Energy and exergy in moist fuels

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1 Heating value and chemical exergy

We define *heating value* by thinking of a combustion chamber. Fuel and air are supplied at a certain temperature (that we have to chose based on some standard). It burns, and we take out so much heat that the combustion products are cooled down to the same temperature that the air and fuel had. Then, the released heat is the heating value.

Lower heating value (Norw.: “nedre brennverdi”) is defined such that the reaction is complete and that all H_2O of the combustion product is in vapor form. *Higher heating value* (Norw.: “øvre brennverdi”) is defined correspondingly, except that all H_2O of the combustion product is in liquid form. The difference between these two is equal to the heat of condensation of the water.

Other terms for these quantities can also be found in literature:
Net calorific value is a synonym of lower heating value.
Gross calorific value, *upper heating value* and *gross heating value* are other terms for the *higher heating value.* And - of course - all terms are given three-letter-abbreviations: LHV, NCV, HHV, GCV, UHV, GHV.

The distinction between *lower* and *higher* appears for all fuels containing hydrogen, thus producing H_2O by combustion. Solid fuels (biomass, coal) usually contain water which follows the combustibles and is mixed with the products. This leads to the issue of defining the mass, and consequently, the heating values of the fuel:

The heating value can be specified on *dry basis* (d.b.) or on *wet basis* (w.b.). Supplementary terms are *as received* (AR) or *moist fuel* for the wet basis and *dry fuel* or *dry matter* (dm) (Norw: “tørrstoff”, ts) for the dry basis. A third option is *dry, ash free* (DAF).

Evaporation of the water contained by the solid fuel takes some of the energy. We define *effective heating value* (Norw.: “effektiv brennverdi”) as the lower heating value of the moist fuel (dry matter and water together). Thus this will be equal to the LHV (w.b.). The term *effective heating value* (and similar) is used in several European countries/languages. It should, however, be noted that the term can have a different meaning in North-American literature.

Chemical exergy is the work that can be obtained from the fuel when it is brought to equilibrium with the surroundings through a reversible process. Thus, this is the maximum work from the fuel. The value is often close to the heating value.

When energy in fuels is quantified, it is (with some special exceptions) the lower heating value. For moist fuels, it is the effective heating value (lower heating value of the moist fuel).

2 Relations between heating values

Heating values are always enthalpies. They are given either as molar or specific values (i.e. energy per mole of substance or energy per unit of mass). Solid fuels are usually given on the basis of mass (J/kg).

The relation between LHV and HHV can be expressed as

$$h_{\mathrm{LHV}} = h_{\mathrm{HHV}} - \frac{m_{\mathrm{H_2O,prod}}}{m_{\mathrm{fu}}} h_{\mathrm{fg}} = h_{\mathrm{HHV}} - 8.94 \cdot X_{\mathrm{H}} \cdot h_{\mathrm{fg}} \tag{1}$$

Here, $m_{\mathrm{H_2O,prod}}$ is the mass of H_2O produced by combustion of the mass of fuel, m_{fu}. This ratio can be found from the mass fraction of hydrogen, X_{H} of the fuel, $m_{\mathrm{H_2O,prod}}/m_{\mathrm{fu}} = 8.94 \cdot x_{\mathrm{H}}$. The numerical value 8.94 is the mass of H_2O per mass of hydrogen. h_{fg} is the enthalpy of evaporation of water. Equation (1) follows from the definitions of higher and lower heating values.

The lower heating value of the dry matter $h_{\mathrm{LHV(dm)}}$ is denoted h_{ts} (kJ/kg) and the moisture content is $w = m_{\mathrm{water}}/(m_{\mathrm{dm}} + m_{\mathrm{water}})$ (kg water per kg moist fuel). The effective heating value then is

$$h_{\mathrm{eff}} = h_{\mathrm{LHV(dm)}} = h_{\mathrm{ts}} \cdot (1 - w) - h_{\mathrm{fg}} \cdot w = h_{\mathrm{ts}} - (h_{\mathrm{ts}} + h_{\mathrm{fg}})w. \tag{2}$$

This is the lower heating value of the mixture of dry matter and water; we have assumed that the water in the flue gas is vapor. Equation (2) is obtained by assuming the the dry matter and eater forms a mechanical (i.e. not chemically bound) mixture.

The enthalpy of evaporation, h_{fg}, for water can be found from steam tables, e.g. in a thermodynamics text book. The value is 2442.3 kJ/kg at 25 °C, 2465.9 kJ/kg at 15 °C, and 2501.3 kJ/kg at 0 °C.

The HHV of the wet fuel can be expressed from the HHV of the dry matter:

$$h_{\mathrm{HHV(w.b.)}} = h_{\mathrm{HHV(dm)}} \cdot (1 - w) \tag{3}$$

and furthermore from the LHV(dm) by using Eq. (1). Like Eq. (2), this equation is obtained by assuming a mechanical mixture of dry matter and water.

The relations of this section are valid for all moist solid fuels, and also for liquid fuels containing water. This includes emulsions (mixtures) of water and (coal) particles and water emulsions of very heavy oil or tar.

3 Obtaining heating values

Heating values can be obtained in different ways. If the type of fuel is well known (and well defined), the heating value can be obtained from literature. Alternatively, the heating value can be measured in a laboratory. A third possibility is to perform only a gravimetric analysis (that is, determine the mass fraction of the elements) in the laboratory, and then use some empirical formula for the heating value. An example (here taken from [1]) is

$$h_{\mathrm{HHV(dm)}} = 34.91 \cdot X_{\mathrm{C}} + 117.83 \cdot X_{\mathrm{H}} + 10.05 \cdot X_{\mathrm{S}} - 1.51 \cdot X_{\mathrm{N}} - 10.34 \cdot X_{\mathrm{O}} - 2.11 \cdot X_{\mathrm{ash}} \text{ (MJ/kg)}, \tag{4}$$

where X_i denotes the mass fraction of carbon (C), hydrogen (H), sulphur (S), nitrogen (N), oxygen (O) and ash in the dry matter.

The literature shows considerable variation among measured heating values, even for similar fuels. This is partly due to variation in growt of the tree (or other plant). However, it also reflects the challenges of accurate measurement of heating values and contents of the biomass. For many biomass fuels, the LHV(dm) is found between 16 and 21 MJ/kg (HHV(dm) between 18 and 22 MJ/kg).

For estimates and exercises we can use $h_{\mathrm{LHV(dm)}} = h_{\mathrm{ts}} = 19\,\mathrm{MJ/kg}$ (that is, per kg dry matter) for solid biomass fuels.

Example: Fresh bark typically has approximately 60 % moisture ($w = 0.60$).
With $h_{\mathrm{ts}} = 19\,\mathrm{MJ/kg}$ and h_{fg} taken at 15 °C, we obtain $h_{\mathrm{eff}} = (19 \cdot 0.40 - 2.47 \cdot 0.60)\,\mathrm{MJ/kg} = 6.1\,\mathrm{MJ/kg}$.

Example: A gravimetric analysis for dry wood shows 50.0 % C, 6.1 % H, 42.2 % O, 0.7 % N and 1.0 % ash.
Equation (4) gives $h_{\mathrm{HHV(dm)}} = (34.91 \cdot 0.500 + 117.83 \cdot 0.061 - 1.51 \cdot 0.007 - 10.34 \cdot 0.422 - 2.11 \cdot 0.010)\,\mathrm{MJ/kg} = 20.2\,\mathrm{MJ/kg}$.
With this result, Eq. (4) gives, with h_{fg} taken at 15 °C, $h_{\mathrm{LHV(dm)}} = (20.2 - 8.94 \cdot 0.061 \cdot 2.47)\,\mathrm{MJ/kg} = 18.9\,\mathrm{MJ/kg}$

Some warnings should be issued:
1) Formulations like Eq. (4) are developed from experiments of certain fuels. Thus, type of fuel and limits of the contents should be observed. For instance, an expression for wood should not be used for coal or fatty acids.
2) Formulations like Eq. (4) or Eq. (6) below contains several numerical figures. When these are reproduced and re-reproduced in reports, notes (like this one), etc., a misprint can readily occur. Hence, it is recommended to consult original literature.
3) It is important to make sure which heating value that is given (higher/lower, wet/dry matter, etc.). This also includes making sure how the terminology is used by the author(s).

4 Chemical exergy

Empirical expressions for the chemical exergy of solid and liquid fuels were developed by Szargut and co-workers. The main work was presented by Szargut and Styrylska [2], where the ratio of the chemical exergy to the lower heating value of the dry matter was expressed as a function of the elemental contents.

$$\varphi_{\mathrm{dry}} = \left(\frac{\varepsilon_{\mathrm{dm}}}{h_{\mathrm{LHV(dm)}}} \right) \tag{5}$$

For dry, solid fuels with a certain content of oxygen, the ratio of chemical exergy to lower hating value for dry matter is expressed as

$$\varphi_{\mathrm{dry}} = \frac{1.0438 + 0.1882\frac{h}{c} - 0.2509\frac{o}{c}\left(1 + 0.07256\frac{h}{c}\right) + 0.0383\frac{n}{c}}{1 - 0.3035\frac{o}{c}} \tag{6}$$

Here, h/c is the ratio of hydrogen mass to carbon mass in the fuel, and n/c and o/c correspondingly for nitrogen and oxygen. This expression is valid for o/c from 0.667 to 2.67 (i.e. biomass), and is expected to be accurate within $\pm 1\%$. Similar expressions are given for other ranges of c/h/o/n/s contents. Strictly, the values were taken at the reference state (25 °C, 1 atm), although the variation due to deviating state will usually be less than the uncertainty of the value calculated.

The numerical factors in Eq. (6) and similar expressions have been slightly adjusted by Szargut in later publications e.g. [3,4].

The value above is for the dry matter. For moist fuel, the ratio of chemical exergy to effective heating value becomes

$$\varphi = \frac{(\varepsilon)_{\mathrm{moist}}}{h_{\mathrm{eff}}} = \frac{(1-w)\varepsilon_{\mathrm{dm}}}{(1-w)h_{\mathrm{LHV(dm)}} - wh_{\mathrm{fg}}} = \left(1 - \frac{w}{1-w}\frac{h_{\mathrm{fg}}}{h_{\mathrm{LHV(dm)}}}\right)^{-1} \varphi_{\mathrm{dry}}. \tag{7}$$

In the numerator here, the relation $(\varepsilon)_{\mathrm{moist}} = (1-w)\varepsilon_{\mathrm{dm}}$ is based on the assumption that dry matter and water have no chemical bonds and are not molecularly mixed. Furthermore, the chemical exergy of liquid water is neglected. Strictly, the ratio $w\varepsilon_{\mathrm{water}}/h_{\mathrm{eff}}$ should be added to the expression of Eq. (7). As the chemical exergy of liquid water is rather small (0.05 MJ/kg), this quantity rarely has a significant contribution even at a large moisture content.

Example: For bark we can use the composition (mass basis) 50.0 % C, 6.1 % H, 42.7 % O, and 1.2 % N (analysis data may vary). This gives $h/c = 0.122$, $n/c = 0.024$, $o/c = 0.853$, and $\varphi_{\mathrm{dry}} = 1.15$.

With $w = 0.60$, $h_{\mathrm{ts}} = 19\,\mathrm{MJ/kg}$, and $h_{\mathrm{fg}} = 2.47\,\mathrm{MJ/kg}$, we get $\varphi = 1.43$, $h_{\mathrm{eff}} = 6.1\,\mathrm{MJ/kg}$, and $\varepsilon_{\circ} = \varphi \cdot h_{\mathrm{eff}} = 8.7\,\mathrm{MJ/kg}$.

References

[1] S. van Loo, J. Koppejan: *The handbook of biomass combustion and co-firing.* Earthscan, London 2008.

[2] J. Szargut, T. Styrylska: Angenährte Bestimmung der Exergie von Brennstoffen. *Brennstoff-Währme-Kraft*, 1964, 16(12):589-596.

[3] J. Szargut, D.R. Morris, F.R. Steward: *Exergy analysis of thermal, chemical and metallurgical processes.* Hemisphere Publ. Corp., New York, 1988.

[4] Jan Szargut: *Exergy method: Technical and ecological applications.* WIT Press, Southampton 2005.

Any textbook (thermodynamics, chemistry) defining the heating values. Any tables for saturated water/steam.