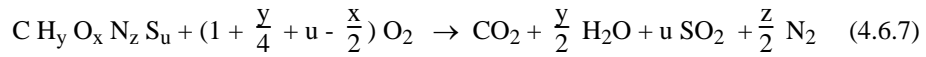### 4.6.2.3 Stoichiometric combustion

We call a stoichiometric combustion a combustion without excess or lack of air, where all available oxygen is completely consumed.

Assuming that nitrogen reacts only in negligible proportions and is found after combustion in molecular form, the general equation of a stoichiometric combustion is:

$$C\,H_y\,O_x\,N_z\,S_u + (1 + \frac{y}{4} + u - \frac{x}{2})\,O_2 \;\rightarrow\; CO_2 + \frac{y}{2}\,H_2O + u\,SO_2 + \frac{z}{2}\,N_2 \quad (4.6.7)$$

Depending on circumstances, coefficient $(1 + \frac{y}{4} + u - \frac{x}{2})$ may be greater or less than unity, depending on the existing availability of oxygen in the fuel. In most cases $x \leq y/2 + 2\,u$, but for some lean gases, the reverse situation may exist

For most conventional fuels, the values of z and u are very low and often negligible, while the condition $x \leq y/2$ is always verified. We can then simplify the symbolic formulation above by writing:
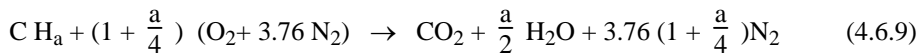
$$1 + \frac{y}{4} - \frac{x}{2} = 1 + \frac{a}{4} \tag{4.6.8}$$

which leads to the conclusion that formula $C\,H_y\,O_x$ becomes:
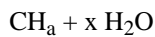
$CH_a + x\,H_2O$

a represents what is called hydrogen available for combustion referred to the complete oxidation of a carbon unit, and $a = y - 2\,x$.

With these conventions, the complete oxidation of fuels of formula $(CH_a + x\,H_2O)$ can be described by the equation:

$$C\,H_a + (1 + \frac{a}{4})\,(O_2 + 3.76\,N_2) \;\rightarrow\; CO_2 + \frac{a}{2}\,H_2O + 3.76\,(1 + \frac{a}{4})\,N_2 \tag{4.6.9}$$

while there is conservation of the constitutive water $x\,H_2O$.

This reaction is the fuel combustion without excess or lack of air.

If there is lack of air, some of the carbon is oxidized into carbon monoxide CO. To completely determine the reaction we have seen above that it is necessary to study the conditions of chemical equilibrium of the dissociation reaction of carbon dioxide, which depend primarily on temperature and correspond to the equation:

$$CO_2 \leftrightarrow CO + \frac{1}{2}\,O_2$$
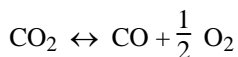
Combustion quality

The combustion quality is primarily determined by two factors:

- the combustion efficiency, which characterizes the degree of fulfillment of the chemical reaction, or if one prefers, the absence of unburned hydrocarbons or incompletely oxidized compounds;
- the level reached by the combustion temperature, determined by the ratio of the amount of heat released by burning to the amount of reactants and products.

In practice, we can optimize combustion by playing on an excess of air. A large excess air ensures that at any point, enough oxygen is available for combustion and therefore reduces the risk of unburned hydrocarbons. However, it dilutes the fumes, whose temperature drops.

4.6.2.4 Non stoichiometric combustion

When the combustion is not stoichiometric, it can be defined in several ways, usually by its excess air e, or its lack of air (- e), or the richness R already introduced in section 4.6.1.2, or its inverse the air factor λ. The formulations vary according to existing professional practice. For example, it is customary to speak of richness for gasoline engines, or excess air for boilers. In Thermoptim, we have selected the air factor, very useful in practice.

Excess air is the percentage of air not consumed by the stoichiometric reaction.
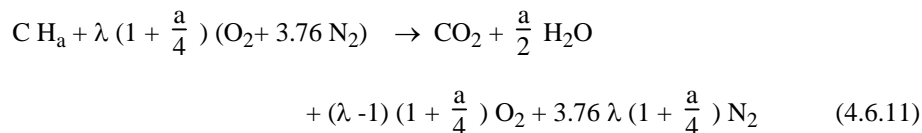
Richness R is defined as the ratio of the number of fuel moles in a given quantity of mixture, to the number of fuel moles in the stoichiometric mixture.

From these definitions, it follows the equivalence:

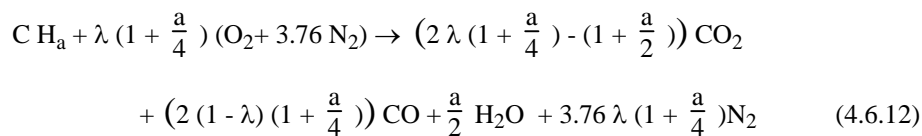$$R = \frac{1}{1 + e} \quad \text{and} \quad \lambda = 1 + e = \frac{1}{R} \tag{4.6.10}$$

Let us consider how a non-stoichiometric reaction is written as a function of air ratio λ:

In case of excess air, λ is greater than 1, and there is too much oxygen. The reaction writes:

$$C\,H_a + \lambda\,(1 + \frac{a}{4}\,)\,(O_2 + 3.76\,N_2) \;\rightarrow\; CO_2 + \frac{a}{2}\,H_2O$$

$$+ (\lambda - 1)\,(1 + \frac{a}{4}\,)\,O_2 + 3.76\,\lambda\,(1 + \frac{a}{4}\,)\,N_2 \tag{4.6.11}$$

In case of lack of air, λ is less than 1, and while there is enough oxygen to oxidize all the carbon in carbon monoxide, and a fraction in carbon dioxide, the reaction becomes:

$$1 > \lambda \; > \; \frac{(1 + \frac{a}{2})}{2\,(1 + \frac{a}{4})} \qquad \text{(neglecting dissociation of } CO_2 \text{ in } H_2O)$$

$$C\,H_a + \lambda\,(1 + \frac{a}{4}\,)\,(O_2 + 3.76\,N_2) \rightarrow \left(2\,\lambda\,(1 + \frac{a}{4}\,) - (1 + \frac{a}{2}\,)\right) CO_2$$

$$+ \left(2\,(1 - \lambda)\,(1 + \frac{a}{4}\,)\right) CO + \frac{a}{2}\,H_2O \; + 3.76\,\lambda\,(1 + \frac{a}{4}\,)N_2 \tag{4.6.12}$$

If the lack of air is more important, there is not even enough oxygen to form all the carbon monoxide.

4.6.3 STUDY OF INCOMPLETE COMBUSTION

In most cases, the combustion is not complete: for many reasons, various products including unwanted pollutants exist in the flue gas. Efforts are generally made to minimize this phenomenon penalizing both energy production and the environment, but it cannot be completely avoided.

4.6.4.5 Higher and Lower Heating Value

In most cases, the reaction products are found in the gaseous state at the end of combustion, but it is possible at low temperature, that some of them are liquid or even solidify, releasing a heat of condensation or solidification.

The problem arises especially during the combustion of hydrocarbons, water appearing among the products. The maximum energy release is obtained when the water contained in the fume is liquefied. The complete value of the heat of reaction is named Higher Heating Value or HHV. Where all the water produced remains in the vapor state, it is given the name of Lower Heating Value or LHV. If only a fraction of the water condenses, the heat of reaction is an intermediate value between the HHV and LHV.

Based on the above definitions, we identify four heating values which are particularly interesting: at constant pressure or volume, and lower or higher.

In fact, heating values at constant pressure and volume are substantially equal. However, enthalpies of vaporization are far from negligible (for water, it is approximately 45 MJ/kmol at 0 °C). So there are significant differences between the values of fuel HHV and LHV, and it is important to specify which one is used.

In conclusion, therefore, to determine the energies involved in a complete combustion reaction, you should use the fuel heating value, specifying whether it is the higher heating value (HHV) or the lower heating value (LHV).

The heating values of specific fuels commonly used in internal combustion engines are fairly close to each other. One can indeed show that hydrocarbon LHV range is from 44 MJ/kg to 40 MJ/kg when we consider products of distillation of increasing molar weight.

For gaseous fuels, heating values are generally expressed in kJ/m^3_N. They are obtained by dividing the heat of reaction in kJ/kmol by the volume occupied by a normal kilomol (0 °C, 1 bar), i.e. 22.414 m^3.

In Thermoptim, the LHV values of gases are displayed in the compound gas editor screen.

4.6.4.6 Adiabatic flame temperature

If we assume that the reaction takes place without heat exchange with the outside, that is to say adiabatically, it is possible to calculate the temperature reached by the mixture.

To do this, simply write that the enthalpy of the products is equal to that of the reactants in the initial state.

Temperature T_{ad} is thus given by:

$$H_p = H_{p0} + \int_{T_0}^{T_{ad}} Cp_p(t)\, dt = H_r \qquad (4.6.31)$$

with

$$H_r = H_{r0} + \int_{T_0}^{T_r} Cp_r(t)\, dt$$

Values with index 0 are relative to the reference state (298.15 K, 1 bar), and T_r is the temperature of the reactants when the combustion has been initiated.

We therefore should resolve:
$$\int_{T_0}^{T_{ad}} Cp_p(t)\, dt = H_{r0} - H_{p0} + \int_{T_0}^{T_r} Cp_r(t)\, dt$$

Since by definition $(- \Delta H_r) = H_{r0} - H_{p0}$

$$\int_{T_0}^{T_{ad}} Cp_p(t)\, dt = (- \Delta H_r) + \int_{T_0}^{T_r} Cp_r(t)\, dt \qquad (4.6.32)$$

In the general case of an equilibrium reaction in the presence of dissociation, this equation can be very complex, since ΔH_r depends on T_{ad} by the law of mass action.

In the case where the reaction is complete, (4.6.32) corresponds to solving a polynomial with real coefficients in T_{ad}, which can be done iteratively, for example.

In practice, the calculation of adiabatic temperature T_{ad} has a number of pitfalls. It is particularly important to take into account the variation in the number of moles during the reaction. For this, the best way is probably to think in molar units and to use the coefficients of the chemical reaction.

With the general equation considered earlier in this chapter:

$$\nu_1 A_1 + \nu_2 A_2 \quad \leftrightarrow \quad \nu_3 A_3 + \nu_4 A_4$$
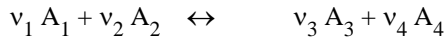
We have seen that the calculation of the heat of reaction is very simple by writing:

$$- \Delta H_r = \nu_1 \Delta h_{01} + \nu_2 \Delta h_{02} - \nu_3 \Delta h_{03} - \nu_4 \Delta h_{04}$$

For this reaction, the general equation (4.6.32) becomes:

$$(\nu_3 + \nu_4) \int_{T_0}^{T_{ad}} Cp_p(t)\, dt = (- \Delta H_r) + (\nu_1 + \nu_2) \int_{T_0}^{T_r} Cp_r(t)\, dt$$

Where Cp represents the molar heat capacity.

It is also possible to take into account incomplete reactions (non-stoichiometric conditions, dissociation), provided the value of equilibrium constants Kp are set, iterating once the temperature T_{ad} is known.

4.6.4.7 Combustion in boilers

To design and conduct boilers, the assumption is often made that the combustions are complete, to avoid too complex calculations. Moreover, volume flows involved