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TP

Fuel heating value (HHV) and Dulong formula

Fuel : $C_a H_b O_c S_d$

$$\approx a \cdot C(s) + x \cdot H_2(g) + c \cdot H_2O(l) + d \cdot S(s)$$

element balance for H:

$$b = 2x + 2c \Rightarrow x = \frac{1}{2} b - c$$

$$\Rightarrow \text{Fuel} \approx a \cdot C(s) + (\tfrac{1}{2} b - c) \cdot H_2(g)$$

$$+ c \cdot H_2O(l) + d \cdot S(s)$$

Combustion reaction of the fuel:

$$\text{(R1)} \quad C_a H_b O_c S_d + y \cdot O_2 \longrightarrow$$

$$\rightarrow a \cdot CO_2(g) + \tfrac{1}{2} b \cdot H_2O(l) + d \cdot SO_2(g)$$

Solve y from element balance for oxygen:

$$\underbrace{c + 2y}_{LHS} = \underbrace{2a + \frac{1}{2}b + 2d}_{RHS}$$

$$\Rightarrow \quad y = a + \frac{1}{4}b - \frac{1}{2}c + d$$

$\Rightarrow$ (R1) becomes

$$(R1): \; C_aH_bO_cS_d + \left(a + \frac{1}{4}b - \frac{1}{2}c + d\right) \cdot O_2$$

$$\rightarrow a \cdot CO_2(g) + \frac{1}{2}b \cdot H_2O(l) + d \cdot SO_2(g)$$

which can be approximated with

$$(R2) \; a \cdot C(s) + \left(\frac{1}{2}b - c\right) \cdot H_2(g) + c \cdot H_2O(l)$$

$$+ d \cdot S(s) + \left(a + \frac{1}{4}b - \frac{1}{2}c + d\right) \cdot O_2(g)$$

$$\rightarrow a \cdot CO_2(g) + \frac{1}{2}b \cdot H_2O(l) + d \cdot SO_2(g)$$

but

$$(R2) = a \cdot (R3) + \left(\tfrac{1}{2}b - c\right) \cdot (R4) + d \cdot (R5)$$

where

(R3) $C(s) + O_2 \rightarrow CO_2(g)$ $\quad \Delta H_{m,R3} = -394 \frac{kJ}{mol}$

(R4) $H_2(g) + O_2 \rightarrow H_2O(l)$ $\quad \Delta H_{m,R4} = -286 \frac{kJ}{mol}$

(R5) $S(s) + O_2 \rightarrow SO_2(g)$ $\quad \Delta H_{m,R5} = -297 \frac{kJ}{mol}$

(Reaction enthalpies from HC pp. 1109, 1116, 1120)

$\Rightarrow$ Reaction enthalpy for (R2) is

$$\Delta H_{m,R2} = a \cdot \Delta H_{m,R3} + \left(\tfrac{1}{2}b - c\right) \cdot \Delta H_{m,R4} + d \cdot \Delta H_{m,R5}$$

and the <u>molar</u> higher heating value (HHV) of the fuel is

$$Q_{m,H} = -\Delta H_{m,R2} = -a \cdot \Delta H_{m,R3} - \ldots$$

Now what remains to be done is:

1° Convert from molar HHV (kJ/mol) into heating value (kJ/kg)

2° Convert from "stoichiometric coefficients" a, b, c, d into mass fractions w_C, w_H, w_O, w_S.

To begin with, compute the "molar mass" of the fuel:

$$M_F = a \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S$$

Now obtain HHV by

$$q_H = \frac{Q_{m,H}}{M_{Fuel}} = \frac{-a \cdot \Delta H_{m,R1} - \ldots}{a \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S}$$

However, note that

$$w_C = \frac{m_C}{m_{Fuel}} = \frac{n_C \cdot M_C}{n_{Fuel} \cdot M_{Fuel}}$$

$$= \frac{a \cdot M_C}{a \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S}$$

$\left(\frac{n_C}{n_{Fuel}} = a \right.$, since there are a atoms of C in one mole of the fuel$\left. \right)$

$$\Rightarrow \frac{a}{a \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S} = \frac{w_C}{M_C}$$

Similarly:

$$\frac{\frac{1}{2} b - c}{a \cdot M_C + b \cdot M_H + c \cdot M_O + d \cdot M_S} = \frac{1}{2} \frac{w_H}{M_H} - \frac{w_O}{M_O}$$

and

$$\frac{d}{a \cdot M_C + \ldots} = \frac{w_S}{M_S}$$

Inserting back into the equation for q_H in p. (4), we obtain

$$q_H = -\frac{w_C}{M_C} \cdot \Delta H_{m,R3} - \left(\frac{1}{2} \frac{w_H}{M_H} - \frac{w_O}{M_O} \right) \cdot \Delta H_{m,R4}$$

$$- \frac{w_S}{M_S} \cdot \Delta H_{m,R5}$$

$$\frac{\Delta H_{m,R3}}{M_C} = \frac{-394 \frac{kJ}{mol}}{12 \frac{g}{mol}} \approx -32{,}8 \frac{kJ}{g}$$

$$\frac{\Delta H_{m,R4}}{2 M_H} = \frac{-286 \frac{kJ}{mol}}{2 \cdot 1 \frac{g}{mol}} = -143 \frac{kJ}{g}$$

$$\frac{\Delta H_{m,R4}}{M_O} = \frac{\Delta H_{m,R4}}{8 \cdot 2 M_H} = \frac{1}{8} \cdot \left(-143 \frac{kJ}{g} \right)$$

$$\frac{\Delta H_{m,R5}}{M_S} = \frac{-297 \frac{kJ}{mol}}{32 \frac{g}{mol}} = -9{,}3 \frac{kJ}{g}$$

$$\Rightarrow q_H = -w_C \cdot \left(-32{,}8\ \frac{kJ}{g}\right)$$

$$- \left(w_H - \frac{1}{8} w_O\right) \cdot \left(-143\ \frac{kJ}{g}\right)$$

$$- w_S \cdot \left(-9{,}3\ \frac{kJ}{g}\right)$$

$$\Rightarrow q_H = 32{,}8\ \frac{kJ}{g} \cdot w_C + 143\ \frac{kJ}{g} \cdot \left(w_H - \frac{1}{8} w_O\right) + 9{,}3\ \frac{kJ}{g} \cdot w_S$$

The original Dulong formula as quoted by Channiwala and Parikh (2002):

$$HHV = 0.3383\, C^* + 1.443\left(H^* - \frac{O^*}{8}\right) + 0.0942\, S^*$$

where C^*, H^*, O^*, S^* are mass fractions in % on a dry basis.

Example: ethanol C_2H_5OH

$(a = 2,\ b = 6,\ c = 1)$

$$M_{Fuel} = aM_C + bM_H + cM_O$$

$$= 2 \cdot 12 \frac{g}{mol} + 6 \cdot 1 \frac{g}{mol} + 1 \cdot 16 \frac{g}{mol}$$

$$= 46 \frac{g}{mol}$$

mass fractions of C, H, O:

$$w_C = \frac{a \cdot M_C}{M_{Fuel}} = \frac{2 \cdot 12 \frac{g}{mol}}{46 \frac{g}{mol}} = 0.522$$

$$w_H = \frac{b \cdot M_H}{M_{Fuel}} = \frac{6 \cdot 1 \frac{g}{mol}}{46 \frac{g}{mol}} = 0.130$$

$$w_O = \frac{c \cdot M_O}{M_{Fuel}} = \frac{1 \cdot 16 \frac{g}{mol}}{46 \frac{g}{mol}} = 0.348$$

$(w_C + w_H + w_O = 0.522 + 0.130 + 0.348 = 1.000$ OK$)$

$$q_H = 32.8\ \frac{kJ}{g} \cdot w_C + 143\ \frac{kJ}{g} \cdot \left(w_H - \frac{1}{8} w_O\right)$$

$$= 32.8\ \frac{kJ}{g} \cdot 0.522 + 143\ \frac{kJ}{g} \cdot \left(0.130 + \frac{0.348}{8}\right)$$

$$= 29.5\ \frac{kJ}{g} = 29.5\ \frac{MJ}{kg}$$

BR App. A Table A.1 p. 567:

For ethanol, $HHV = 29.7\ \frac{MJ}{kg}$

⇒ Dulong-type calculation resulted in an error of ≈ − 0.7 %

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