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Mass-fraction of oxygen as a predictor of HHV of gaseous, liquid and solid fuels

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Abstract

The higher heating value (HHV) of gaseous, liquid and solid fuels is demonstrated to be a strong function of the mass fraction of oxygen required for combustion, and suitable correlations are proposed to describe this relationship accurately. A 4th order correlation was found to be the best for estimating HHV as an all-purpose correlation with a root-mean-square error (RMSE) of 1.2 MJ/kg, coefficient of determination (R^2) value of 0.9900 and mean bias error (MBE) of 0.40 %. A 3rd order correlation was as accurate with an RMSE of 1.2 MJ/kg, R^2 value of 0.9898 and an MBE of – 0.16 %. In addition, the linear relationship between the HHV and oxygen required for combustion on a mole basis is demonstrated and an alternative mole-based correlation is proposed. A total of 311 HHV data from various sources are used to validate these correlations and 13 other correlations available in the literature are used for further comparison.

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1. Introduction

Energy is an essential and intrinsic part of any economy with both the quantity and quality of energy directly affecting the short and long-term outcomes of GDP [1]. Measuring and estimating the higher heating value (HHV) of fuels is crucial during the first stages of fuel utilisation 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 [2]. Numerous correlations for estimating HHV have been developed previously, most of which are applicable only to coals (discussed in more detail by Channiwala & Parikh [3]). The majority of correlations rely on knowing how C, H, N and S oxidise to their respective combustion products [4-13,15], while

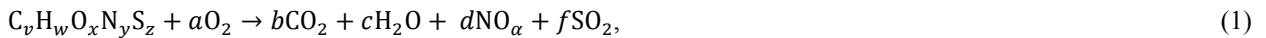
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others assume HHV is directly proportional to oxygen required for combustion [3,14]. From a thermodynamic consideration that both fuel and oxidant prescribe the thermochemical outcomes of combustion processes (comparable to the redox reactions governing electrochemistry), we revisit heat of combustion treating oxygen and fuel as both mutually inclusive to the outcomes of the combustion process. Oxygen present intrinsically as oxygenates within the (partially oxidised) fuel is also accounted for since the former reduces the oxidizing potential of the latter. A total of 19 correlations predicting the HHV for various fuel types identified in the literature were initially used for comparison [3-6,8,10-23], but for the sake of brevity only 13 of the more applicable correlations are discussed further, namely from references 3-6, 8, &10-15.

2. Derivation of correlations

Combustion of conventional fuels proceeds via the exothermic oxidation of carbon, hydrogen, sulfur and nitrogen according to the redox reaction:



with the moles of oxygen required for complete combustion, a , given by:

$$a = b + \frac{c}{2} + \frac{ad}{2} + f - \frac{x}{2} \quad (2)$$

A linear relationship is observed when plotting the moles of O_2 required for combustion for a variety of fuels against their respective measured HHV on a mole basis (Fig. 1). Nitrogen-containing compounds deviated the least from this trend when $\alpha = 0.2$. This is possibly due to nitrogen being present mostly in its native form of N_2 in the flue gas. A correlation for this relationship was obtained using the Curve Fitting Toolbox™ in MATLAB®. Elemental and HHV data for 311 fuels comprising of hydrocarbons (including oxygenated hydrocarbons) and nitrogenous compounds [24], various grades of coal [25,26], as well as diverse types of biomass [3,27-29] and biodiesel [30-32] were used to fit a straight line for HHV_{mol} as a function of a on a mole basis:

$$HHV_{mol} = -433.8a - 46.89 \text{ (MJ/kmol)} \quad (3)$$

The same approach on a mass basis yields a similar, albeit less accurate, relationship. Accuracy was found to increase when converting the oxygen data to a mass fraction basis instead of the conventional mass basis (Fig. 1, left). The transformation to the mass fraction of O_2 required for combustion, β , is defined as:

$$\beta = \text{mass fraction. } O_2 = \frac{\text{mass. } O_2}{\text{mass. fuel} + \text{mass. } O_2} = 1 - \frac{\text{mass. fuel}}{\text{mass. fuel} + \text{mass. } O_2} \quad (4)$$

Choosing a 3rd order correlation to approximate the HHV_{mass} as function of β (Fig. 1, right), and solving the three coefficients using the Curve Fitting Toolbox™ yields:

$$HHV_{mass} = 88.1\beta^3 - 8.909\beta^2 - \frac{24.34\beta}{(1-\beta)} \quad (5)$$

Note that β may alternatively be calculated as $1 - \text{mass fraction of fuel combusted}$ according to Equation 4. Increasing the order of Equation 5 yields:

$$HHV_{mass} = 118\beta^4 - 52.46\beta^3 + 40.74\beta^2 - \frac{26.29\beta}{(1-\beta)} \quad (6)$$

Increasing the order of Equation 6 further did not achieve significant improvements while lower orders were insufficient for estimating HHV_{mass} accurately. Both Equations 5 and 6 were derived on the assumption that as β approaches zero, so does the calorific value of fuels. This further corresponds to the final oxidative states of fuel constituents, namely CO_2 , H_2O , SO_2 and N_2/NO_x where no further oxygen is consumed via the combustion reaction.

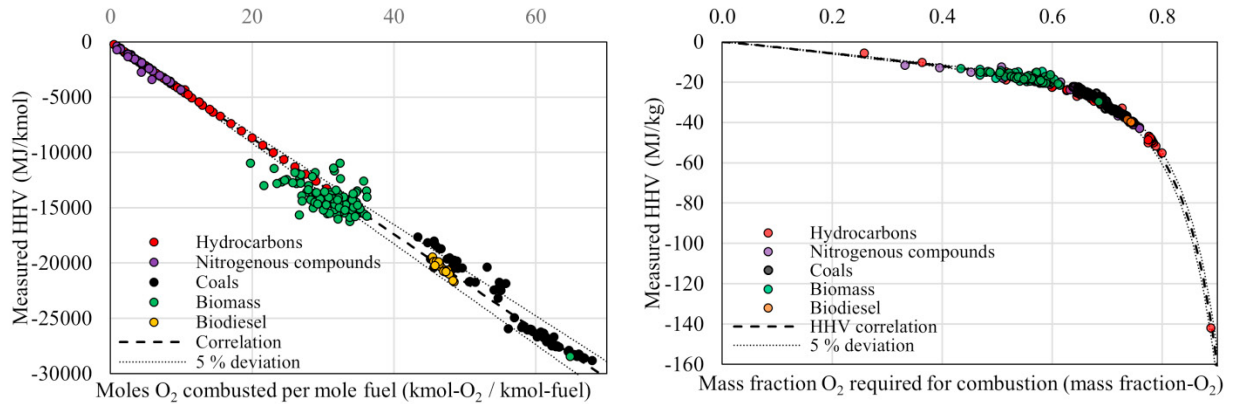


Fig. 1. (Left) HHV data plotted against moles O_2 required per mole fuel with linear correlation; (right) HHV data plotted against the mass-fraction of O_2 required for combustion with non-linear 3rd order trendline.

3. Evaluation of correlations

The coefficient of determination (R^2), the mean bias error (MBE), and the root-mean-square error (RMSE) were used to fit the correlations of Equations 3, 5 and 6 to the data and compare these correlations to those in the literature [3-6,8,10-15], computed respectively as follows:

$$R^2 = 1 - \frac{SSE_{res}}{SS_{total}} \quad (7)$$

$$MBE (\%) = \frac{1}{n} \sum_{i=1}^n \frac{HHV_{correlation} - HHV_{measured}}{HHV_{measured}} \times 100\% \quad (8)$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (HHV_{correlation} - HHV_{measured})^2} \quad (9)$$

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

$$SSE_{res} = \sum_i^n (HHV_{correlation} - HHV_{measured})^2 \quad (10)$$

$$SS_{total} = \sum_i^n [HHV_{correlation} - \text{Mean}(HHV_{measured})]^2 \quad (11)$$

The 3rd and 4th order correlations achieved the best overall approximations for the HHV with R^2 values of 0.9898 and 0.9900, respectively, compared to other correlations evaluated (Fig. 2). The correlations of Zhu & Venderbosch

[14] ($R^2 = 0.9761$) and Channiwala & Parikh [3] ($R^2 = 0.9751$), being somewhat analogous to correlations proposed by Equations 3, 5 & 6, achieved less favourable approximations in comparison, while correlations of Gumz [6] ($R^2 = 0.9811$) and Mott & Spooner [8] ($R^2 = 0.9770$) achieved slightly better approximations. The correlation by Sumegi [12] was found to be the least accurate approximation with $R^2 = 0.9369$ and an RMSE of 3.07 (Fig. 2). The mole-based correlation of Equation 3 achieved an R^2 value of 0.9890, with a RMSE of 916.1 MJ/kmol (equivalent to 1.50 MJ/kg).

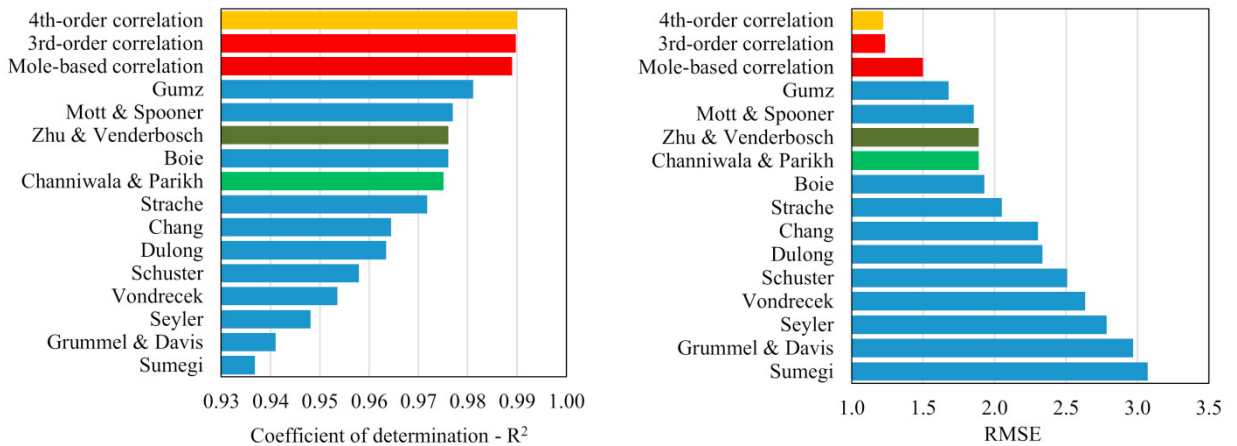


Fig. 2. (Left) overall R² and (right) RMSE values for correlations evaluated against HHV data.

The lowest RMSE was obtained for the 4th-order correlation at 1.22 MJ/kg followed by the 3rd-order correlation at 1.23 MJ/kg. Correlations by Zhu & Venderbosch and Channiwala & Parikh both obtained a higher RMSE of 1.89 MJ/kg. For specific fuel types, the mole-based correlation gave the closest approximations for R² except for biomass, which was better approximated with correlations by Boie [4] and Zhu & Venderbosch (Table 1). The 4th-order correlation achieved the lowest RMSE for hydrocarbon based fuels at 1.2 MJ/kg, while the 3rd-order correlation achieved the lowest RMSE for nitrogenous-type fuels at 1.1 MJ/kg (Table 1). The 3rd-order correlation also attained the lowest RMSE of 1.3 MJ/kg for biomass-based fuels together with correlations by Channiwala & Parikh, Boie, and Zhu & Venderbosch. The correlation by Seyler [10] gave the lowest RMSE of 0.9 MJ/kg for coals. The lowest RMSE for biodiesel was obtained by the mole-based correlation and Chang’s correlation, at 0.5 MJ/kg, with 0.6 MJ/kg achieved with the 3rd-order correlation. Eight out of the sixteen correlations evaluated achieved an MBE of less than ±1.0 %, namely the mole-based correlation, the 4th and 3rd-order correlations, as well as the correlations of Mott & Spooner, Seyler, Channiwala & Parikh, Strache, and Boie (Fig. 3).

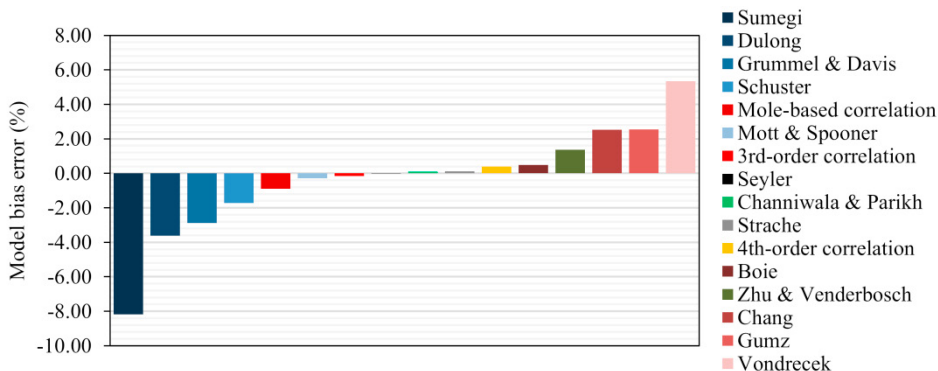


Fig. 3. Comparison of measured and calculated HHV values across a range of fuels on a mass and mole basis.

Figure 4 shows HHV data obtained from Equation 3 and 6 respectively, plotted against measured HHV for gaseous,

Table 1: R^2 and RMSE values computed for correlations estimating HHV for various types of fuel

Correlation	HC ¹		NC ²		C ³		BM ⁴		BD ⁵		Total	
	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE
Mole-based correlation	1.000	1.5	0.9996	1.9	0.9948	1.1	0.6747	1.8	0.9988	0.5	0.9890	1.5
4 th -order correlation	0.9951	1.2	0.9842	1.2	0.9591	1.1	0.9840	1.4	0.9962	0.7	0.9900	1.2
3 rd -order correlation	0.9938	1.4	0.9862	1.1	0.9618	1.0	0.9851	1.3	0.9966	0.6	0.9898	1.2
Channiwala & Parikh [3]	0.9742	2.6	0.9430	2.6	0.9457	1.1	0.9860	1.3	0.9956	0.7	0.9751	1.9
Boie [4]	0.9767	2.8	0.9266	2.3	0.9563	1.2	0.9870	1.3	0.9953	0.7	0.9761	1.9
Schuster [3]	0.9504	3.9	0.9054	3.0	0.9432	1.2	0.9839	1.4	0.9935	0.9	0.9579	2.5
Gumz [6]	0.9855	2.1	0.9631	1.9	0.9210	1.5	0.9831	1.4	0.9939	0.8	0.9811	1.7
Strache [11]	0.9777	2.6	0.9155	2.8	0.9554	1.1	0.9784	1.6	0.9551	2.3	0.9718	2.1
Mott & Spooner [8]	0.9837	2.2	0.9244	2.7	0.9563	1.1	0.9799	1.6	0.9689	1.9	0.9770	1.9
Grummel & Davis [3]	0.9261	4.7	0.9039	3.0	0.9545	1.1	0.9737	1.8	0.9857	1.3	0.9410	3.0
Seyler [10]	0.9754	2.7	0.5571	6.5	0.9731	0.9	0.9810	1.5	0.9567	2.2	0.9482	2.8
Vondracek [13]	0.9575	3.6	0.9006	3.1	0.8725	1.9	0.9798	1.6	0.8990	3.4	0.9535	2.6
Dulong [5]	0.9783	2.6	0.8952	3.1	0.9655	1.0	0.9471	2.5	0.9665	2.0	0.9635	2.3
Sumegi [12]	0.9732	2.8	0.8595	3.6	0.9535	1.1	0.8670	4.0	0.9758	1.7	0.9369	3.1
Chang [15]	0.9635	3.3	0.9723	1.6	0.9275	1.4	0.9647	2.1	0.9977	0.5	0.9644	2.3
Zhu & Venderbosch [14]	0.9767	2.6	0.9266	2.6	0.9563	1.1	0.9870	1.3	0.9953	0.7	0.9761	1.9

¹ HC = hydrocarbons; ² NC = nitrogenous compounds; ³ C = coals; ⁴ BM = biomass; ⁵ BD = biodiesel

liquid, and solid fuels according to their class. A 5 % deviation line is included to illustrate the extent of scatter of data around the line $y = x$. The smallest deviation in HHV occurs within the hydrocarbons fuels while biomass-based fuels have the largest deviation. Likewise, the higher grade of coals deviates less than coals with higher oxygen content (i.e. lignites). HHV for hydrocarbon, biodiesel and nitrogenous-type fuels deviate the least on a mole basis (well within the 5 % deviation mark).

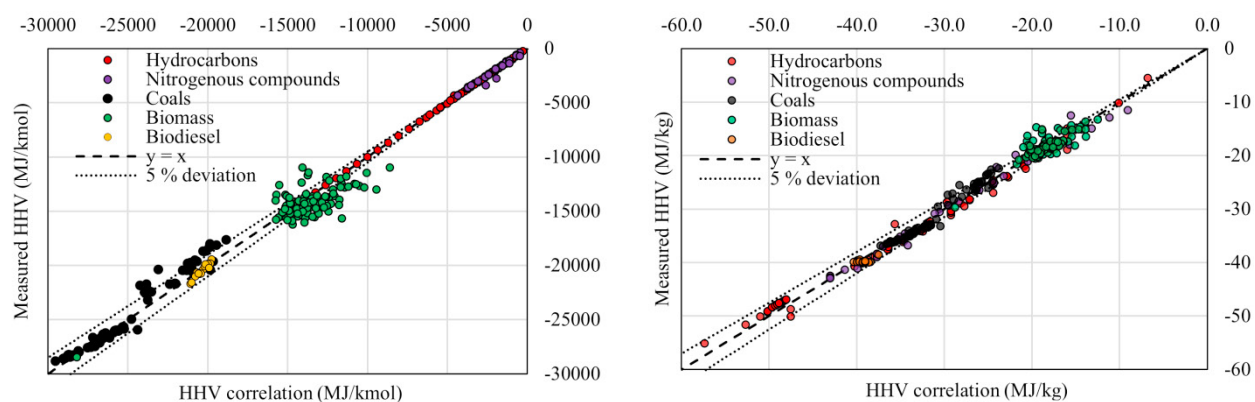


Fig. 4. Comparisons between measured and predicted HHV on a mole (left) and mass (right) basis.

4. Applications of correlations

The efficiency of combustion processes (e.g. internal combustion engines, industrial furnaces, boilers, gas turbines, etc.) is the highest for stoichiometric combustion. However, in practice stoichiometric air-to-fuel ratios are

not achievable due to factors such as imperfect mixing of reagents by burners. To ensure complete combustion with maximum efficiency, these processes typically aim to operate using the minimum excess air/oxygen and thereby minimise heat rejected to the stack, avoid unnecessary heating of the air and avoid deficient oxidation [33]. Air-fuel ratio meters such as zirconia oxygen sensors are typically employed to monitor the oxygen present in the flue gas and adjust the inflow of air/oxygen accordingly. In this case, the amount of oxygen consumed during combustion is easily calculated from the oxygen entering and leaving the process. The proposed correlations (i.e. Equations 3, 5 & 6) are most suited for application in these processes since they allow HHV to be calculated from knowing only the quantities of oxygen and fuel consumed during combustion, irrespective of the composition of the fuel and combustion products.

5. Conclusions

Three correlations were derived for approximating HHV of various fuels as a function of oxygen required for combustion. Higher heating values of gaseous and liquid fuels can be approximated accurately on a mole by the simple linear equation $\text{HHV}_{\text{mol}} = -433.8x - 46.89$ (MJ/kmol) where x is the kmol O_2 required for combustion per kmol fuel. Accuracy is much lower for coals and more so for biomass-based fuels. A 3rd order correlation relating HHV as a function of the mass fraction of oxygen was found to be more accurate overall for approximating all types of gaseous, liquid and solid fuels compared with other correlations found in literature, although HHV for coal was better approximated using the correlation by Seyler. The accuracy achieved using a 4th order correlation was comparable to the 3rd order correlation.

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