Calculating the heat content of fuels

Under conditions of constant pressure and with work restricted to PV work, the heat produced by a chemical reaction is equal to the enthalpy change of the reaction, ΔH. If a mole of fuel is combusted the heat of the reaction is equal to the molar enthalpy change. Enthalpies of combustion are measured experimentally (Table 1) or may be calculated in several different ways.

One way to think of heats of combustion is to consider that chemical reactions are simply the reorganization of the reactants to produce new products. In other words, heats of reaction are the energy of breaking all the bonds in the reactants and then recovering energy by forming new bonds in the products. To get the correct sign for the enthalpy change of the system (reaction) we calculate enthalpy change of a reaction as the energy of all bonds broken minus the energy of bonds formed. Considering the combustion of a

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$

mole of methane we would need to break four moles of C-H bonds in CH_4, break two moles of O=O double bonds in two moles of oxygen gas, form two moles of C=O double bonds in CO_2, and form four moles of H-O bonds in two moles of H_2O. Notice that I use the balanced chemical reaction to calculate the numbers of bonds broken and formed. The following table illustrates the bond accounting.

broken	Moles of Bonds		Bond Energy kJ/mol	total kJ/mol reactant
C-C bonds	0		346	0
C-H bonds	4		411	1644
O=O	2		498	996
formed				
C=O	2		805	1610
O-H	4		464	1856

Sum bonds broken - Sum bonds formed **-826**

The calculated heat of combustion, -826 kJ/mol, is close to the experimental value obtained using a calorimeter of, -798 kJ/mol.

Another way to calculate heats of reaction is take the heats of formation, $_f\Delta H$, of the products minus the reactants of the combustion reaction. The heat of formation is the heat given off when a mole of molecules is formed from pure elements at room temperature, Table 2. This is really the same as the calculation above except we break each molecule down to pure stable elements instead of atoms (O_2 instead of O, H_2 instead of H) and then rebuild the products from the pure elements. For example, the reaction for combustion of methane to carbon dioxide and steam is

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$

where the molar enthalpy of the reaction is the heat of formation of products minus reactants.

$$\Delta H \text{ combustion} = {}_f\Delta H\,(CO_2) + 2\ {}_f\Delta H\,(H_2O\,(g)) - {}_f\Delta H\,(CH_4) - 2\ {}_f\Delta H\,(O_2)$$

$$\Delta H \text{ combustion} = -393 + 2*(-241.8) - (-74.9) - 2*(0) = -801.7 \text{ kJ/mol}$$

Notice that this value is in very good agreement with the experimental value (-798) because heats of formation are measured experimentally and are specific to each product and reactant while bond energies are averages.

The heats of formation change depending on the phase of the molecule. If water is condensed to a liquid it releases heat so the ${}_f\Delta H\,(H_2O\,(g) > {}_f\Delta H\,(H_2O\,(l))$. Making the change to liquid water causes

$$\Delta H \text{ combustion} = -393 + 2*(\mathit{-285.8}) - (-74.9) - 2*(0) = -889.7 \text{ kJ/mol}$$

the enthalpy of the reaction increases (becomes more negative) because the condensation of water releases more heat. The heat of reaction of fuels to produce liquid water is called the ***gross heat of combustion*** and the heat of reaction of fuels to produce steam is called the ***net heat of combustion***. The difference is about 10% depending on the amount of water produced. Boilers that condense the water produced during combustion are about 10% more efficient than conventional boilers but must operate at lower temperatures – typically less than 140 ^{o}F.

Table 2. Heats of Formation

Formula	Name	${}_f\Delta H$ kJ/mol
H_2	Hydrogen	0.0
CO_2	Carbon Dioxide	-393.5
O_2	Oxygen	0.0
H_2O	Water (g)	-241.8
H_2O	Water (l)	-285.8
CH_4	Methane	-74.9
C_2H_6	Ethane	-83.7
C_2H_2	Acetylene	226.8
C_3H_8	n-Propane	-104.6
C_4H_{10}	n-Butane	-125.5
C_5H_{12}	n-Pentane	-146.9
C_6H_{14}	n-Hexane	-167.4
C_7H_{16}	n-Heptane	-187.9
C_8H_{18}	n-Octane	-208.4
C_9H_{20}	n-Nonane	-229.3
$C_{10}H_{22}$	n-Decane	-249.4

Procedure:

1) Write the balanced combustion reactions for hydrogen (H_2), CH_4 (methane), C_3H_8 (propane), C_4H_{10} (butane), $C_{12}H_{22}O_{11}$ (sucrose – close to wood) and C_8H_{18} (octane or “gasoline”).
2) Make ball-and-stick models of the first four fuels and oxygen. Now reorganize the atoms and bonds (sticks) to make the combustion products.
3) Determine the moles of bonds broken and formed for each combustion reaction.
4) Calculate the enthalpy of combustion of each fuel using the energy of bonds broken minus the energy of bonds formed. Use and Excel table like the one shown above to help organize your calculations.
5) Calculate the enthalpy of combustion of each fuel using the enthalpies of formation.
6) Compare both calculations to the values in Table 2. You will need to do some unit conversions to make the comparisons. Since this is a practical course, lets do the comparison using units of BTU/pound of fuel. Use the following data to compare fossil fuels to wood.
7) Compute the pounds of carbon dioxide produced per BTU (kJ) of heat content for each fuel.

Lab Report:

1) In an Excel spreadsheet show your calculations. Which fuel is the most economical and which fuel will produce the least carbon dioxide to heat a home?

Current fuel prices: *http://maine.gov/energy/fuel_prices/index.shtml*

Extra Credit: A lot has been written about the hydrogen economy and the advantages of carbon free, high energy content hydrogen. However, the most cost effective industrial method to produce hydrogen gas is a reaction called steam reforming.

Stage 1. $CH_4 + H_2O + \text{heat} \rightarrow CO + 3H_2$
Stage 2. $CO + H_2O + \text{heat} \rightarrow CO_2 + H_2$

Net reaction $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

This reaction requires heat (from the combustion of fossil fuels) to proceed. How does the practical source of hydrogen change your opinion of this fuel?