

Furnaces and boilers. Review of combustion.

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(version 3e)

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0. Introduction to boilers and furnaces

Furnace or boiler is here referred to any fossil-fuel fired combustion system where energy generated in a combustion chamber is used to heat or boil a fluid. The fluid (water or other type of fluid) can be contained in a vessel or circulated in tubes located in the combustion chamber.

In the context of HVAC a **boiler** boils/heats water while a **furnace** heats air. In material processing furnaces are used to heat/melt solids.

The examples presented in this section show the complexity of the different **heat transfer modes** involved in these equipment: pure conduction heat transfer through solid elements, natural and forced turbulent convection of the fluids, combustion in the firebox, radiation heat transfer, two-phase flows (boiling) in many applications.

The figure below, Fig. 0.1, shows a diagram of a **steam generator for a power plant**.

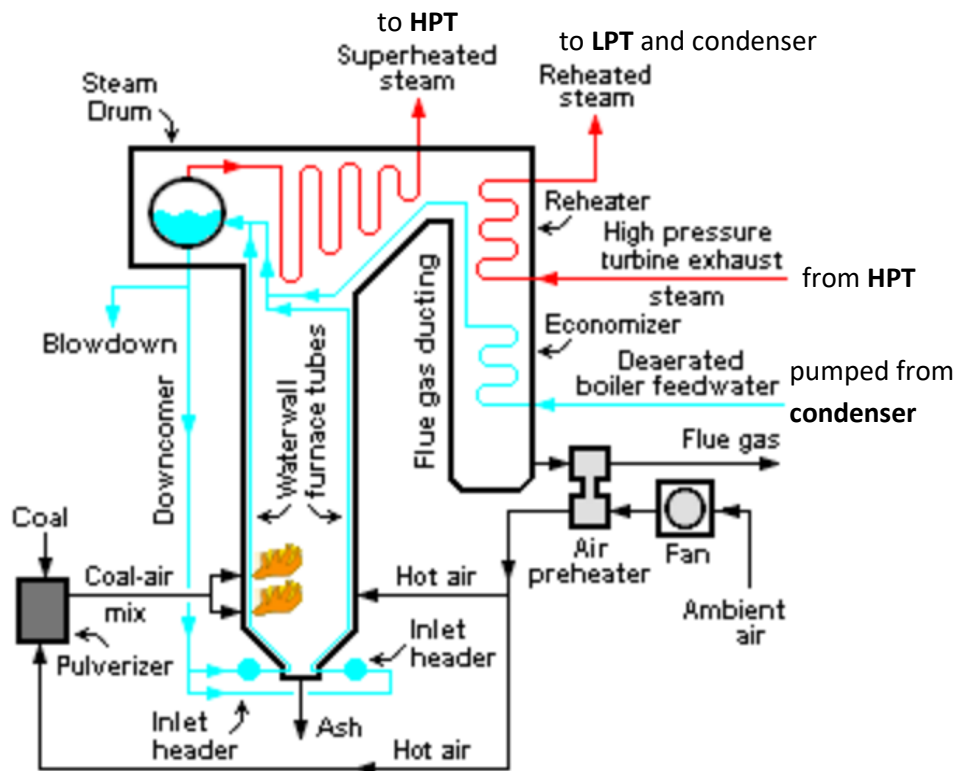


Figure 0.1 Boiler or steam generator for a power plant¹

The two figures below, Fig. 0.2 and Fig. 0.3, show a **fire-tube boiler** (combustion products goes inside the tubes) and a **water-tube boiler**, Fig. 0.4, (fluid goes inside the tubes).

¹ Figure from [https://en.wikipedia.org/wiki/Boiler_\(power_generation\)](https://en.wikipedia.org/wiki/Boiler_(power_generation)).

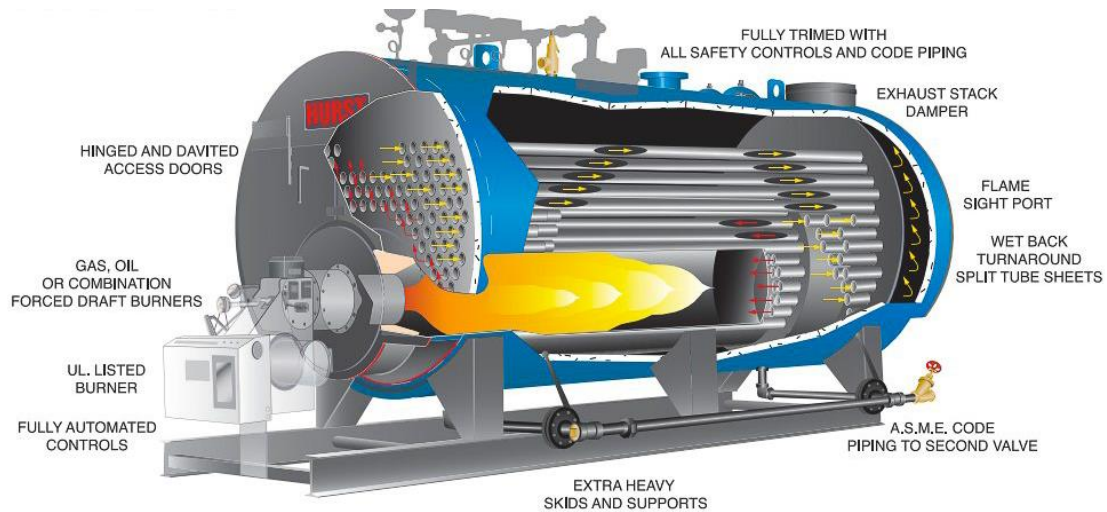


Figure 0.2 Fire-tube boiler²

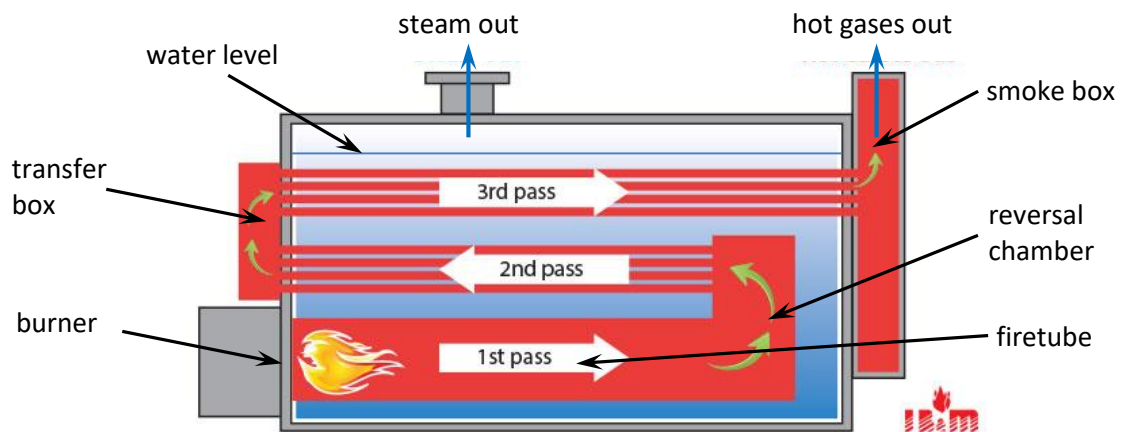


Fig. 0.3. Three-pass fire-tube boiler³

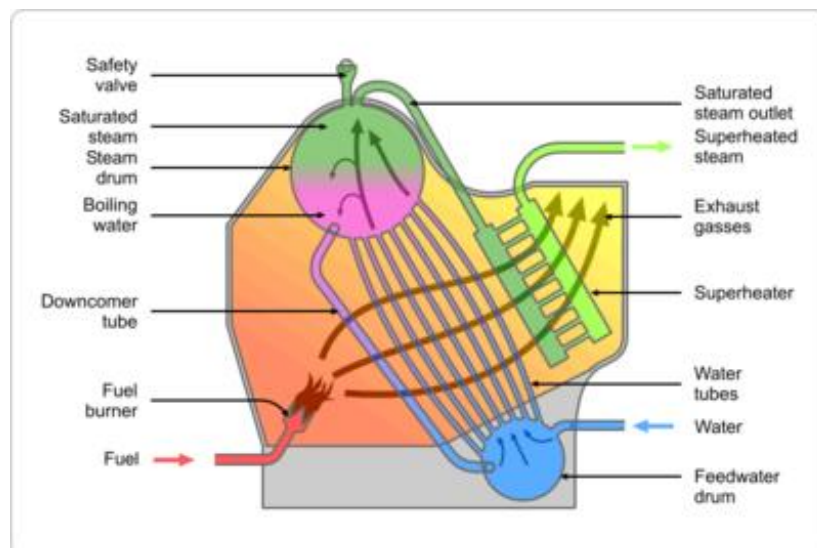


Figure 0.4 Water-tube boiler⁴

² Figure from http://www.hurstboiler.com/boilers/scotch_marine/euro_series.

³ Figure from <http://www.industrialboiler.com/boilers/firetube-boilers/3-pass-firetube-boilers.aspx>.

⁴ Figure from https://en.wikipedia.org/wiki/Water-tube_boiler

1. Basic concepts and combustion fundamentals

1.1. Basic concepts

1.1.1. Mixture of perfect gases

Consider a mixture of **perfect gases** containing N_s species in a volume δV and at a temperature T . If the species k was alone in the volume δV , its pressure would be the partial pressure of k . It must be verified that

$$\rho_k = \frac{m_k}{\delta V}; \quad p_k = \rho_k \frac{\hat{R}}{W_k} T; \quad p = \sum_{k=1}^{N_s} p_k; \quad \rho = \frac{m}{\delta V} = \sum_{k=1}^{N_s} \rho_k; \quad p = \rho \frac{\hat{R}}{W} T \quad (1.1.1)$$

where p, ρ, T , and W are the pressure, density, absolute temperature and the mean molar mass of the mixture, p_k is the partial pressure of species k , ρ_k is its density, and \hat{R} is the universal gas constant ($\hat{R} = 8.314 \text{ kJ/kmol}$).

The mean molar mass is related to the molar mass of the species from: $W = \sum_{k=1}^{N_s} \chi_k W_k$ or $W = [\sum_{k=1}^{N_s} Y_k / W_k]^{-1}$, where $\chi_k = n_k / n$ and $Y_k = m_k / m$ are the mole fraction and mass fraction of species k , and n_k and m_k refer to the moles and mass of species k .

In terms of the volume, the gas state equation is written as $pV = n\hat{R}T$, where n is the total number of moles. Then, the partial pressure for species k is given by $p_k V = n_k \hat{R}T$, while its partial volume is obtained from $pV_k = n_k \hat{R}T$. Therefore, the mole fraction of species k is:

$$\chi_k = \frac{n_k}{n} = \frac{V_k}{V} = \frac{p_k}{p} \quad (1.1.2)$$

1.1.2. Dry and humid air

Standard composition of dry air: $\chi_{N_2}^{da} = 0.7809$; $\chi_{O_2}^{da} = 0.2095$; $\chi_{Ar}^{da} = 0.0093$; $\chi_{CO_2}^{da} = 0.0003$.

Simplified (or regular) dry air is considered to contain 21% O_2 (in volume) and 79% N_2 (all components of air other than O_2 are lumped together with nitrogen). Its chemical formula is $0.21O_2 + 0.79N_2$ or, per mole of oxygen, $O_2 + 3.76N_2$. Note: $W_{air} = \sum \chi_k W_k = 28.86 \text{ kg/kmol}$.

Air frequently contains water vapour, a condensable gas at normal operating conditions. Air is then referred to as **humid air**.

Consider air at a given temperature T , pressure p and relative humidity ϕ . The **saturation vapour pressure**, p_{vs} , i.e. the one water vapour condenses, is given by the expression⁵:

⁵ Psychrometrics. ASHRAE Fundamentals.

$$\ln p_{vs} = -\frac{5.8002206 \times 10^3}{T} + 1.3914993 - 4.8640239 \times 10^{-2}T + 4.1764768 \times 10^{-5}T^2 - 1.4452093 \times 10^{-8}T^3 + 6.5459673 \ln T \quad (T > 273.15 \text{ K}) \quad (1.1.3)$$

where T refers to the absolute temperature (K) and p_{vs} is given in Pa.

The **vapour pressure of water**, p_v , is the partial pressure of water vapour in air. This important value can be calculated from the **relative humidity**, ϕ , which is defined as the ratio of the moles of water vapour contained in the air respect to the maximum amount of water the air can contain, i.e.

$$\phi = \left(\frac{n_v}{n_{vs}} \right)_{p,T} \approx \frac{p_v}{p_{vs}} \rightarrow p_v = \phi p_{vs} \quad (1.1.4)$$

The **moist air density**, ρ , can be evaluated using the ideal state equation of gases:

$$\rho = \rho_{da} + \rho_v = \frac{p - p_v}{R_{da}T} + \frac{p_v}{R_vT} \quad (1.1.5)$$

where $R_{da} = 287.042 \text{ J/kgK}$ and $R_v = 461.524 \text{ J/kgK}$. Note: $p_{da} = p - p_v$.

The **humidity ratio**, ϕ , represents the moisture content in air. Using the state equation:

$$\phi = \frac{m_v}{m_{da}} = \frac{W_v n_v}{W_{da} n_{da}} \approx \frac{R_{da}}{R_v} \frac{p_v}{p - p_v} \quad (1.1.6)$$

The humidity ratio ϕ is frequently given as $g_{\text{water}}/kg_{\text{dry - air}}$.

The **vapour mass fraction** (or specific humidity), Y_v , can be calculated from

$$Y_v = \frac{m_v}{m_{da} + m_v} = \frac{\phi}{1 + \phi} \quad (1.1.7)$$

Another important quantity is the **dew-point temperature**, T_{dp} . It represents the temperature the air must be cooled down (at a given p_v) to start water condensation. It can be calculated from⁶

$$T_{dp} = 6.54 + 14.526\alpha + 0.7389\alpha^2 + 0.09486\alpha^3 + 0.4569(p_v)^{0.1984} \quad (0 \leq T_{dp} \leq 93^\circ\text{C}) \quad (1.1.8)$$

where $T_{dp}(^\circ\text{C})$, $\alpha = \ln(p_v)$ and $p_v(\text{kPa})$.

Absolute specific **humid air enthalpy**, h_{ha} , can be obtained weighting the dry air and water vapour specific enthalpies, i.e.

$$h_{ha}(T, p, Y_v) = (1 - Y_v)h_{da} + Y_v h_v \quad (1.1.9)$$

where,

⁶ Psychrometrics. ASHRAE Fundamentals.

$$h_{da}(T, p) = h_{da}^o + \int_{T^o}^T c_{pda} dT; \quad h_{da}^o = 0; \quad c_{pda} \approx 1006 \frac{J}{kgK} \quad (1.1.10)$$

$$h_v(T, p) = h_{fv}^o + \int_{T^o}^T c_{pv} dT; \quad h_{fv}^o = -13423959 \frac{J}{kg}; \quad c_{pv} = 1860 \frac{J}{kgK} \quad (1.1.11)$$

In these expressions, h_{da}^o and h_{fv}^o are the enthalpies of formation of dry air and water vapour (reference conditions at $p^o = 1 \text{ atm} = 101325 \text{ Pa}$ and $T^o = 25^\circ\text{C} = 298.15 \text{ K}$).

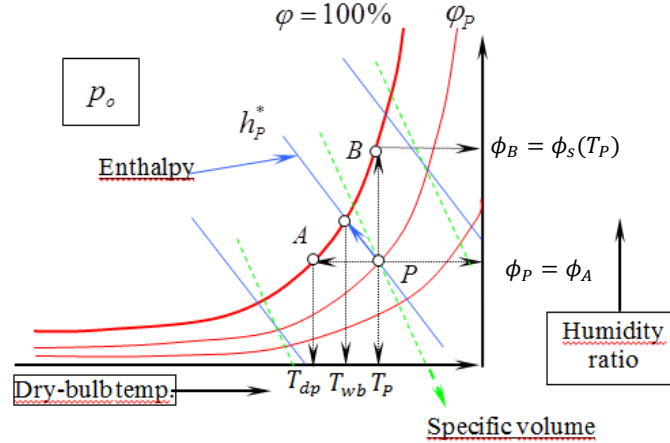
Absolute **enthalpy of liquid water**, h_l , can be calculated in a similar way:

$$h_l(T, p) = h_{fl}^o + \int_{T^o}^T c_{pl} dT + \frac{p - p^o}{\rho_l}; \quad h_{fl}^o = -15865987 \frac{J}{kg}; \quad c_{pl} \approx 4186 \frac{J}{kgK} \quad (1.1.12)$$

Note: $h_{fv}^o - h_{fl}^o = 2.4420 \times 10^6 \text{ kJ/kg}$.

Wet-bulb temperature (or adiabatic saturation temperature). Temperature when air is brought to saturation adiabatically (this is an isenthalpic process). From an energy balance of humid air at given T , p and ϕ , the wet-bulb temperature T_{wb} can be iteratively solved: $T_{wb} = T - \frac{(\phi_{wb} - \phi)[h_v(T_{wb}) - h_l(T_{wb})]}{1006 + 1860\phi}$ (1.1.13)

Previous information for humid air can also be obtained from the **psychrometric chart**:



1.2. Transport equations

Mass, energy and mass transfer equation of species k can be written in integral form for a control volume V_a , surrounded by a surface S_a with a unit normal vector \vec{n} pointing outwards:

$$\frac{\partial}{\partial t} \int_{V_a} \rho dV + \int_{S_a} \rho \vec{v} \cdot \vec{n} dS = 0 \quad (1.2.1)$$

$$\frac{\partial}{\partial t} \int_{V_a} \left(h - \frac{p}{\rho} + e_k + e_p \right) \rho dV + \int_{S_a} (h + e_k + e_p) \rho \vec{v} \cdot \vec{n} dS = - \int_{S_a} \vec{q}^{C+R} \cdot \vec{n} dS + \int_{S_a} \vec{v} \cdot \vec{f}_{(\vec{n})}^T dS \quad (1.2.2)$$

$$\frac{\partial}{\partial t} \int_{V_a} Y_k \rho dV + \int_{S_a} Y_k \rho \vec{v} \cdot \vec{n} dS = - \int_{S_a} \vec{j}_k \cdot \vec{n} dS + \int_{S_a} \dot{\omega}_k dS \quad (1.2.3)$$

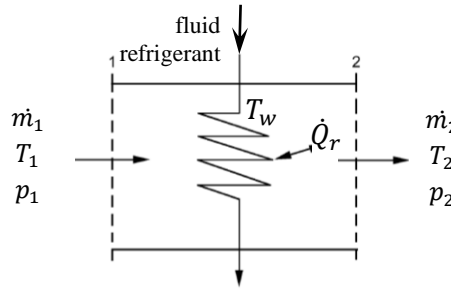
where h , e_k and e_k represent the specific enthalpy, kinetic energy and potential energy respectively; \vec{v} the flow velocity and ρ its density; \vec{q}^{C+R} the heat transfer rate (by conduction and radiation) per unit area; $\vec{f}_{(\vec{n})}^{\tau}$ the viscous forces; Y_k the mass fraction of species k ; \vec{j}_k the mass diffusion of the species k in the mixture; $\dot{\omega}_k$ the mass generation (or destruction) of species k per unit volume and time.

The transport of entropy can be written as,

$$\frac{\partial}{\partial t} \int_{V_a} s \rho dV + \int_{S_a} s \rho \vec{v} \cdot \vec{n} dS = - \int_{S_a} \frac{\vec{q}^{C+R}}{T} \cdot \vec{n} dS + \int_{S_a} \dot{s}_{gen} dS \quad (1.2.4)$$

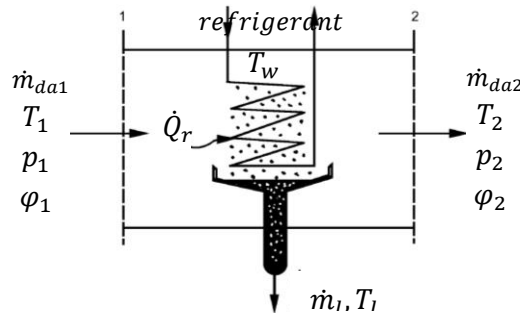
where s the specific entropy and \dot{s}_{gen} the generated entropy (always, $\dot{s}_{gen} \geq 0$).

Exercise 1.2a: Dry air circulates in a channel and through a cold coil at these entrance conditions: $\dot{m}_1 = 6 \text{ kg/s}$, $T_1 = 30^\circ\text{C}$, $p_1 = 1.3 \text{ bar}$. The superficial temperature of the coil is $T_w = 7^\circ\text{C}$, and the air is cooled down to $T_2 = 12^\circ\text{C}$ and the outlet pressure is $p_2 = 1.25 \text{ bar}$. Evaluate the power energy lost by the air and the generated entropy. Consider adiabatic channel walls.



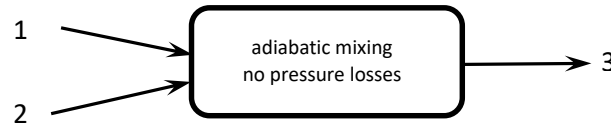
Sol. $\dot{Q}_r = 109 \text{ kW}$, $\dot{s}_{gen} = 85.9 \text{ W/K}$

Exercise 1.2b: Consider exercise 1.2a but humid air circulates in the channel at these entrance conditions: $\dot{m}_{da1} = 6 \text{ kg/s}$, $T_1 = 30^\circ\text{C}$, $p_1 = 1.3 \text{ bar}$, $\phi_1 = 0.64$. The superficial temperature of the coil is $T_w = 7^\circ\text{C}$, the condensed water is at $T_l = 9^\circ\text{C}$, and the air is cooled down to $T_2 = 12^\circ\text{C}$ and $\phi_2 = 0.5$. Exit pressure is $p_2 = 1.25 \text{ bar}$. Evaluate the dew point temperature of the air at the inlet and outlet conditions, the power energy lost by the air, and the water condensed. Consider adiabatic channel walls.



Sol. $\dot{Q}_r = 254 \text{ kW}$, $\dot{m}_l = 0.0575 \text{ kg/s}$, $T_{dp2} = 1.9^\circ\text{C}$, $T_{wb2} = 7.69^\circ\text{C}$, $\phi_2 = 0.0035 \text{ kg/s}$

Exercise 1.2c: Two flows of humid air enter in a chamber at $p = 1 \text{ bar}$. The inlet conditions for the first flow are: $T_1 = 4^\circ\text{C}$, $\varphi_1 = 70.7\%$, $\dot{G}_1 = 2 \text{ m}^3/\text{s}$. For the second flow: $T_2 = 25^\circ\text{C}$, $\varphi_2 = 50\%$, $\dot{G}_2 = 6.25 \text{ m}^3/\text{s}$. The chamber is adiabatic. Evaluate the outlet mixture conditions (humidity ratio, dry-bulb and wet-bulb temperatures, air mass flow rate, relative humidity).



Sol. $\dot{m}_{da3} = 9.69 \text{ kg/s}$; $T_3 = 19.63^\circ\text{C}$, $\varphi_3 = 58.04\%$, $T_{wb3} = 14.54^\circ\text{C}$, $\phi_3 = 8.29 \text{ gv/kgda}$.

1.3. Chemical reaction and combustion

A **chemical reaction** involves the exchange and/or rearrangement of atoms between colliding molecules. Therefore, reactant molecules are rearranged to become product molecules.

Combustion is a fast chemical reaction where a fuel (usually a hydrocarbon) reacts with oxygen (oxidizer) to produce oxidized products (e.g. carbon dioxide, water, etc.). Combustion is an exothermic reaction where energy is liberated as thermal energy (in the form of high-temperature gases).

For example, the complete combustion of methane with oxygen is $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$. It reads one mole of methane combines with two moles of oxygen to give one mole of carbon dioxide and two moles of water.

Any chemical reaction must verify that the **number of reactants atoms** before and after the reaction must be conserved (however, number of moles or molecules are not necessarily conserved). As a consequence, **mass is also conserved**. In the previous chemical reaction we have 1 atom of C (reactants and products), 4 atoms of H and 4 atoms of O . Per unit of kmol of CH_4 , we have 80.042 kg of reactants and exactly the same quantity of products. **Electric charge** is also conserved. However, **chemical potential** is conserved under chemical equilibrium conditions.

Note: in this document, a specific variable **per unit mole** or **per unit mass** is indicated with a lower case letter with or without a hat, i.e. $\hat{\phi}$ represents a quantity per unit mole and ϕ per unit mass. E.g. $h \text{ (J/kg)}$ but $\hat{h} \text{ (J/kmol)}$. Both properties are related through the molar mass $W \text{ (kg/kmol)}$, i.e. $\hat{h} = Wh$ (in general, $\hat{\phi} = W\phi$).

Exercise 1.3a: Write the complete combustion of methane with regular air and complete consumption of oxygen. If the combustion is at atmospheric pressure, evaluate the partial pressure of the combustion gases.

Sol. $\text{CH}_4 + 2(\text{O}_2 + 3.76\text{N}_2) \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2$; $p_{\text{CO}_2} = 9632 \text{ Pa}$; $p_{\text{H}_2\text{O}} = 19263 \text{ Pa}$, $p_{\text{N}_2} = 72430 \text{ Pa}$

1.4. Fuels

Most of the combustion systems use air or oxygen as oxidizers.

Most common fuels are based on hydrocarbons. They are usually classified according to their physical state: gas, liquid or solid. Gaseous fuels are burned in premixed or diffusion burners. Atomization or vaporization is needed when liquids fuels are used; adequate mixing of the fuel and air is also needed. Solid fuels must be heated to vaporize sufficiently volatiles to initiate and sustain the combustion.

As it was mentioned, hydrocarbon fuels can be into gaseous, liquid and solid forms, i.e.

- **Gases:**
 - NG (natural gas), mainly composed by methane (from 70 to 96%) (other components are ethane, propane, butane, pentane, etc.)
 - LPG (liquefied petroleum gas), commonly mixes including both propane and butane
 - Commercial propane consists basically of propane but generally contains propylene (5 to 10%). It shows low boiling point at atmospheric pressure (good property for cold climates)
 - Commercial butane consists basically of butane but may contain up to 5% of butylene. It has relatively high boiling point at atmospheric pressure (about 0°C)
 - Syngas, or synthesis gas, formed primarily by hydrogen, carbon monoxide, and very often with some carbon dioxide.
 - Biogas, from organic matter, mainly composed by methane and carbon dioxide. It is produced in the absence of oxygen (anaerobically) by the breakdown of organic matter (agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste).
 - Manufactures gases are produced from coal, coke, oil, LPG or NG. They are mainly used for industrial in-plant operations or as specialty fuels, e.g. acetylene used in gas welding, cutting, etc.
- **Liquids:**
 - In general, liquid fuels are mixtures of hydrocarbons extracted from crude oil after a refining process, which gives a variety of fuels and other products.
 - Lighter hydrocarbons are refined into distillate fuel oils like gasoline, kerosene, jet fuels, diesel fuels or light heating oils.
 - Heavy hydrocarbons are refined into residual fuel oils and other products (e.g. lubricating oils, asphalt, etc.).
 - According to ASTM Standard D396, fuel oils are divided into different grades: distillates (grades 1 and 2), light (4 and 5-light), heavy (5-heavy), residual (6).
 - Brief description of the grade system according to ASHRAE (Fundamentals 2009): “**Grade No. 1** is a light distillate intended for vaporizing-type burners. High volatility is essential to continued evaporation with minimum residue. This fuel is also used in extremely cold climates for residential heating using pressure-atomizing burners. **Grade No. 2** is heavier than No. 1 and is used primarily with pressure-atomizing (gun) burners that spray oil into a combustion

chamber. The atomized oil vapour mixes with air and burns. This grade is used in most domestic burners and many medium-capacity commercial/industrial burners. A dewaxed No. 2 oil with a pour point of -50°C is supplied only to areas where regular No. 2 oil would jell. Grade No. 2—low sulphur is a relatively new category that has a sulphur content of 0.05%. Lower fuel sulphur content reduces fouling rates of boiler heat exchangers. **Grade No. 4** is an intermediate fuel that is considered either a heavy distillate or a light residual. Intended for burners that atomize oils of higher viscosity than domestic burners can handle, its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. **Grade No. 5 (light)** is a residual fuel of intermediate viscosity for burners that handle fuel more viscous than No. 4 without preheating. Preheating may be necessary in some equipment for burning and, in colder climates, for handling. **Grade No. 5 (heavy)** is a residual fuel more viscous than No. 5 (light), but intended for similar purposes. Preheating is usually necessary for burning and, in colder climates, for handling. **Grade No. 6**, sometimes referred to as Bunker C, is a high viscosity oil used mostly in commercial and industrial heating. It requires preheating in the storage tank to permit pumping, and additional preheating at the burner to permit atomizing”.

- **Solids:**

- Coal, wood, charcoal, coke, grains (corn, wheat, rye, etc.), etc. These fuels are used for heating and cooling applications (burners, furnaces, etc.).
- The most important is coal. It is usually classified as: i) anthracite (high carbon content and energy density; repels moisture; domestic/industrial uses; HHV=30-32 MJ/kg), ii) bituminous (some moisture content; for thermal or metallurgical applications; HHV=25-33 MJ/kg), iii) sub-bituminous (for electricity generation; HHV=20-21 MJ/kg), iv) lignite coal (high moisture content, low energy density, electricity generation; HHV=16 MJ/kg).
- A first estimation of the HHV of a higher-quality coals can be obtained by the Dulong formula: $HHV \text{ (MJ/kg)} = 33.820C + 144.28(H - O/8) + 9.42S$, where C, H, O, S are the mass fractions of these species obtained from the ultimate analysis (see exercise 1.5d).

Characterization of fuels:

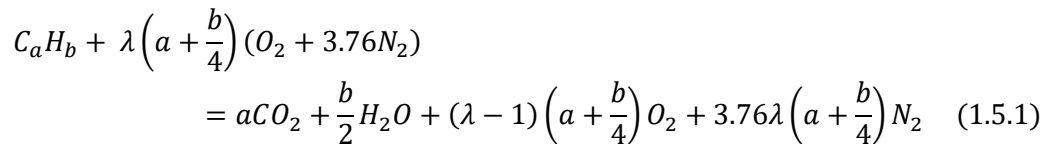
- Chemical formula, W (molecular mass), HHV (higher heating value), LHV (lower heating value), ρ , c_p , λ , μ (liquids, gases), etc. (see Annex 1 and 2).
- For a self-sustained combustion reaction the volume percentage of fuel and air must be within the flammability limits of the combustible substance (see Annex 1 for lower and upper flammable or explosive limits).
- Ignition temperature: lowest temperature at which combustion of a substance becomes self-propagating (see Annex 1).
- For solids or liquids fuels, prior to combustion a phase change to the gas state must take place.

1.5. Complete, stoichiometric, lean and rich combustion

In a **complete combustion** all combustible elements are fully oxidized. Then, all the carbon present in the fuel is consumed to give carbon dioxide, all the hydrogen is burned to water or all the sulphur (if present) is burned to sulphur dioxide.

In a **stoichiometric combustion** the fuel (e.g. a hydrocarbon) and the oxidizer (e.g. oxygen, O_2 or air) consume each other completely. In a **lean combustion** there is an excess of oxygen while in a **rich combustion** there is an excess of fuel.

E.g. the lean combustion of a **hydrocarbon** C_aH_b in theoretical (dry) air gives:

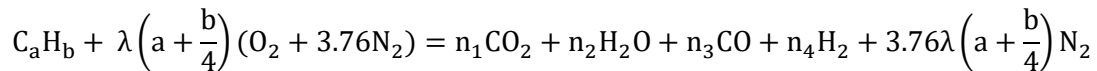


where the parameter λ indicates the excess/deficit of air, i.e.

$$\lambda = \frac{(\dot{m}_A/\dot{m}_F)}{(\dot{m}_A/\dot{m}_F)_{stoic}}$$

Then, $\lambda = 1$ means stoichiometric combustion, while $\lambda > 1$ indicates **lean combustion** (excess of air) and $\lambda < 1$ indicates **rich combustion** (defect of air). E.g., if one says “octane, C_8H_{18} , is burned with 50% excess air...”, wants to say $\lambda = 1.5$.

In case of **rich combustion** ($\lambda < 1$), CO and H_2 can be found in products but not O_2 (there is not enough oxygen to allow the fuel to react completely to produce CO_2 and H_2O). The reaction could be:



To determine the number of moles of products the atom conservation property is not enough. We have more unknowns than equations. If we assume equilibrium condition, the following equilibrium reaction can be used: $CO + H_2O \rightleftharpoons CO_2 + H_2$. Therefore, the extra equation is based on the principle that the total Gibbs free energy of the mixture reaches a minimum value.

The equivalence ratio ϕ is defined as

$$\phi = \frac{(\dot{m}_F/\dot{m}_A)}{(\dot{m}_F/\dot{m}_A)_{stoic}}$$

Then, $\phi = 1/\lambda$. For a fuel-rich mixture $\phi > 1$ ($\lambda < 1$); for a fuel-lean mixture $\phi < 1$ ($\lambda > 1$).

Exercise 1.5a: 2 kmol of methane is burned with regular air that contains 16 kmol of oxygen. Evaluate the excess of air, the equivalence ratio and the air-fuel ratio assuming complete combustion. Write the chemical equation.

Sol. $\lambda = 4$, $\phi = 0.25$, $AF = 68.47 \text{ kg}_A/\text{kg}_F$

Exercise 1.5b: A combustion chamber at atmospheric pressure (1 atm) is fed with $\dot{m}_F = 0.32 \text{ kg/s}$ of liquid n-decane $C_{10}H_{22(l)}$ and excess air of 70% ($\lambda = 1.7$). Assuming complete combustion with simplified air and under thermodynamic equilibrium, evaluate the mass flow rate of the products, \dot{m}_k , and their partial pressure. p_k .

Sol. $\dot{m}_{\text{CO}_2} = 0.990 \text{ kg/s}$; $\dot{m}_{\text{H}_2\text{O}} = 0.446 \text{ kg/s}$; $\dot{m}_{\text{O}_2} = 0.781 \text{ kg/s}$; $\dot{m}_{\text{N}_2} = 6.242 \text{ kg/s}$; $p_{\text{CO}_2} = 7739 \text{ Pa}$, $p_{\text{H}_2\text{O}} = 8513 \text{ Pa}$, $p_{\text{O}_2} = 8397 \text{ Pa}$, $p_{\text{N}_2} = 76676 \text{ Pa}$.

Exercise 1.5c: Propane is burned with 70% of excess of regular air at 1 bar. Assuming complete combustion, evaluate the air-fuel ratio and the dew-point temperature of the flue gases.

Sol. $AF = 26.47 \text{ kg}_A/\text{kg}_F$, $T_{dp} = 44.9^\circ\text{C}$

Exercise 1.5d: Coal is burned in a boiler with a 20% of excess of air at 1 atm. An ultimate analysis of the coal gives the following mass percentage of the fuel constituents: 82% C, 5% H_2 , 5.2% O_2 , 1.5% N_2 , 0.5% S and 5.8% ash. Evaluate the air-fuel ratio, an approximate value of its HHV, and the dew-point temperature.

Sol. $AF = 13.86 \frac{\text{kg}_A}{\text{kg}_F}$, $HHV = 34 \frac{\text{MJ}}{\text{kg}}$, $T_{dp} = 34^\circ\text{C}$.

1.6. Elementary vs. overall reactions

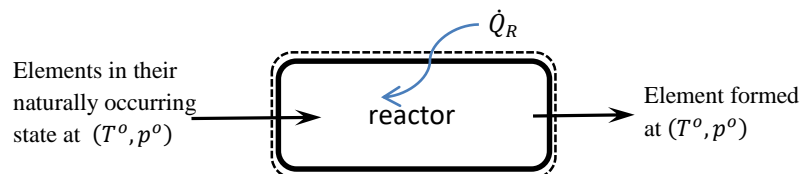
Elementary reactions occur on a molecular level, exactly in the way which is described by the reaction equation. For example, $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$, i.e. due to molecular motion in the gas, hydroxy radicals collide with hydrogen molecules. Some collisions occur without molecular rearrangement (non-reactive collisions), but others give water and hydrogen (reactive collisions).

However, the already mentioned reaction of methane, $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$, is not an elementary reaction. The reaction is called **net reaction or overall reaction**. Carbon dioxide and water are not produced by a single collision between the methane and oxygen. Instead, many reactive intermediates like H, O and OH are formed (e.g. the GRI-Mech 3.0 mechanism for methane involves 53 species and 325 elementary reactions!).

1.7. Formation enthalpy

The standard **enthalpy of formation** of an element k , h_{fk}^o or \hat{h}_{fk}^o , is the enthalpy needed to form the element at a given reference state (T^o, p^o) . The reference state is: $p^o = 1 \text{ atm} = 101325 \text{ Pa}$; $T^o = 25^\circ\text{C} = 298.15 \text{ K}$.

Brief explanation of its evaluation:



From an **energy balance**, $h_{PR} - h_{REACT} = \dot{Q}_R/\dot{m}$ (products and reactants at T^o, p^o). For convention, enthalpy of formation is zero for the elements in their naturally occurring state at (T^o, p^o) . E.g. $\hat{h}_{fk}^o = 0$ for $k = \text{O}_{2(g)}$, $\text{N}_{2(g)}$, $\text{H}_{2(g)}$, $\text{He}_{(g)}$, $\text{Ar}_{(g)}$, $\text{C}_{(s)}$. Therefore, if $h_{REACT} = 0$ (reactants are composed by elements in their naturally occurring state), $h_{PR} = \dot{Q}_R/\dot{m}$ and represents the energy delivered to the system to form the element.

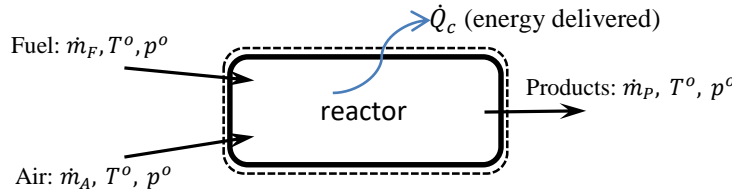
For example, oxygen monoatomic can be formed by dissociation of molecules of O_2 , $O_2 \rightarrow 2O$. The bond dissociation energy of 1 mole of O_2 at (T^o, p^o) is 498390 kJ/kmol . Therefore, the enthalpy of formation of O is $\hat{h}_{f,O}^o = 249170 \text{ kJ/kmol}$. In these processes energy is delivered to the system (i.e. $\dot{Q}_R > 0$, endothermic reaction), and then $\hat{h}_{f,k}^o > 0$.

To form water vapour (or liquid), $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. In this case, energy is delivered by the system ($\dot{Q}_R < 0$, exothermic reaction), and then $\hat{h}_{f,k}^o < 0$ (for water, $\hat{h}_{f,H_2O(g)}^o = -241818 \text{ kJ/kmol}$ and $\hat{h}_{f,H_2O(l)}^o = -285830 \text{ kJ/kmol}$). See Annex 1.

1.8. Heat of combustion, HHV and LHV

The **enthalpy (or heat) of combustion** is the heat released when 1 *mole* of fuel is completely burned, products and reactants at the reference conditions of $T^o = 25^\circ\text{C}$, $p^o = 1 \text{ at}$.

Consider the combustion of a hydrocarbon C_aH_b in the reactor of the figure:



An energy balance assuming steady state, $\dot{W}_s = 0$, $\Delta e_c = \Delta e_p = 0$ reads as:

$$\sum_P \dot{m}_k h_k - \sum_{R=F+A} \dot{m}_k h_k = -\dot{Q}_c \quad (1.8.1)$$

However, $\dot{m}_k h_k = \dot{n}_k W_k h_k = \dot{n}_k \hat{h}_k$, and dividing by \dot{n}_F :

$$\sum_P \frac{\dot{n}_k}{\dot{n}_F} \hat{h}_k - \sum_{R=F+A} \frac{\dot{n}_k}{\dot{n}_F} \hat{h}_k = -\frac{\dot{Q}_c}{\dot{n}_F} \quad (1.8.2)$$

Considering that $\hat{h}_k = \hat{h}_{f,k}^o + \Delta \hat{h}_k = \hat{h}_{f,k}^o + \int_{T=T^o}^{T^o} \hat{c}_{p,k} dT = \hat{h}_{f,k}^o$ and $\hat{h}_{f,O_2}^o = \hat{h}_{f,N_2}^o = 0$:

$$\frac{\dot{Q}_c}{\dot{n}_F} = \hat{h}_{f,C_aH_b}^o - a \hat{h}_{f,CO_2}^o - \frac{b}{2} \hat{h}_{f,H_2O(x)}^o \quad (1.8.3)$$

This is the heat of combustion or heating value of the fuel. It is called **lower heating value (LHV)** when water leaves the reactor in gas state:

$$\widehat{LHV} = \frac{\dot{Q}_{c(g)}}{\dot{n}_F} = \hat{h}_{f,C_aH_b}^o - a \hat{h}_{f,CO_2}^o - \frac{b}{2} \hat{h}_{f,H_2O(g)}^o \quad \left(\frac{\text{kJ}}{\text{kmol}_F} \right) \quad (1.8.4)$$

The **higher heating value (HHV)** is when the water is condensed:

$$\widehat{HHV} = \frac{\dot{Q}_{c(l)}}{\dot{n}_F} = \hat{h}_{f,C_aH_b}^o - a \hat{h}_{f,CO_2}^o - \frac{b}{2} \hat{h}_{f,H_2O(l)}^o \quad \left(\frac{\text{kJ}}{\text{kmol}_F} \right) \quad (1.8.5)$$

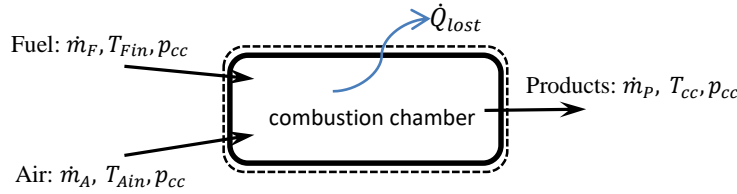
Obviously, $\widehat{HHV} = \widehat{LHV} + \frac{b}{2} (\hat{h}_{f,H_2O(g)}^o - \hat{h}_{f,H_2O(l)}^o) = \widehat{LHV} + \frac{b}{2} \Delta \hat{h}_{fg,H_2O}^o$.

Note: $HHV = \widehat{HHV}/W_F$ and $LHV = \widehat{LHV}/W_F$.

Exercise 1.8. Evaluate the LHV and HHV of methane, acetylene and propane using eq. (1.8.4) and (1.8.5). Use Annex 1 for the enthalpies of formation. Compare your results with the ones given on the same annex.

1.9. Temperature of the combustion products

Consider the combustion of a hydrocarbon C_aH_b in the combustion chamber of the figure:



where \dot{Q}_{cc} represents the energy exchanged with the walls (sometimes energy losses).

An **energy balance** on the CV indicated in the figure assuming: steady state, constant pressure, $\Delta e_k = \Delta e_p \approx 0$, and $\dot{W}_s \approx 0$, has the form:

$$\sum_P \dot{m}_k h_k - \sum_R \dot{m}_k h_k = -\dot{Q}_{lost} \quad (1.9.1)$$

dividing by \dot{m}_F

and considering: $\frac{\dot{m}_k}{\dot{m}_F} h_k = \frac{\dot{n}_k W_k}{\dot{n}_F W_F} h_k = \frac{v_k}{W_F} \hat{h}_k$

$$\sum_P v_k \hat{h}_k - \sum_R v_k \hat{h}_k = -\frac{W_F \dot{Q}_{lost}}{\dot{m}_F} \quad (1.9.2)$$

For the products: $\hat{h}_k = \hat{h}_{fk}^o + \bar{c}_{pk}(T_{cc} - T^o)$

$$\sum_P v_k \hat{h}_{fk}^o + \sum_P v_k \bar{c}_{pk}(T_{cc} - T^o) - \sum_R v_k \hat{h}_k = -\frac{W_F \dot{Q}_{lost}}{\dot{m}_F} \quad (1.9.3)$$

$$T_{cc} = T^o + \frac{\sum_R v_k \hat{h}_k - \sum_P v_k \hat{h}_{fk}^o - W_F \dot{Q}_{lost}/\dot{m}_F}{\sum_P v_k \bar{c}_{pk}} \quad (1.9.4)$$

where enthalpy of reactants can be calculated directly: $\sum_R v_k \hat{h}_k = \hat{h}_{fF}^o + \int_{T^o}^{T_{Fin}} \hat{c}_{p,F} dT + v_{O_2} \hat{h}_{fO_2}^o + v_{O_2} \int_{T^o}^{T_{Ain}} \hat{c}_{p,O_2} dT + v_{N_2} \hat{h}_{fN_2}^o + v_{N_2} \int_{T^o}^{T_{Ain}} \hat{c}_{p,N_2} dT$ (for oxygen and nitrogen, $\hat{h}_{fO_2}^o = \hat{h}_{fN_2}^o = 0$). Introducing these terms:

$$T_{cc} = T^o + \frac{\hat{h}_{fF}^o - \sum_P v_k \hat{h}_{fk}^o + \int_{T^o}^{T_{Fin}} \hat{c}_{p,F} dT + v_{O_2} \int_{T^o}^{T_{Ain}} \hat{c}_{p,O_2} dT + v_{N_2} \int_{T^o}^{T_{Ain}} \hat{c}_{p,N_2} dT - W_F \dot{Q}_{lost}/\dot{m}_F}{\sum_P v_k \bar{c}_{pk}} \quad (1.9.5)$$

where $\hat{h}_{fF}^o - \sum_P v_k \hat{h}_{fk}^o$ is the \widehat{LHV} .

The calculation needs an **iterative process**. Firstly, T_{cc} is estimated to evaluate the mean specific heat of each one of the species k :

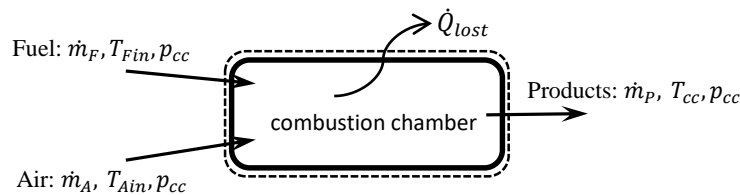
$$\bar{\hat{c}}_{pk} = \frac{1}{T_{cc} - T^o} \int_{T^o}^{T_{cc}} \hat{c}_{pk} dT \quad (1.9.6)$$

Then, from the energy equation, (1.9.5), T_{cc} is calculated. The process is repeated until convergence is reached.

The **adiabatic flame temperature** is obtained when the combustion is complete and stoichiometric, and without heat losses ($\dot{Q}_{lost} = 0$). This is the maximum temperature. In technical applications the temperature of the combustion products is lower than the adiabatic flame temperature because:

- the combustion is incomplete,
- frequently with excess of air (lean combustion, $\lambda > 1$),
- there are energy losses,
- combustion products can dissociate (endothermic reaction),
- etc.

Exercise 1.9a. A combustion chamber burns propane (C_3H_8) with 50% of excess of regular (simplified) air. The flow of air is $\dot{m}_A = 10 \text{ kg/s}$.



Questions:

- Write the chemical formula considering complete combustion
- Evaluate the mass flow rate of propane \dot{m}_F , and the mass flow rate of CO_2 and H_2O
- The LHV of propane is 46360 kJ/kg. Explain the meaning of this quantity and how it is obtained.
- Evaluate the \widehat{LHV} and \widehat{HHV} using the formation enthalpies of the Annex 1.
- Obtain from the energy equation the temperature T_{cc} of the combustion gases. Consider as input data $\dot{m}_F, T_{Fin}, p_{cc}, \dot{m}_A, T_{Ain}, \dot{Q}_{lost}$, the molar formation enthalpy of the species \hat{h}_{fk}^o ($k = C_3H_8, O_2, N_2, CO_2, H_2O$), and their molar heat capacities $\hat{c}_{pk}(T)$.

Exercise 1.9b: Consider combustion of methane (CH_4) at atmospheric pressure. Fuel and air inlet temperatures are: $T_{Fin} = 400 \text{ K}$, $T_{Ain} = 300 \text{ K}$. The mass flow of air is $\dot{m}_A = 0.1 \text{ kg/s}$ and the excess air is 100 %. Evaluate the mass flow rates of the products and the temperature of the gases. It is assumed adiabatic combustion ($\dot{Q}_{lost} = 0$). Repeat the exercise with an excess of air of 50% and under stoichiometric conditions.

Sol. $T_{cc} = 1556.19 \text{ K}$ (100% excess air); $T_{cc} = 1859.58 \text{ K}$ (50%); $T_{cc} = 2389.20 \text{ K}$ (stoichiometric conditions).

All this part is necessary for the analysis and design of combustion thermal equipment, e.g. heaters, ovens, stoves, boilers, furnaces, fireplaces, steam generators, dryers, burners, etc.

Next section is focussed on a particular application where the analysis of the whole equipment is taken into account.

2. Heat transfer in well-stirred furnaces

2.1 Introduction

Now, we follow the analysis by Hottel described in Viskanta's book⁷ based on a zero-dimensional model. The considered system consists of:

- a. single gas zone of the **well-mixed combustion products** at a uniform temperature T_g and composition;
- b. the **load** (i.e. **heat sink**) to be heated inside the chamber is at constant and uniform temperature T_s ; and
- c. the **rest of the walls** of the combustion chamber are refractory at constant and uniform temperature T_w .

Gas recirculation is needed if the assumption of well-stirred system is applied. According to Viskanta, homogeneity of temperature and composition of the combustion gases must be promoted by **recirculation of the gases** in the chamber by means of a fan or by design.

The model is **steady-state**. The figure below shows a schematic representation of the considered furnace.

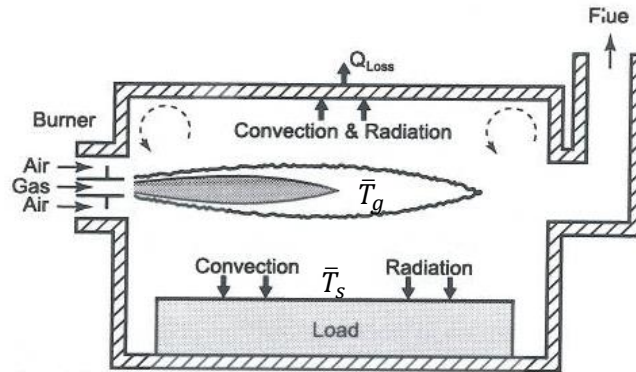


Figure 2.2.1 Schematic representation of a furnace⁸

The load has a surface heat transfer area A_s . The remaining part of the combustion chamber walls represents an area A_w .

2.2 Overall energy balance and heat transfer to the load

An overall **energy balance** on the combustion chamber gives:

$$\sum_P \dot{m}_k h_k - \sum_R \dot{m}_k h_k = -\dot{Q}_s - \dot{Q}_w \quad (2.2.1)$$

The total **heat transfer to the load**, \dot{Q}_s , is by radiation ($\dot{Q}_{s,rad}$) and convection ($\dot{Q}_{s,conv}$), i.e.

⁷ R.Viskanta, Radiative Transfer in Combustion Systems: Fundamentals and Applications, Begell House Publishers Inc., U.S., 2005.

⁸ Figure from R.Viskanta's book (op. cit.).

$$\dot{Q}_s = \dot{Q}_{s,rad} + \dot{Q}_{s,conv} \quad (2.2.2)$$

The radiant heat exchanged between the flame and combustion gases and the heat sink can be evaluated from this expression:

$$\dot{Q}_{s,rad} = \varepsilon_{eff} \sigma (\bar{T}_g^4 - \bar{T}_s^4) A_s \quad (2.2.3)$$

where $\sigma = 5.67 \times 10^{-8} W/m^2 K^4$ is the Stefan-Boltzmann constant and ε_{eff} is an effective emittance of the gas (assumed as grey) and the combustion chamber⁹:

$$\frac{1}{\varepsilon_{eff}} = \frac{1}{\varepsilon_s} - 1 + \frac{1/\varepsilon_g}{1 + \frac{A_r/A_s}{1 + \frac{\varepsilon_g}{(1 - \varepsilon_g)F_{rs}}}} \quad (2.2.4)$$

In this expression ε_s is the emissivity of the sink, ε_g is the gas emittance, A_r is the refractory area, and F_{rs} is the view factor between the refractory and the sink. Gas emittance ε_g must be calculated considering the isothermal gas volume and the walls containing the gas. This issue is out of the scope of this report.

The product $A_s \varepsilon_{eff}$ is also known as the Hottel's total exchange area between the gas and the sink.

The convection heat transfer between the gas and the load (sink) is evaluated using the average heat transfer coefficient $\bar{\alpha}_s$:

$$\dot{Q}_{s,conv} = \bar{\alpha}_s (\bar{T}_g - \bar{T}_s) A_s \quad (2.2.5)$$

2.3 Heat losses through the refractory walls

Assuming refractory walls, the **heat losses through these walls** from the chamber to the external ambient can be evaluated by an overall heat transfer coefficient U_w :

$$\dot{Q}_w = U_w (\bar{T}_g - T_{ext}) A_w \quad (2.3.1)$$

where T_{ext} represents an effective external ambient temperature.

Radiation in the refractory walls has been neglected because the inner surface temperature of the wall is close to the mean furnace temperature (especially if the wall is well insulated).

The overall heat transfer coefficient considers the internal convective process, fouling layer, the conduction heat transfer through the refractory wall (composed of N layers of different materials) and the convection with the external ambient, i.e.

$$U_w = \left[\frac{1}{\alpha_w} + R_{fi} + \sum_{k=1}^N \frac{e_k}{\lambda_k} + \frac{1}{\alpha_{ext}} \right]^{-1} \quad (2.3.2)$$

⁹ J.S.Trulove, Furnaces and combustion chambers, Heat Exchanger Design Handbook, Volume 3, Chapter 11, Hemisphere Publishing Corporation, 1983.

In this expression α_w is the convective heat transfer coefficient in the combustion chamber, e_k and λ_k are the thickness and thermal conductivity of layer k (refractory wall is composed of N layers of different materials), and α_{ext} is the external convective heat transfer coefficient. In case of cylindrical walls:

$$U_w = \left[\frac{1}{\alpha_w} + R_{fw} + \sum_{k=1}^N \left(\frac{D_w}{2\lambda_k} \ln \frac{D_{k+1}}{D_k} \right) + \frac{D_w}{D_{ext}} \frac{1}{\alpha_{ext}} \right]^{-1} \quad (2.3.3)$$

2.4 Temperature of the gas

Introducing these heat exchanges in the **energy equation** (see eq. 2.2.1), the following expression is obtained:

$$\sum_P \dot{m}_k h_k - \sum_R \dot{m}_k h_k = -\varepsilon_{eff} \sigma (\bar{T}_g^4 - \bar{T}_s^4) A_s - \bar{\alpha}_s (\bar{T}_g - \bar{T}_s) A_s - U_w (\bar{T}_g - T_{ext}) A_w \quad (2.4.1)$$

Dividing by \dot{m}_F , and following sections 1.8 and 1.9 (remember, $\dot{m}_k h_k / \dot{m}_F = v_k \hat{h}_k / W_F$, and $\hat{h}_k = \hat{h}_{fk}^o + \int \hat{c}_{pk} dT$), this equation can also be written in the following form:

$$\begin{aligned} \frac{\dot{m}_F}{W_F} \left[\sum_P v_k \left[\hat{h}_{fk}^o + \int_{T^o}^{T_g} \hat{c}_{pk} dT \right] - \left[\hat{h}_{fF}^o + \int_{T^o}^{T_{F,in}} \hat{c}_{pF} dT \right] - v_{O_2} \left[\hat{h}_{fO_2}^o + \int_{T^o}^{T_{A,in}} \hat{c}_{pO_2} dT \right] - v_{N_2} \left[\hat{h}_{fN_2}^o + \int_{T^o}^{T_{A,in}} \hat{c}_{pN_2} dT \right] \right] \\ = -\varepsilon_{eff} \sigma (\bar{T}_g^4 - \bar{T}_s^4) A_s - \bar{\alpha}_s (\bar{T}_g - \bar{T}_s) A_s - U_w (\bar{T}_g - T_{ext}) A_w \quad (2.4.2) \end{aligned}$$

Rearranging this equation, using the mean specific heats (see eq. 1.9.6), and taking into account that enthalpy of formation of both oxygen and nitrogen are zero (in reactants and products):

$$\begin{aligned} \frac{\dot{m}_F}{W_F} \left[-(\hat{h}_{fF}^o - v_{CO_2} \hat{h}_{fCO_2}^o - v_{H_2O} \hat{h}_{fH_2O}^o) + \sum_P v_k \bar{\hat{c}}_{pk} (\bar{T}_g - T^o) - \bar{\hat{c}}_{pF} (T_{F,in} - T^o) - (v_{O_2} \bar{\hat{c}}_{pO_2} + v_{N_2} \bar{\hat{c}}_{pN_2}) (T_{A,in} - T^o) \right] \\ = -\varepsilon_{eff} \sigma (\bar{T}_g^4 - \bar{T}_s^4) A_s - \bar{\alpha}_s (\bar{T}_g - \bar{T}_s) A_s - U_w (\bar{T}_g - T_{ext}) A_w \quad (2.4.3) \end{aligned}$$

where the species in the reactants and products are determined by the combustion process. E.g. in case of a single-step chemical equilibrium model of methane with regular air: $CH_4 + 2\lambda(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 2(\lambda - 1)O_2 + 7.52\lambda N_2$. Notice that the three first terms in previous equation are related to the \widehat{LHV} (see eq. 1.8.4).

If the temperature \bar{T}_s of the load is given, the above energy equation allows the evaluation of the mean gas temperature \bar{T}_g . After that, the heat transfer to the sink, \dot{Q}_s , and the heat losses through the walls, \dot{Q}_w , can be determined using equations (2.2.5 and 2.2.1 respectively).

Equation 2.4.3 can be iteratively solved in the following way:

1. Evaluate enthalpies of formation, $\bar{\hat{c}}_{pF}$, $\bar{\hat{c}}_{pO_2}$, $\bar{\hat{c}}_{pN_2}$
2. Estimate the mean gas temperature, \bar{T}_g^*
3. Evaluate $\bar{\hat{c}}_{pk}$
4. Calculate \bar{T}_g from eq. (2.4.3)
5. If $|\bar{T}_g^* - \bar{T}_g| < \delta$ go to step 6. If not, go to step 3 using $\bar{T}_g^* = \bar{T}_g$ (δ is an arbitrary small value, e.g. $\delta = 10^{-6} K$)
6. End