IMPACT 2 ON TECHNOLOGY

Thermochemical aspects of fuels and foods

The thermochemical properties of fuels and foods are commonly discussed in terms of their **specific enthalpy**, the enthalpy of combustion divided by the mass of material (typically in kilojoules per gram), or the **enthalpy density**, the magnitude of the enthalpy of combustion divided by the volume of material (typically in kilojoules per cubic decimetre or, equivalently, kilojoules per litre). Thus, if the standard enthalpy of combustion is $\Delta_c H^\ominus$ and the molar mass of the compound is M, then the specific enthalpy is $\Delta_c H^\ominus/M$. This relation follows from the fact that the enthalpy change for material of mass m, which corresponds to an amount (in moles) $n = m/M$ of molecules, is $n\Delta_c H^\ominus = (m/M)\Delta_c H^\ominus$, so the enthalpy change divided by the mass of the sample is $\Delta_c H^\ominus/M$. Similarly, the enthalpy density is $\Delta_c H^\ominus/V_m$, where V_m is the molar volume of the material under the same conditions of pressure and temperature. This relation follows from the fact that the enthalpy change for a sample of volume V corresponds to an amount $n = V/V_m$ of molecules, is $n\Delta_c H^\ominus = (V/V_m)\Delta_c H^\ominus$, so the enthalpy change divided by the volume of the sample is $\Delta_c H^\ominus/V_m$.

Table 1 lists the specific enthalpies and enthalpy densities of several fuels. The most suitable fuels may be those with high specific enthalpies, as the advantage of a high molar enthalpy of combustion may be eliminated if a large mass of fuel is to be transported. Thus, H_2 gas compares very well with more traditional fuels such as methane (natural gas), iso-octane (a component of gasoline), and methanol. However, H_2 gas has a very low enthalpy density, so the advantage of a high specific enthalpy is undermined by the large volume of fuel to be transported and stored.

To assess the factors that optimize the heat output of carbon-based fuels, consider the combustion of 1 mol $CH_4(g)$, the main constituent of natural gas. The combustion of 1 mol $CH_4(g)$ releases 890 kJ of energy as heat. Now consider the combustion of 1 mol $CH_3OH(g)$:

$$CH_3OH(g) + \tfrac{3}{2}\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H^\ominus = -764\ \text{kJ}$$

This reaction is also exothermic, but only 764 kJ of energy is released as heat per mole of molecules. The replacement of a C—H bond by a C—O bond renders the carbon in methanol more highly oxidized than the carbon in methane, so it is reasonable to expect that less energy is released to complete the oxidation of carbon to CO_2 in methanol.

The fuel of living organisms is their food. A typical 18–20 year old human requires a daily input of about 9–12 MJ (1 MJ = 10^6 J). If the entire consumption were in the form of glucose, which has a specific enthalpy of 16 kJ g^{-1}, meeting their energy needs would require the consumption of 560–750 g of glucose. In fact, the complex carbohydrates (polymers of carbohydrate units, such as starch) more commonly found in our diets have slightly higher specific enthalpies (17 kJ g^{-1}) than glucose itself, so a carbohydrate diet is slightly less daunting than a pure glucose diet, as well as being more appropriate in the form of fibre, the indigestible cellulose that helps move digestion products through the intestine.

The specific enthalpy of fats, which are long-chain esters like tristearin (beef fat), is much greater than that of carbohydrates, at around 38 kJ g^{-1}, slightly less than the value for the hydrocarbon oils used as fuel (48 kJ g^{-1}). The reason for this difference lies in the fact that, unlike in fats, many of the carbon atoms in carbohydrates are bonded to oxygen atoms and are already partially oxidized.

Proteins are also used as a source of energy, When they are oxidized (to urea, $CO(NH_2)_2$), the equivalent enthalpy density is comparable to that of carbohydrates. However, there are advantages in avoiding this complete oxidation because the components of proteins, the amino acids, can be used more effectively in the body to construct other proteins.

Table 1
Thermochemical properties of some fuels

Fuel	Combustion equation	$\Delta_c H^\ominus$/(kJ mol^{-1})	Specific enthalpy/ (kJ g^{-1})	Enthalpy density*/ (kJ dm^{-3})
Hydrogen	$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$	–286	142	13
Methane	$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$	–890	55	40
Iso-octane†	$2\,C_8H_{18}(l) + 25\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(l)$	–5461	48	3.3×10^4
Methanol	$2\,CH_3OH(l) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 4\,H_2O(l)$	–726	23	1.8×10^4

* At atmospheric pressures and room temperature.
† 2,2,4-Trimethylpentane.