

Application of the First Law to Complex Fuels

An example of a simple reacting First Law problem is a furnace that burns a fuel with air to heat water and produce a warm exhaust gas. We can find the amount of heat going into the water by our usual First Law balance:

$$Q = \sum_P n_i h_i - \sum_R n_i h_i$$

To do this calculation, we need the enthalpy of formation of the fuel; for simple fuels like CH₄ we can get this from the table.

For a complex fuel, such as wood, the energy content is reported as a "Heat of Combustion" or a "Heating Value". These terms refer to the same thing: how much heat do you get when you burn a given amount of fuel in stoichiometric air (all at 298 K) to CO₂ and water when the products are cooled to 298 K. This is *not* the same as an enthalpy of formation, and you need to be able to convert one value to the other to be able to easily do First Law Applications on complex fuels. (Remember, the enthalpy of formation is the heat needed to create the fuel from the elements, not the heat released on burning the fuel to CO₂ and H₂O.) Let's step through how the conversion is done for a typical wood fuel, in this case Douglas Fir.

The ultimate analysis is (basis is raw fuel)¹:

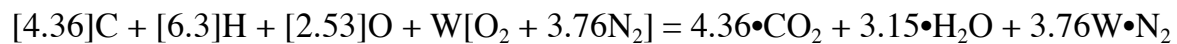
<u>Element</u>	<u>Mass %</u>
Ash	0.90
C	52.30
H	6.30
O	40.50

Higher Heating Value (MJ/kg) = 21.05

We will work with a basis of 100 kg of raw fuel.

<u>Element</u>	<u>Mass %</u>	<u>Mass (kg)</u>	<u>kmoles</u>
Ash	0.90	0.90	-
C	52.30	52.30	4.36
H	6.30	6.30	6.30
O	40.50	40.50	2.53

The reaction equation becomes:

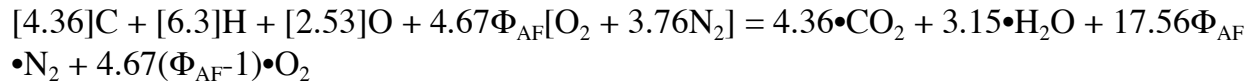


¹ <http://www.woodgas.com/proximat.htm/> Note that I ignored the very small nitrogen content (0.1%) for simplicity, adding it to the ash to keep the sum at 100%

Doing an O-atom balance:

$$2.53 + 2W = (2)(4.36) + 3.15 \quad \text{Yields } W = 4.67$$

Thus, the general combustion equation becomes:



The higher heating value (HHV) is defined as the amount of heat given up when 1 kg of raw fuel is burned with stoichiometric air to yield products at 298 K. (The water is assumed to be liquid, so the enthalpy of formation for liquid water is used in the following table. If the LHV was specified, the only change would be to use the vapor enthalpy of formation.) Since $Q(=HHV) = H_p - H_R$, if we set up a First Law balance for this situation we will see that the only unknown is the enthalpy of formation of the wood.

<u>Species</u>	<u>kmoles</u>	<u>h_f°</u>	<u>$h-h_{298}$</u>
Wood	100 kg	$h_{f,wood}^\circ$	0
O ₂	4.67	0	0
N ₂	17.56	0	0
CO ₂	4.36	-393,520	0
H ₂ O (f)	3.15	-285,830	0
N ₂	17.56	0	0

This yields $H_R = h_{f,wood}^\circ$ and $H_p = -2,616,112$ kJ/100 kg wood

Now we do the HHV First Law:

$$Q = H_p - H_R$$

$$-2,105,000 = -2,616,112 - h_{f,wood}^\circ \quad \text{which yields } h_{f,wood}^\circ = -511,112 \text{ kJ/100 kg wood}$$

Note that the Q is on our 100 kg wood basis, as is the final value for the enthalpy of formation of the wood. Now we can use our enthalpy of formation to do non-standard First Law calculations.

Assume you have a furnace burning pulverized Douglas Fir with 20% excess air to heat water. The products of combustion are at 500 K and the reactants are at 298 K. Find the heat passed to the water for 100 kg of wood.

We set up our usual table, with the kmoles and $h-h_{298}$ adjusted to the new situation:

<u>Species</u>	<u>kmoles</u>	<u>h_f°</u>	<u>$h-h_{298}$</u>
Wood	100 kg	-551,112	0
O ₂	5.60	0	0
N ₂	21.07	0	0
CO ₂	4.36	-393,520	17,678 - 9,364
H ₂ O (g)	3.15	-241,820	16,828 - 9,904
N ₂	21.07	0	14,581 - 8,669
O ₂	0.93	0	14,770 - 8,682

So, $H_R = -551,112$ kJ/100 kg wood, and $H_P = -2,289,193$ kJ/100 kg wood

And $Q = -1,738,081$ kJ/100 kg wood