is in that they all fail to explain adequately the thermodynamic fundamentals of the combustion process. Attempts at applying certain concepts are made, such as using heats of formation (which are themselves mostly derived from heats of combustion), bond dissociation enthalpies and the association of atoms with each other. The matter is discussed in much detail by Schmidt-Rohr [26], who demonstrates semi-quantitatively that the exothermicity of the combustion reaction is due to the weaker bonds in diatomic oxygen forming much stronger bonds in the combustion products of water and CO_2, while bond changes of the fuels play only a minor role. Schmidt-Rohr further demonstrates the proportionality between HHV and oxygen consumed, with a correlation of the lower heating value (LHV) of fuels on a mole basis, as $\Delta_c H^{\circ}{}_m|_{LHV} = -418\,n_{O_2}$ (MJ kmol^{-1}) where n_{O_2} is the moles of oxygen required for combustion. The complexity of most fuel oils and the feedstock from which they are derived do not easily allow for the determination of these quantities on a molar basis. Nonetheless, the implication of this relationship is simple: the heat of combustion is directly proportional to the oxygen required by combustion, and the latter depends on the composition of the fuel. From a thermodynamic consideration, this implies that all reactants (i.e. fuel and oxidant) prescribe the thermochemical outcomes of combustion processes and are equivalent to the redox reactions governing electrochemistry. It is therefore worth considering the mutual inclusiveness of oxygen and fuel with respect to the outcomes of the combustion process and consider the respective reduction and oxidation half reactions. Doing so would provide further guidelines and insight into the development of biofuels to improve and enhance the energy quality required from them. Here, we define energy quality of combustible substances as the quantity of energy released per unit matter, either on the mass, mole, or volume basis.

2. Thermodynamic Derivation of Heat of Combustion

Consider the combustion of a fuel with chemical formula $C_{v_C} H_{v_H} O_{v_O} N_{v_N} S_{v_S} P_{v_P}$ in oxygen, which is described by the reaction

$$C_{v_C} H_{v_H} O_{v_O} N_{v_N} S_{v_S} P_{v_P} + n_{O_2} O_2 \rightarrow v_C CO_2 + \frac{v_H}{2} H_2O + \frac{v_N}{2} N_2 O_x + v_S SO_2 + \frac{v_P}{2} P_2 O_5 \qquad (1)$$

where, based on 1 mol fuel, the oxygen required for combustion is

$$n_{O_2} = v_C + \frac{v_H}{4} + \frac{x v_N}{4} + v_S + \frac{5 v_P}{4} - \frac{v_O}{2} \qquad (2)$$

The heat liberated by Reaction (1) at standard conditions $\Delta_c H^{\circ}_m$ may be evaluated with some degree of accuracy as the difference in the sum of bond dissociation enthalpies $D_{H,m}(j,T)$ of reactants and products:

$$\Delta_c H^{\circ}{}_m \approx \sum_{i,reactants} v_i \sum_j D_{H,m}(j,T) - \sum_{i,products} v_i \sum_j D_{H,m}(j,T) \qquad (3)$$

where $\sum_j D_{H,m}(j,T)$ represents all bond cleavages and formation j with respect to component i. In the case of H_2 combusting with O_2 according to the reaction:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$
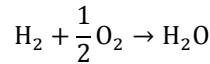
$\Delta_c H^{\circ}_m$ is calculated as:

$$\Delta_c H^{\circ}{}_m \approx D_{H,m}(H-H)_{H_2} + n_{O_2} D_{H,m}(O=O)_{O_2} - 2\frac{v_H}{2}\frac{2}{3} D_{H,m}(O-H)_{H_2O} - 2\frac{v_H}{2}\frac{1}{3} D_{H,m}(O-H)_{H_2O} \qquad (4)$$

which assumes that the bond enthalpies are shared equally between the respective atoms and the product is in the vapour phase. By rearranging Equation (4), the total change in the bond dissociation energy with respect to the hydrogen species, $\Delta_c D_{H,m}(H)$, may be expressed as:

$$\Delta_c D_{H,m}(H) = D_{H,m}(H-H)_{H_2} - 2\frac{v_H}{2}\frac{2}{3} D_{H,m}(O-H)_{H_2O} \qquad (5)$$

Evaluation of Equation (5) yields $\Delta_c D_{H,m}(H) = -180.0$ MJ kmol^{-1}. Similarly, for the oxygen species, $\Delta_c D_{H,m}(O) = -59.0$ MJ kmol^{-1}. Summation of $\Delta_c D_{H,m}(H)$ and $\Delta_c D_{H,m}(O)$ yields $\Delta_c H^{\circ}{}_m(H_2)|_{calc.,LVH} \approx -239.0$ MJ kmol^{-1}. This value is close to the measured LHV of $\Delta_c H^{\circ}{}_m(H_2)|_{meas.,LHV} = -245.2$ MJ kmol^{-1}. The hydrogen bonding in the condensed product (H_2O) is significant, being 16.4 % of the total HHV measured for

hydrogen, at ~ -46.7 MJ kmol^{-1}. It just so happens that the difference between LHV and HHV is also 16.4 %. If hydrogen bonding present in the product $n_{\text{bonds}}(\text{H}\cdots\text{O})\overline{D}^{\circ}_{H,m}(\text{H}\cdots\text{O})\frac{v_H}{2}$ is included in Equation (4), the HHV may be easily determined as $\Delta_c H^{\circ}_{m}(\text{H}_2)|_{\text{calc.,HHV}} = -285.7$ MJ kmol^{-1}, which is only 0.4 % larger than the measured HHV of $\Delta_c H^{\circ}_{m}(\text{H}_2)|_{\text{meas.,HHV}} = -284.6$ MJ kmol^{-1}. Similarly for the combustion of methane, where $\Delta_c H^{\circ}_{m}(\text{CH}_4)|_{\text{meas.,HHV}} = -890.7$ MJ kmol^{-1}, $\Delta_c H^{\circ}_{m}(\text{CH}_4)|_{\text{calc.}}$ may be determined by the following Equation:

$$\Delta_c H^{\circ}_{m}(\text{CH}_4)|_{\text{calc.}} = \Delta_c D_{H,m}(\text{C}) + \Delta_c D_{H,m}(\text{H}) + \Delta_c D_{H,m}(\text{O}) - \Delta_c D_{H,m}(\text{H}\cdots\text{O}) \tag{6}$$

This gives $\Delta_c H^{\circ}_{m}(\text{CH}_4)|_{\text{calc.}} = -895.4$ MJ kmol^{-1}. When evaluating $\Delta_c H^{\circ}_{m}(\text{CH}_4)|_{\text{calc.}}$, it is realized that $\Delta_c D_{H,m}(\text{O}) = -689.3$ MJ kmol^{-1}, while $\Delta_c D_{H,m}(\text{fuel}) = -112.7$ MJ kmol^{-1} [$\Delta_c D_{H,m}(\text{C}) = 289.3$ MJ kmol^{-1} and $\Delta_c D_{H,m}(\text{H}) = -402.0$ MJ kmol^{-1}]. Heat liberated during methane combustion is therefore primarily due to oxygen being reduced to the combustion products CO_2 and H_2O and accounts for 86.0 % of the total heat of combustion of methane. In fact, of the 359 fuels evaluated in this way [27,28], only 9 fuels (2.5 %, mass basis) had an oxygen contribution towards $\Delta_c h^{\circ}|_{\text{calc.}}$ of less than 100 % (Fig. 1A). Some carbonaceous fuels for instance have changes in dissociation enthalpy of carbon that results in a negative contribution towards the heat of combustion of more than 100 %, while the contribution by hydrogen is only modest, between -2 % and 16 %.
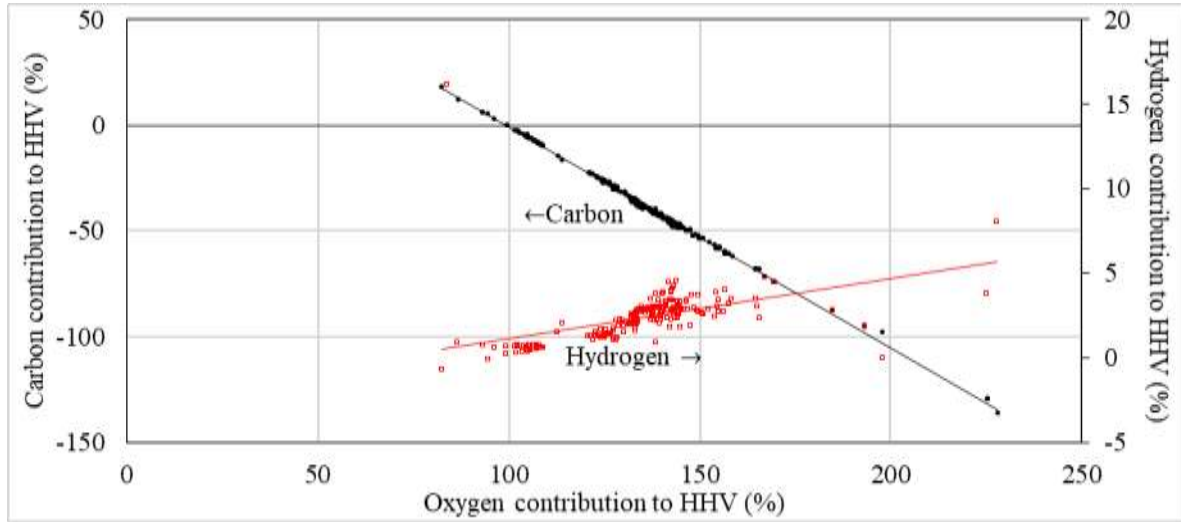

Figure 1: Comparison between the contribution of O$_2$ required for combustion and C, and H in fuel to $\Delta_c h^{\circ}|_{\text{calc.}}$

By applying the rearrangement of Equation (6) to Equation (3) and dividing by the molar mass of fuel one obtains an expression that describes $\Delta_c h^{\circ}$ on a mass basis:

$$\Delta_c h^{\circ}|_{\text{HHV}} = \Delta_c D_H(\text{fuel}) + \Delta_c D_H(\text{O}_2) - \Delta_c D_{H,m}(\text{H}\cdots\text{O}) + \Delta_{RS} h^{\circ} \tag{7}$$

Here $\Delta_{RS} h^{\circ}$ represents resonance energies that may be significant depending on the bond configurations. It is helpful to consider the half-reactions related to the changes in bond enthalpies expressed in Equation (7). In the case of methane, the oxidation and reduction half-reactions are, respectively:

i. $\quad \text{C}^{4-} \rightarrow \text{C}^{4+} + 8e^{-} \qquad (\Delta_r h^{\circ} = +289.3 \text{ MJ kmol}^{-1})$
ii. $\quad 2\text{O}_2 + 8e^{-} \rightarrow 4\text{O}^{2-} \qquad (\Delta_r h^{\circ} = -689.3 \text{ MJ kmol}^{-1})$
iii. $\quad 4\text{H}^{+} \rightarrow 4\text{H}^{+} \qquad (\Delta_r h^{\circ} = -402.0 \text{ MJ kmol}^{-1})$

Repetition of this exercise for all 359 data points analyzed shows that the reduction of oxygen always results in a negative (exothermic) change in bond dissociation enthalpy, while the oxidation of carbon almost always results in a positive (endothermic) change in bond dissociation enthalpy apart from three data points (Fig. 2A).
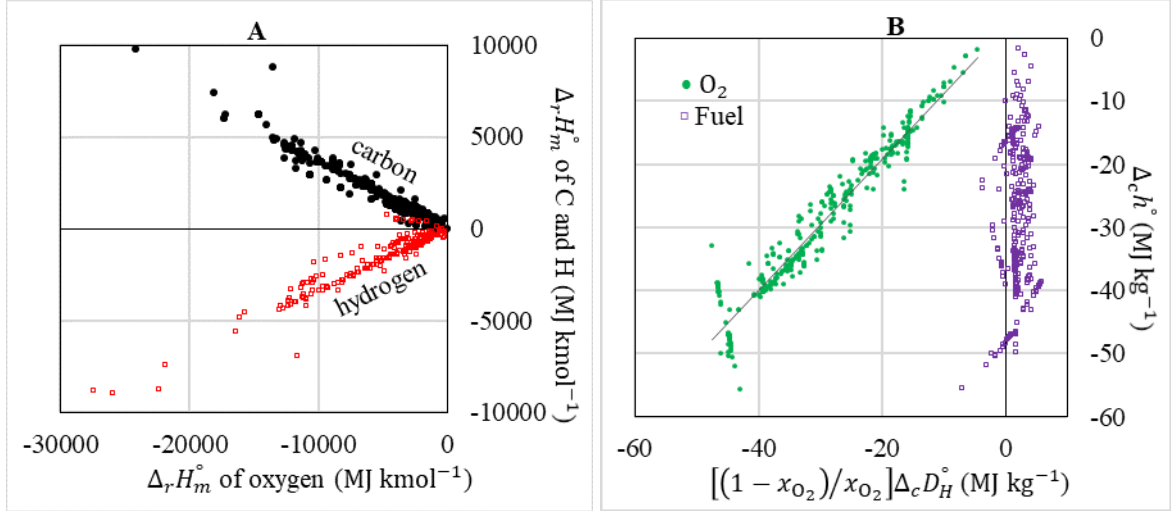
Figure 2: Comparison between the changes in dissociation enthalpies associated with the half-reactions undertaken by oxygen and fuel-based carbon and hydrogen (A), and plot of $\Delta_c h^°$ against $\frac{x_{O_2}}{x_{\text{fuel}}} \Delta_c D_H^°(O_2)$ and $\frac{x_{O_2}}{x_{\text{fuel}}} \Delta_c D_H^°(\text{fuel})$ (B).

This suggests that the reduction half-reaction resulting from the evolution of oxygen bonds during combustion is responsible for the liberation of heat during combustion of fuels, while the oxidation half-reaction of carbon absorbs some of this energy, and thus the apparent gross heat of combustion $\Delta_c h^°|_{\text{HHV,gross}}$ would be interpreted mathematically as:

$$\Delta_c h^°|_{\text{HHV,gross}} = \left(\Delta_c h^°|_{\text{HHV,meas.}} - \Delta_c D_H(\text{fuel})\right) = \Delta_c D_H(O_2) - \Delta_c D_{H,m}(\text{H} \cdots \text{O}) + \Delta_{RS} h^°$$

Although hydrogen does not change oxidation state during methane combustion, the bond changes it undergoes still release energy due to the differences in electronegativity χ_r between carbon and oxygen. This change in energy is easily determined from this associated electronegativity difference as $\Delta_{\chi_r} h^° = -405.5$ MJ kmol^{-1}, which is close to $\Delta_c D_{H,m}(\text{H}) = -402.0$ MJ kmol^{-1}. Because the electronegativity of carbon will always be lower than oxygen, the change in dissociation energy associated with this electronegativity difference will almost always be negative (exothermic) for hydrogen.

As combustion reactions are described on both an energy and mass basis, it is useful to rewrite Equation (7) by adding the mass ratio of fuel-to-oxidant in the following way:

$$\Delta_c h^°|_{\text{HHV}} = \frac{m_{O_2}}{m_{\text{fuel}}} \left[\frac{m_{\text{fuel}}}{m_{O_2}} [\Delta_c D_H^*(\text{fuel}) + \Phi_c] + \frac{m_{\text{fuel}}}{m_{O_2}} \Delta_c D_H(O_2) \right] - \Delta_c D_{H,m}(\text{H} \cdots \text{O}) + \Delta_{RS} h^° \qquad (8)$$

or alternatively, if mass fractions are used instead, Equation (8) takes the form of:

$$\Delta_c h^°|_{\text{HHV}} = \frac{x_{O_2}}{1-x_{O_2}} \left[\frac{1-x_{O_2}}{x_{O_2}} [\Delta_c D_H^*(\text{fuel}) + \Phi_c] + \frac{1-x_{O_2}}{x_{O_2}} \Delta_c D_H(O_2) \right] - \Delta_c D_{H,m}(\text{H} \cdots \text{O}) + \Delta_{RS} h^° \qquad (9)$$

Here additional energy associations such as differences in electronegativity are included in the term Φ_c (i.e. $\Delta_c D_H(\text{fuel}) = \Delta_c D_H^*(\text{fuel}) + \Phi_c$). As a completely theoretical determination of $\Delta_c h^°|_{\text{meas.,HHV}}$, it is possible to achieve a high level of accuracy using Equation (9), but knowledge of all bond configurations, resonance enthalpies, as well as elemental composition is required with respect to the reactants. The usefulness of Equation (9) is therefore limited to those fuels for which these particulars are fully specified, and immediately disqualifies complex fuels such as coals and biomass-based energy products. A graphical examination of the first two terms on the right-hand side of Equation (9) when applied to 359 fuel data points suggests a strong linear correlation between $\Delta_c h^°|_{\text{meas.,HHV}}$ and $[(1 - x_{O_2})/x_{O_2}]\Delta_c D_H(O_2)$ (Fig. 2B). In comparison, the fuel term $[(1 - x_{O_2})/x_{O_2}]\Delta_c D_H(\text{fuel})$ of Equation (9) results in an undefined gradient when correlated to $\Delta_c h^°|_{\text{meas.,HHV}}$, as the former exhibits very little deviation for more or less all values of $\Delta_c h^°|_{\text{meas.,HHV}}$ (also inferred indirectly

from Fig. 3). This insight confirms again the extensive contribution of oxygen towards heat liberation of combustion reactions (Fig. 1B) and may be used in simplifying Equation (9) further. Fig. 3A suggests that $[(1 - x_{O_2})/x_{O_2}]\Delta_c D_H(O_2)$ may be represented as a function of the mass fraction of oxygen required for combustion as:

$$-[\Delta_c D_H(O_2)] \approx \mu_{D_H}(x_{O_2}) = -13.87\, e^{-0.092\, x_{O_2}} \text{ (MJ kg}^{-1}) \tag{10}$$

where the constants have been determined for 1087 fuel data points [27-37]. Equation (10) is in principle a modifier function and substituted into Equation (9) yields:

$$\Delta_c h^\circ|_{\text{HHV}} = \frac{x_{O_2}}{1 - x_{O_2}} \mu_{D_H} - \Delta h_{\text{vap}} + \Delta_{RS} h^\circ = \mu_{D_H} m_{O_2} - \Delta h_{\text{vap}} + \Delta_{RS} h^\circ \tag{11}$$

which assumes $\Delta_c h^\circ|_{\text{HHV}}$ to be a function of x_{O_2} only, and where $\Delta_c D_{H,m}(\text{H} \cdots \text{O})$ is approximated by Δh_{vap}. This functionality becomes obvious when plotting $\Delta_c h^\circ|_{\text{meas.,HHV}}$ against x_{O_2} (Fig. 3A), and a similar equation as Equation (11) could have been obtained based on this observation where μ_{D_H} takes the form of some appropriate constant or variable. Taking the limits of $\Delta_c h^\circ|_{\text{HHV}}$ as $x_{O_2} \to \{0; 1\}$ yields the following results:

1. $\lim\limits_{x_{O_2} \to 0} \Delta_c h^\circ|_{\text{HHV}} = \lim\limits_{x_{O_2} \to 0} \left[\frac{\langle 0 \rangle}{1 - \langle 0 \rangle} \left(-13.87\, e^{-0.092\langle 0 \rangle} \right) - \Delta h_{\text{vap}} + \Delta_{RS} h^\circ \right] = -\Delta h_{\text{vap}} + \Delta_{RS} h^\circ$

2. $\lim\limits_{x_{O_2} \to 1} \Delta_c h^\circ|_{\text{HHV}} = \lim\limits_{x_{O_2} \to 1} \left[\frac{\langle 1 \rangle}{1 - \langle 1 \rangle} \left(-13.87\, e^{-0.092\langle 1 \rangle} \right) - \Delta h_{\text{vap}} + \Delta_{RS} h^\circ \right] \to \infty$

In the first instance the fuel would not be able to participate in a combustion reaction since $x_{O_2} = 0$ and since no reaction would take place without an oxidant $\lim_{x_{O_2} \to 0} \Delta_c h^\circ|_{\text{HHV}} = 0$. This would be the case for substances that are either fully oxidised or in an inert state. The second limit $x_{O_2} \to 1$ suggests that if an infinite amount of oxygen is required to combust an infinitesimally small quantity of fuel, the energy released would approach some infinite quantity. Between the limits of $0 < x_{O_2} < 1$ the modifier function takes on values with the range $-13.87 \text{ MJ kg}^{-1} < \mu_{D_H} < -12.65 \text{ MJ kg}^{-1}$, and it is therefore possible to simplify Equation (11) even further through the substitution of μ_{D_H} by a constant value and still approximate $\Delta_c h^\circ|_{\text{HHV}}$ with some accuracy. This is not necessary, however, since Equation (11) requires only knowledge of the mass-fraction (or percentage) of oxygen consumed during combustion and may be used easily. Regardless, Equation (12) is the proposed simplification of Equation (11) assuming a constant value for μ_{D_H}:

$$\Delta_c h^\circ|_{\text{HHV}} = \frac{-13.87}{x_{O_2}^{-1} - 1} - \Delta h_{\text{vap}} + \Delta_{RS} h^\circ \tag{12}$$

which can be simplified further by assuming $\Delta_{RS} h^\circ$ to be negligible (especially if this is not known) to:

$$\Delta_c h^\circ|_{\text{HHV}} = \frac{-13.87}{x_{O_2}^{-1} - 1} - \Delta h_{\text{vap}} = -13.87\, m_{O_2} - \Delta h_{\text{vap}} \tag{13}$$

where the substitution of μ_{D_H} for $-13.87 \text{ MJ kg}^{-1}$ is the value obtained for $\Delta_c h^\circ|_{\text{HHV}}$ when $x_{O_2} = x_{\text{fuel}}$ as indicated by the dashed lines in Fig. 3A.
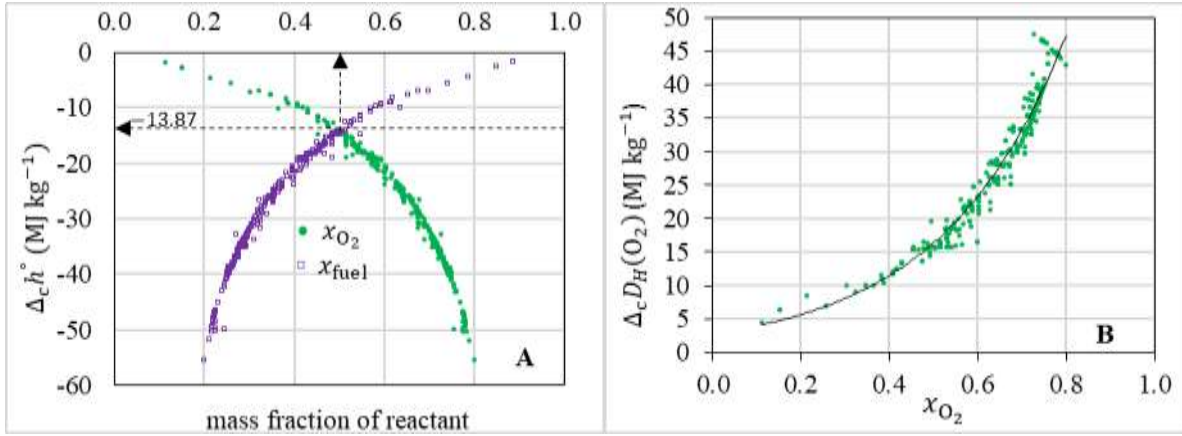
Figure 3: Association of x_{O_2} with $\Delta_c h^{\circ}$ (A) and $\Delta_c D_H(O_2)$ (B), with $\Delta_c D_H(O_2) = -13.87 \text{ MJ kg}^{-1}$ at $x_{O_2} = x_{\text{fuel}}$ (A)

3. Comparisons of correlations

Using conventional statistical methods, the accuracy of Equation (11) and Equation (13) may be validated and compared with previously proposed correlations found in the literature. The coefficient of determination (R^2), the mean bias error (MBE), and the root-mean-square error (RMSE) were used in this case, and computed respectively as follows:

$$R^2 = 1 - \frac{SSE_{\text{res}}}{SS_{\text{total}}} \tag{14}$$

$$\text{MBE (\%)} = \frac{1}{n}\sum_{i=1}^{n} \frac{\Delta_c h^{\circ}|_{\text{HHV,calculated}} - \Delta_c h^{\circ}|_{\text{HHV, measured}}}{\Delta_c h^{\circ}|_{\text{HHV, measured}}} \times 100\% \tag{15}$$

$$\text{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\Delta_c h^{\circ}|_{\text{HHV, calculated}} - \Delta_c h^{\circ}|_{\text{HHV, measured}}\right)^2} \tag{16}$$

where the residual sum of squares SSE_{res} and the total sum of squares SS_{total} are defined respectively as:

$$SSE_{\text{res}} = \sum_{i}^{n}(\Delta_c h^{\circ}|_{\text{HHV, calculated}} - \Delta_c h^{\circ}|_{\text{HHV, measured}})^2 \tag{17}$$

$$SS_{\text{total}} = \sum_{i}^{n}[\Delta_c h^{\circ}|_{\text{HHV, calculated}} - \Delta_c \bar{h}^{\circ}|_{\text{HHV, measured}})]^2 \tag{18}$$

The variances of $\Delta_c h^{\circ}|_{\text{HHV, calculated}}$ from $\Delta_c h^{\circ}|_{\text{HHV, measured}}$ with respect to Equations (9) & (11) show good replicability of $\Delta_c h^{\circ}|_{\text{HHV, measured}}$ based on their respective coefficients of determination, namely $R^2|_{\text{Eq.(9)}} = 0.996$ and $R^2|_{\text{Eq.(11)}} = 0.980$. This variance in $\Delta_c h^{\circ}|_{\text{HHV, calculated}}$ increases expectedly with the substitution of $\mu_{D_H} = -13.87 \text{ MJ kg}^{-1}$ of Equation (13), with $R^2|_{\text{Eq.(13)}} = 0.981$. The MBE (i.e. 2.8 %) of Equation (9) is considerably greater in relation to 13 of the other correlations evaluated (Table 1), possibly due to the inadequately defined energy term Φ_c. But the impracticality of Equation (9) even without fully defining Φ_c is obvious. Equation (9) only serves to develop the thermodynamic justifications used in the derivation of Equations (11) and (13). Equation (11) performs particularly well as a correlation, based on its MBE of -0.2 % and RMSE of 1.5 MJ kg^{-1} while Equation (13) does reasonably well compared to all other correlations evaluated with an MBE of -1.8 % and RMSE of 1.5 MJ kg^{-1}.

Table 1: Summary of statistical data for comparison between various correlations

Correlation	Statistical measures			Rank according to statistical measures		
	|MBE|	RMSE	R^2	|MBE|	RMSE	R^2
Equation (9)[a]	2.8	0.8	0.996	13	1	1
Equation (11)[b]	0.2	1.5	0.980	3	3	3
Equation (13)	1.8	1.5	0.981	8	2	2
Boie [19]	0.1	1.8	0.972	1	7	7
Strache and Lant [15]	0.9	1.7	0.973	6	5	5
Mott and Spooner [14]	2.5	1.7	0.972	11	6	6
Channiwala & Parikh [16]	0.3	1.9	0.968	4	10	10
Zhu and Venderbosch [38]	0.3	1.9	0.968	4	10	10
Gumz [18]	5.4	1.7	0.974	17	4	4
D'Huart *et al.* [16]	2.8	1.9	0.969	12	8	8
Schuster [16]	2.2	2.0	0.964	9	11	11
Demirbas *et al.* [23]	3.1	2.1	0.961	14	12	12
Dulong-Berthelot [16]	1.6	3.1	0.915	7	17	17
Vondrecek [25]	5.0	2.2	0.954	15	13	14
Schmidt-Rohr [26]	6.5	2.4	0.959	19	14	13
Tillman [16]	0.1	6.9	0.574	2	22	22
Beckman *et al.* [16]	5.6	2.8	0.931	18	15	15
Grummel and Davis [16]	2.3	3.9	0.860	10	19	19
IGT [16]	5.1	3.2	0.905	16	18	18
Sumegi [39]	10.9	2.8	0.930	23	16	16
Grabosky and Bain [16]	6.9	6.2	0.646	20	21	21
Seyler [40]	7.9	4.7	0.798	22	20	20
Jenkins [41]	7.9	7.6	0.481	21	23	23
Niessen [21]	35.8	10.0	0.084	24	24	24

[a]The term Φ_c in this case was tedious to specify fully and was therefore not used here.
[b]Calculated using $\Delta_c D_{H,m}(\text{H} \cdots \text{O})$ instead of Δh_{vap}.

The direct comparisons of Equations (9), (11) and (13) with $\Delta_c h°|_{\text{HHV, measured}}$ are plotted graphically in Fig. 4 around the line of symmetry $y = 1.0x$ with dashed trend lines indicating deviation boundaries of ± 5.0 %, showing the slight increase in variance with each simplification from Equation (9) to (13) (hydrogen not shown). Overall, Equation (11) offers acceptable compromise between complexity, by defining the modifier function μ_{D_H}, and simplicity, by eliminating the need for fuel-based parameters such as elemental composition from the correlation. However, Equation (13) is far simpler and, except for the mean bias error, performs statistically as well as Equation (11). It should be mentioned here that the bias relates partly to deviations brought about by not accounting for Φ_c-related energies.
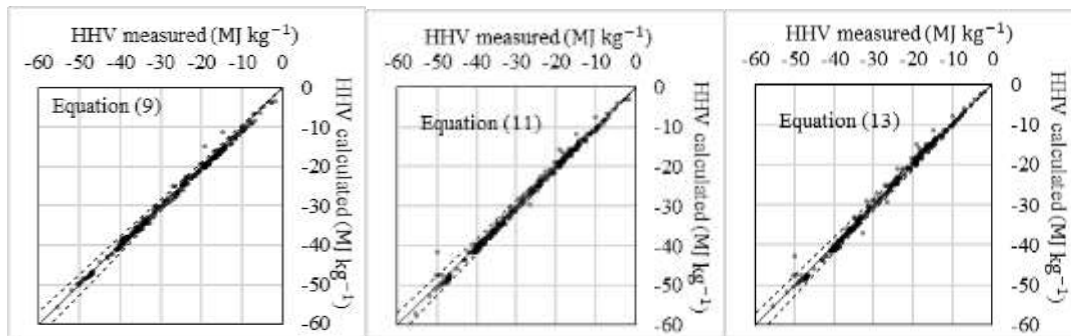

Figure 4: Comparison between calculated and measured $\Delta_c h°|_{\text{HHV}}$ using 1087 data points, with dashed deviation boundaries of ± 5.0 %

4. Implications of the proposed correlations

It must be stressed that the significance of Equations (11) & (13) lies not simply in the statistical performance as demonstrated in Table 1, but also in the thermodynamic principles and implications that underline their derivation. The chemical reduction of oxygen by a fuel as shown in Fig. 2A results in heat being liberated, while

the oxidation of carbon within the fuel conversely consumes some of this energy, resulting in a lowered heat of combustion. The role of oxygen in the combustion reaction is essential, in most cases contributing more than 100 % towards the heat of combustion (Fig. 1A), suggesting that the reduction half-reaction of oxygen is the principal reaction pathway responsible for the heat of combustion, rather than the oxidation half-reaction (pertaining to the fuel). Although hydrogen contributes to the heat of combustion only slightly compared to oxygen (Fig. 1A), because carbon is shown to reduce the heat of combustion, increasing the H/C ratio of fuel would result in enhanced energy quality. Coupled to this are the adverse effects of oxygenates on fuel properties, causing increased acidity, hydroscopicity, polarity and instability in biofuels [8,10–13]. Oxygenates hamper separation processes due to their inherent reactivity, making the separation of complex biofuel mixtures near to impossible.

The energy quality of fuel is also adversely affected with increase in oxygenates and decrease in hydrogen content, and can be demonstrated with the use of either Equation (11) or (13). For example using Equation (11) shows that increases in the O/C of the fuel from 0.0 to 2.0 decreases HHV by 50.0 MJ kg^{-1} (demonstrated in Fig. 5 by the carboxylic acid series), which is synonymous with increased oxidation of fuel. The same increase in the H/C ratio from 0.0 to 4.0 results in a comparatively modest increase in HHV of 22.7 MJ kg^{-1} (demonstrated by the n-alkane series in Fig. 5). Increases in oxygen content of carbon-rich fuel (with little to no hydrogen present), again by increasing the O/C from 0.0 to 2.0, results in a decrease in HHV of 34.6 MJ kg^{-1} (demonstrated by the carbon series of Fig. 5). Considering all three examples, it is obvious that, in the case of fuels completely lacking in hydrogen, the energy quality would have an upper boundary at more or less the HHV of carbon, ~ -33 MJ kg^{-1}, and it is by increasing hydrogen content that the highest energy quality may be achieved for a fuel. Although a second boundary pertaining to hydrogen is implied in Fig. 5 by the dashed line of value 57.5 MJ kg^{-1}, this boundary may be crossed by diatomic hydrogen and hydrogen-containing gaseous fuel mixtures. In the first example, the alteration to HHV from 0.0 MJ kg^{-1} to 50.0 MJ kg^{-1} is due to decreased oxygen content by its dilution as a result of increased change length. Realise that the sum of the changes in HHV for examples 2 & 3 of 57.5 MJ kg^{-1} is more or less the same as example 1 of 50.0 MJ kg^{-1}. This implies that a HHV may be altered in a wider range by changing oxygen content in fuel, compared to changes in either carbon or hydrogen content alone.

Fig. 5 shows that HHV is much more sensitive to oxygen-specific changes in the O/C for higher values of HHV, while sensitivity with respect to hydrogen- and carbon-specific changes in the H/C are less pronounced. Upgrading procedures for biofuels should therefore focus primarily on decreasing oxygen content via routes that are sacrificial towards carbon rather than hydrogen where possible. Catalysts used in upgrading of biofuels for example should be designed to reduce oxygen via decarboxylation and decarbonylation while supporting the hydrogenation of fuels for improved energy quality and stability. Upgrading routes that rely on hydrogenation of the fuel of biofuels similarly would support increases in energy quality athough this may also invariably consume some of the valuable hydrogen via hydrodeoxygenation pathways.
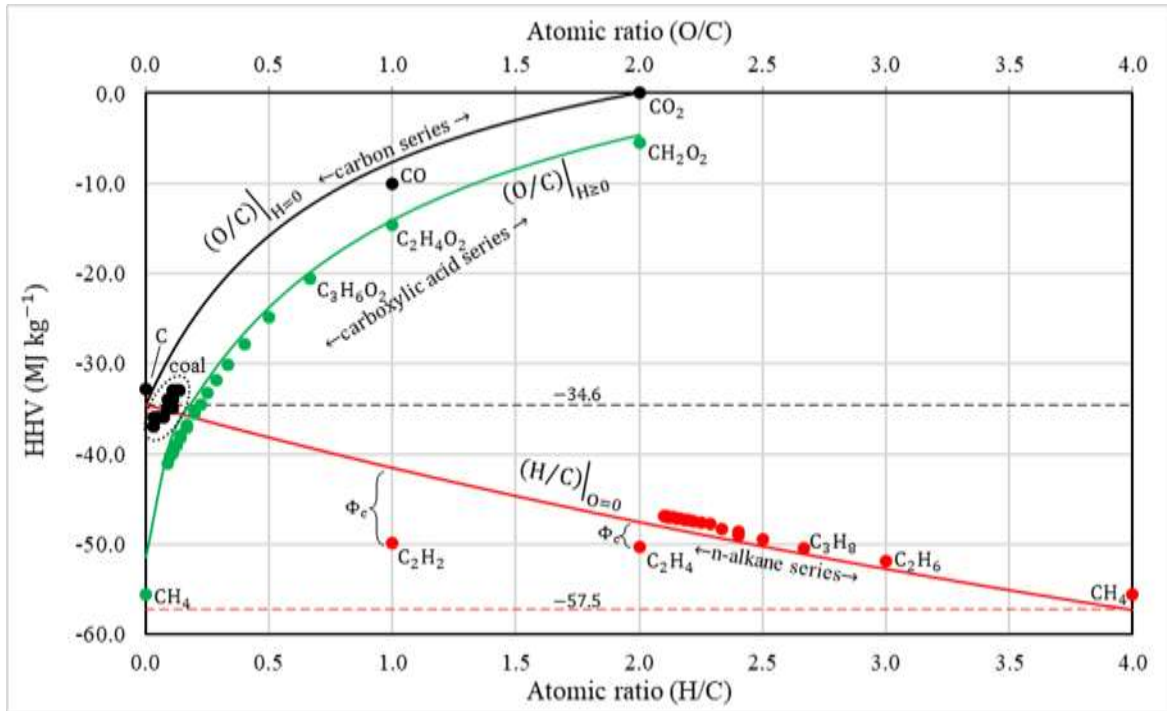
Figure 5: Changes in HHV with respect to changes in fuel atomic ratios O/C and H/C

5. Conclusions

Up until now, correlations available for approximating HHV of fuels have inadequately incorporated the thermodynamic fundamentals of the combustion process into their derivations. A correlation for estimating HHV accurately as a function of the mass fraction of oxygen consumed is presented. The correlation is a simplification of the equation derived using a theoretical and quantitative approach based on the reduction/oxidation half-reactions of the combustion reaction. Although the theoretical equation is impractical to apply directly as is, the heat of combustion is found to be a strong function of changes in bond enthalpies with respect to the oxygen atom, while related changes with respect to the fuel elements have been shown to be comparatively insignificant. It is therefore possible to derive a modifier function $\mu_{D_H}(x_{O_2})$ that reduces complexity in the theoretical equation describing the heat of combustion. Since the modifier function is a function of the mass fraction of oxygen required for combustion only, it is possible to eliminate the prerequisite of specifying fuel-based parameters as coefficients in the resulting correlation. This implies that only the mass of fuel burnt and mass of oxygen consumed during the combustion reaction is necessary to estimate HHV. The coefficients used in the modifier function are determined from a set of 359 data points, and may be adjusted for use with other types of data if need be. Variance in the modifier function between the limits of $x_{O_2} \to \{0; 1\}$ is shown to be small, and can be approximated by a constant, namely $\mu_{D_H} \approx -13.87$ MJ kg^{-1}.

The correlation performs well statistically compared to similar correlations available in the literature. A set of 1087 fuel data points with a wide range of chemical compositions based on the chemical formula of $C_{v_C}H_{v_H}O_{v_O}N_{v_N}S_{v_S}P_{v_P}$ is used for this comparison, and confirms the accuracy of most correlations including the one proposed here. Both equations using the modifier function and substitution of the modifier with a constant perform well statistically when compared to similar correlations from the literature. Since the proposed correlation is derived using a thermodynamic approach that describes the heat of combustion, it is possible to quantify the effects of fuel composition and oxygen consumption on the energy quality of biofuels. HHV is found to be much more sensitive to changes in oxygen content in the fuel compared to similar changes in carbon and hydrogen content, while hydrogen content enhances energy quality much more than carbon. Therefore, reduction of oxygen content in the fuel via deoxygenation pathways such as decarboxylation and decarbonylation is recommended over routes that sacrifice hydrogen (such as hydrodeoxygenation and dehydrogenation) where energy quality is a concern. As the correlation has been applied successfully to fuels containing other elements (i.e. sulfur, nitrogen, and phosphorus), and shows no deviation from trends pertaining to hydrogen and carbon, these same results may hold for other elements too. Looking into other types of oxidants such as fluorine may provide further insight into the development of energy products.

Acknowledgements

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