

Energy Systems

Lecture notes on

Combustion

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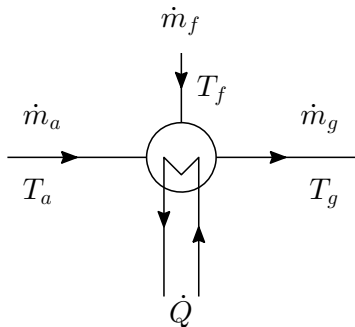
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Combustion

Fuel (\dot{m}_f) + Combustive agent (\dot{m}_a) \longrightarrow Combustion prod. (\dot{m}_g) + Heat (\dot{Q})

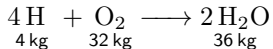
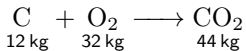


- **Fuel:** substance containing non-oxidized elements capable of developing an exothermic reaction (C,H,S);
- **Combustive agent:** substance containing the oxygen required by the combustion reaction, usually air.
- **Combustion products:** gas products, ash.

Elemental combustion reactions

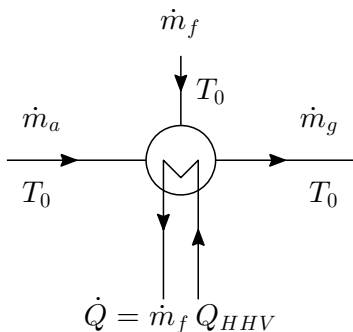
Sulfur oxidation produces a polluting substance (SO_2 , which leads to the problem of acid rain), therefore fuels must be treated so that sulfur content is reduced below an acceptable threshold set by environmental legislation.

The elemental combustion reactions to be considered are those of **carbon** and **hydrogen**:



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Higher Heating Value

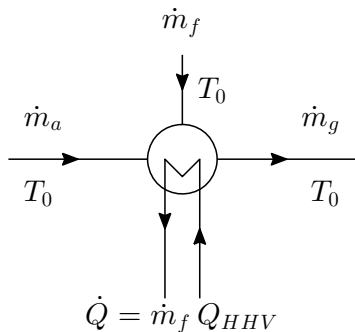


Conceptual scheme for the definition of the fuel's heating value:

- fuel and air both at ambient (reference) temperature
- combustion products cooled down to ambient temperature
- the heat rate given off by the combustion reaction is proportional to the **higher heating value** of the fuel:

$$Q_{HHV} = \frac{\dot{Q}}{\dot{m}_f} \quad [\text{MJ/kg}]$$

Lower Heating Value



- if combustion products (which contain water vapor) are cooled down to ambient temperature, water vapor condenses
- therefore the latent heat of condensation r is released
- in practical situations the combustion products cannot leave the power plant at ambient temperature, but at significantly higher temperatures, therefore water vapor is not condensed
- the **lower heating value** of the fuel takes this into account, subtracting from the higher heating value the heat rate corresponding to water vapor condensation:

$$Q_{LHV} = Q_{HHV} - \frac{\dot{m}_{\text{H}_2\text{O},g}}{\dot{m}_f} r$$

Lower Heating Value

There are 3 possible sources of water vapor in the combustion products:

- hydrogen combustion: $\dot{m}_{\text{H}_2\text{O},g} = 9\dot{m}_{\text{H},f} = 9x_{\text{H}}\dot{m}_f$
- fuel humidity: $\dot{m}_{\text{H}_2\text{O},g} = \frac{X}{1+X}\dot{m}_f$
- air humidity: $\dot{m}_{\text{H}_2\text{O},g} = \frac{X_a}{1+X_a}\dot{m}_a$

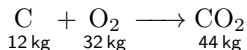
Neglecting air's humidity (in order to make reference to fuel properties only):

$$\dot{m}_{\text{H}_2\text{O},g} = \left(9x_{\text{H}} + \frac{X}{1+X} \right) \dot{m}_f$$

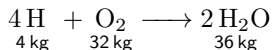
Therefore lower and higher heating value are related in this way:

$$Q_{LHV} = Q_{HHV} - \left(9x_{\text{H}} + \frac{X}{1+X} \right) r$$

Elemental carbon and hydrogen heating values



$$Q_{LHV,C} = 32.76 \text{ MJ/kg} = 393.5 \text{ MJ/kmol}$$



$$Q_{LHV,H} = 120.0 \text{ MJ/kg} = 241.8 \text{ MJ/kmol}$$

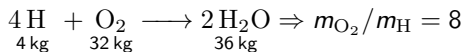
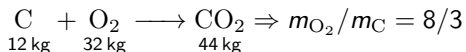
As x_H increases relative to x_C , the heating value (evaluated on a mass basis) also increases.

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Stoichiometric air

Stoichiometric air is defined as the **minimum quantity of air** needed for the fuel to **burn completely**.

Stoichiometric oxygen for elemental carbon and hydrogen:



For a generic fuel with an elemental mass composition defined by mass fractions x_{C} , x_{H} , x_{O} :

$$\dot{m}_{\text{O}_2, st} = \frac{8}{3} \dot{m}_{\text{C}, f} + 8 \dot{m}_{\text{H}, f} - \dot{m}_{\text{O}, f} = \left(\frac{8}{3} x_{\text{C}} + 8 x_{\text{H}} - x_{\text{O}} \right) \dot{m}_f$$

$$\dot{m}_{a, st} = \frac{1}{x_{\text{O}_2, a}} \left(\frac{8}{3} x_{\text{C}} + 8 x_{\text{H}} - x_{\text{O}} \right) \dot{m}_f$$

Stoichiometric ratio

The **stoichiometric ratio** is defined on a mass basis as the ratio between stoichiometric air and fuel mass:

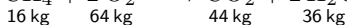
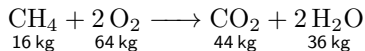
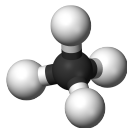
$$\alpha_{st} = \frac{\dot{m}_{a,st}}{\dot{m}_f}$$

With reference to the fuel's elemental composition:

$$\alpha_{st} = \frac{1}{x_{O_2,a}} \left(\frac{8}{3}x_C + 8x_H - x_O \right)$$

As the hydrogen content x_H increases relative to the carbon content x_C , the stoichiometric ratio also increases.

Example: methane (CH₄) stoichiometric ratio

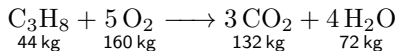
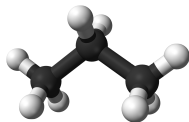


$$\alpha_{st} = \frac{64/16}{0,23} = \frac{4}{0,23} = 17,39$$

Elemental composition: $x_C = 12/16 = 75\%$, $x_H = 4/16 = 25\%$

$$\alpha_{st} = \frac{8/3 \cdot 3/4 + 8 \cdot 1/4}{0,23} = \frac{4}{0,23} = 17,39$$

Example: propane (C₃H₈) stoichiometric ratio

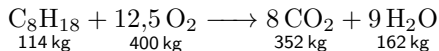
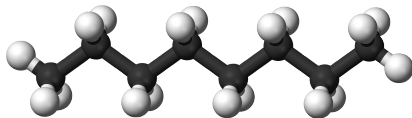


$$\alpha_{st} = \frac{160/44}{0,23} = \frac{40/11}{0,23} = 15,81$$

Elemental composition: $x_C = 36/44 = 81,8\%$, $x_H = 8/44 = 18,2\%$

$$\alpha_{st} = \frac{8/3 \cdot 36/44 + 8 \cdot 8/44}{0,23} = \frac{40/11}{0,23} = 15,81$$

Example: octane (C₈H₁₈) stoichiometric ratio

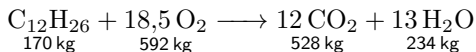
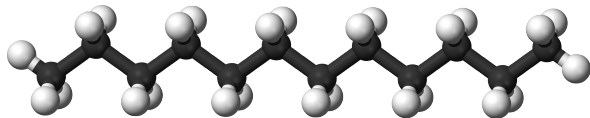


$$\alpha_{st} = \frac{400/114}{0,23} = 15,26$$

Elemental composition: $x_C = 96/114 = 84,2\%$, $x_H = 18/114 = 15,8\%$

$$\alpha_{st} = \frac{8/3 \cdot 96/114 + 8 \cdot 18/114}{0,23} = \frac{8 \cdot 50/114}{0,23} = 15,26$$

Example: dodecane (C₁₂H₂₆) stoichiometric ratio

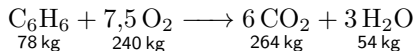
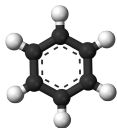


$$\alpha_{st} = \frac{592/170}{0,23} = 15,14$$

Elemental composition: $x_C = 144/170 = 84,7\%$, $x_H = 26/170 = 15,3\%$

$$\alpha_{st} = \frac{8/3 \cdot 144/170 + 8 \cdot 26/170}{0,23} = \frac{8 \cdot 74/170}{0,23} = \frac{592/170}{0,23} = 15,14$$

Example: benzene (C₆H₆) stoichiometric ratio

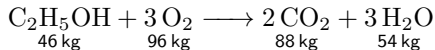
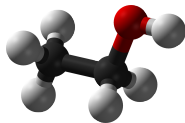


$$\alpha_{st} = \frac{240/78}{0,23} = \frac{40/13}{0,23} = 13,38$$

Elemental composition: $x_C = 72/78 = 92,3\%$, $x_H = 6/78 = 7,7\%$

$$\alpha_{st} = \frac{8/3 \cdot 72/78 + 8 \cdot 6/78}{0,23} = \frac{8 \cdot 30/78}{0,23} = \frac{240/78}{0,23} = 13,38$$

Example: ethanol (C_2H_5OH) stoichiometric ratio



$$\alpha_{st} = \frac{96/46}{0,23} = 9,07$$

Elemental composition:

$$x_C = 24/46 = 52,2\%, \quad x_H = 6/46 = 13,0\%, \quad x_O = 16/46 = 34,8\%$$

$$\alpha_{st} = \frac{8/3 \cdot 24/46 + 8 \cdot 6/46 - 16/46}{0,23} = \frac{96/46}{0,23} = 9,07$$

Excess air

To ensure a **complete combustion**, it is usually necessary to use a larger quantity of air than what would be strictly required by the stoichiometric combustion. Therefore the **percent excess air** is defined:

$$e = \frac{\dot{m}_a - \dot{m}_{a,st}}{\dot{m}_{a,st}}$$

and the **actual air/fuel ratio**:

$$\alpha = \frac{\dot{m}_a}{\dot{m}_f}$$

The air/fuel ratio is dependent on stoichiometric ratio and excess air:

$$\alpha = (1 + e) \alpha_{st}$$

Other parameters used to quantify the excess air

Fuel/air **equivalence ratio**:

$$\phi = \frac{\alpha_{st}}{\alpha} = \frac{1}{1 + e}$$

Excess air ratio:

$$\lambda = \frac{\alpha}{\alpha_{st}} = 1 + e$$

For a “lean” mixture: $\alpha > \alpha_{st}$; $e > 0$; $\phi < 1$; $\lambda > 1$

For a “rich” mixture: $\alpha < \alpha_{st}$; $e < 0$; $\phi > 1$; $\lambda < 1$

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Composition of combustion products

The quantity of combustion products depends on the air/fuel ratio:

$$\dot{m}_g = \dot{m}_a + \dot{m}_f \Rightarrow \boxed{\dot{m}_g = (\alpha + 1) \dot{m}_f}$$

Components of combustion products*:

- H₂O, due to the combustion of H and also to fuel or air humidity;
- CO₂, due to the combustion of C;
- inert substances in the fuel (e.g., elemental nitrogen \longrightarrow molecular nitrogen);
- inert substances in air (nitrogen, excess oxygen, other substances such as Ar).

* only substances with a significant mass fraction are considered; other substances are present (pollutants such as CO, NO_x, particulate matter) but their influence on thermodynamic properties is negligible because of their small quantity.

Composition of combustion products

Other substances are present, but in much smaller quantities (mass fractions are measured in parts per million, orders of magnitude smaller than the main components):

- substances generated by incomplete combustion: CO, HC, particulate matter;
- nitrogen oxides NO_x ;
- sulphur oxide SO_2 if sulphur is significantly present in the fuel.

Composition of combustion products: nitrogen

Nitrogen is an inert substance in the combustion process, therefore all nitrogen present in the combustive air (and possibly in the fuel) is found in the combustion products:

$$\begin{aligned}\dot{m}_{N_2,g} &= \dot{m}_{N_2,a} + \dot{m}_{N,f} \\ &= x_{N_2,a} \dot{m}_a + x_{N,f} \dot{m}_f = (\alpha x_{N_2,a} + x_{N,f}) \dot{m}_f\end{aligned}$$

Therefore nitrogen mass fraction in the combustion products is given by:

$$x_{N_2,g} = \frac{\alpha}{\alpha + 1} x_{N_2,a} + \frac{1}{\alpha + 1} x_{N,f}$$

Composition of combustion products: oxygen

Stoichiometric oxygen is consumed by the combustion process (it is found in H₂O and CO₂), while the excess oxygen is found in the combustion products:

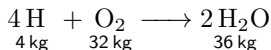
$$\begin{aligned}\dot{m}_{O_2,g} &= \dot{m}_{O_2,a} - \dot{m}_{O_2,a,st} \\ &= x_{O_2,a} (\dot{m}_a - \dot{m}_{a,st}) = e x_{O_2,a} \dot{m}_{a,st}\end{aligned}$$

Therefore oxygen mass fraction in the combustion products is given by:

$$x_{O_2,g} = \frac{e\alpha_{st}}{\alpha + 1} x_{O_2,a} = \frac{\alpha}{\alpha + 1} e\phi x_{O_2,a}$$

Composition of combustion products: water vapor

Elemental hydrogen reaction:



Water vapor in combustion products:

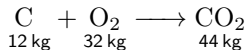
$$\begin{aligned} \dot{m}_{\text{H}_2\text{O},g} &= 9x_{\text{H},f}\dot{m}_f + \dot{m}_{\text{H}_2\text{O},f} + \dot{m}_{\text{H}_2\text{O},a} \\ &= \left(9x_{\text{H},f} + \frac{X}{1+X} \right) \dot{m}_f + \frac{X_a}{1+X_a} \dot{m}_a \end{aligned}$$

Therefore water vapor mass fraction in the combustion products is given by:

$$x_{\text{H}_2\text{O},g} = \frac{1}{\alpha + 1} \left(9x_{\text{H},f} + \frac{X}{1+X} \right) + \frac{\alpha}{\alpha + 1} \frac{X_a}{1+X_a}$$

Composition of combustion products: carbon dioxide

Elemental carbon reaction:



CO₂ in combustion products:

$$\dot{m}_{\text{H}_2\text{O},g} = \frac{11}{3} x_{\text{C},f} \dot{m}_f$$

Therefore carbon dioxide mass fraction in the combustion products is given by:

$$x_{\text{CO}_2,g} = \frac{1}{\alpha + 1} \frac{11}{3} x_{\text{C},f}$$

Composition of combustion products

If air humidity, fuel humidity and elemental nitrogen in the fuel are all neglected, one obtains:

$$x_{N_2,g} = \frac{\alpha}{\alpha + 1} x_{N_2,a}$$

$$x_{O_2,g} = \frac{\alpha}{\alpha + 1} \phi x_{O_2,a}$$

$$x_{H_2O,g} = \frac{1}{\alpha + 1} 9 x_{H,f}$$

$$x_{CO_2,g} = \frac{1}{\alpha + 1} \frac{11}{3} x_{C,f}$$

Combustion products properties and composition: example

Since $\alpha \gg 1$, combustion products' thermodynamic properties (M, c_p) are similar to those of ambient air: $M_g \approx M_a = 28.96 \text{ kg/kmol}$, $c_{pg} \approx c_{pa} = 1.0 \text{ kJ/(kg K)}$. More specifically, $c_{pg} > c_{pa}$ because of two factors:

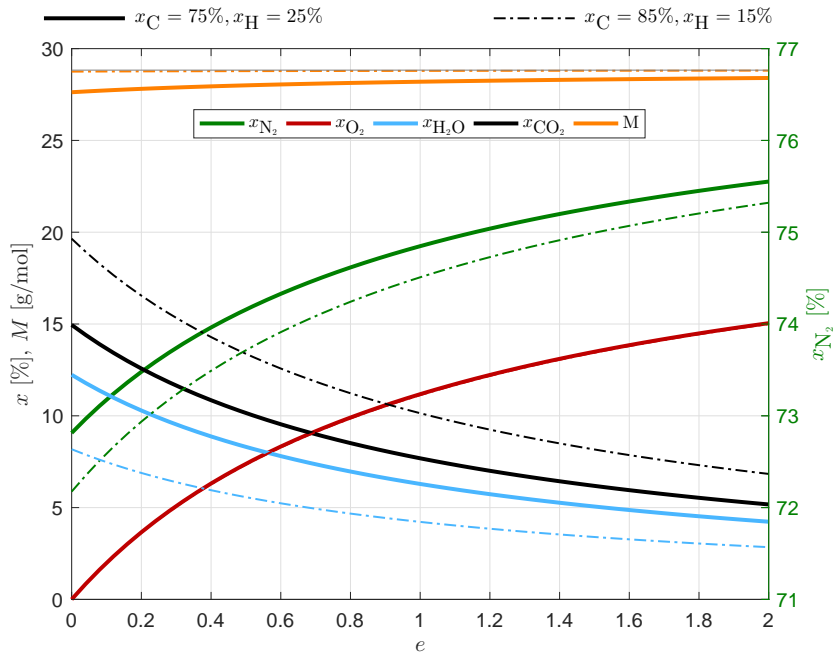
- higher temperature
- high water vapour content ($c_{p,H_2O} \approx 2 \text{ kJ/(kg K)}$)

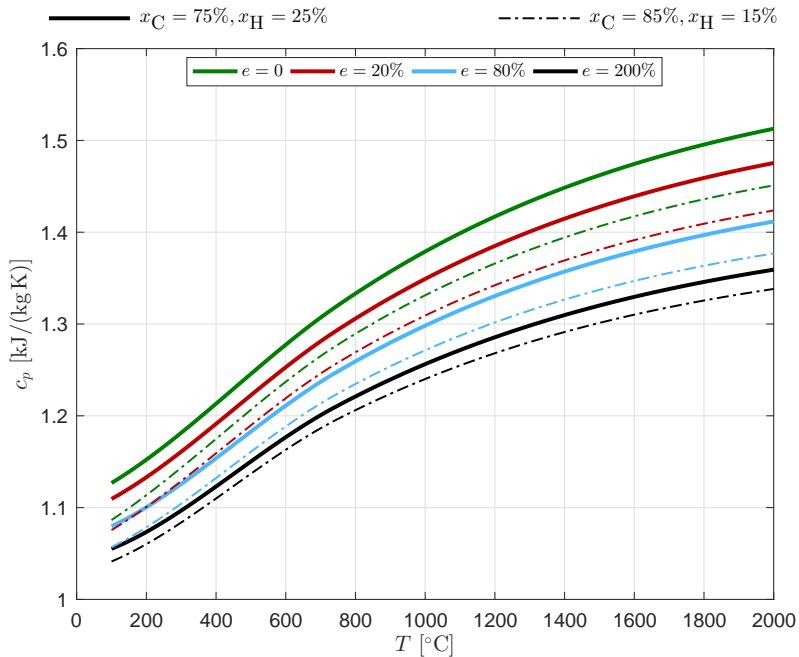
Example:

- 1 methane combustion with $e = 150\%$
- 2 dodecane combustion with $e = 20\%$

	e	α	$x_{N_2,g}$	$x_{O_2,g}$	$x_{H_2O,g}$	$x_{CO_2,g}$	M_g^\dagger
CH ₄	150%	43.48	75.27%	13.49%	5.06%	6.18%	28.32
C ₁₂ H ₂₆	20%	18.17	72.98%	3.63%	7.18%	16.20%	28.68

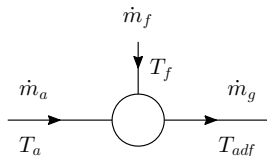
[†] M_g in kg/kmol





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Heating value per unit of mass of combustion products



- **energy vector** in combustion processes: combustion products, rather than fuel alone
- therefore a more relevant parameter than just the heating value is the fuel's heating value divided by the mass of products:

$$Q_{LHV}/(\alpha + 1)$$

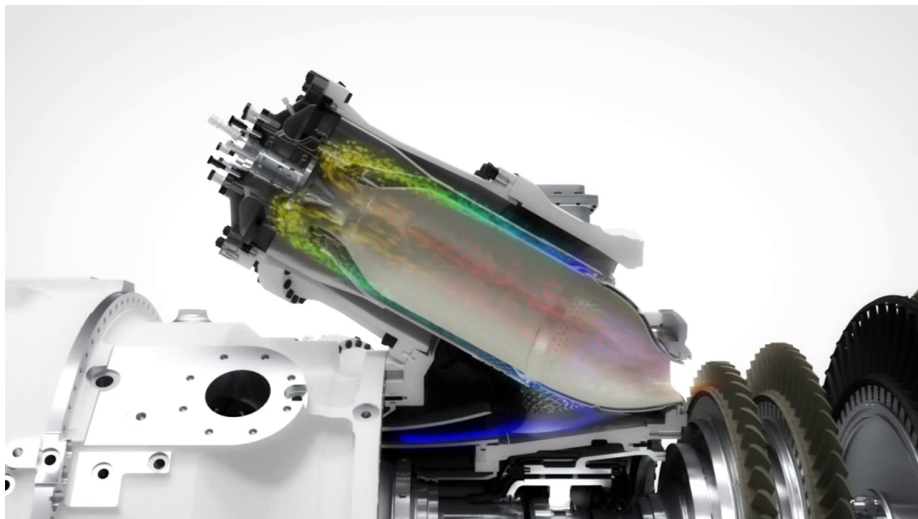
If stoichiometric conditions are considered, this quantity is a property of the fuel alone:

$$\frac{Q_{LHV}}{\alpha_{st} + 1}$$

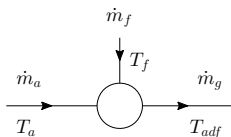
This parameter does not change significantly for different fuels, because both Q_{LHV} and α_{st} increase with x_H .

As it is demonstrated in the following pages, this parameter appears in the expression of adiabatic flame temperature and heat generator efficiency: hence, it is a particularly important property (even more than the heating value).

Combustion chamber



Combustion chamber energy balance



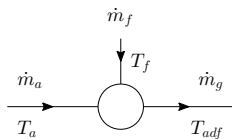
Neglecting heat losses to the environment (adiabatic combustor):

$$\dot{m}_g [c_{p_g}]_{T_0}^{T_{adf}} (T_{adf} - T_0) = \dot{m}_a [c_{p_a}]_{T_0}^{T_a} (T_a - T_0) + \dot{m}_f Q_{LHV}$$

The temperature reached by combustion products in an adiabatic combustor is called *adiabatic flame temperature*:

$$T_{adf} = T_0 + \frac{1}{[c_{p_g}]_{T_0}^{T_{adf}}} \frac{Q_{LHV}}{\alpha + 1} + \frac{[c_{p_a}]_{T_0}^{T_a}}{[c_{p_g}]_{T_0}^{T_{adf}}} \frac{\alpha}{\alpha + 1} (T_a - T_0)$$

Adiabatic flame temperature



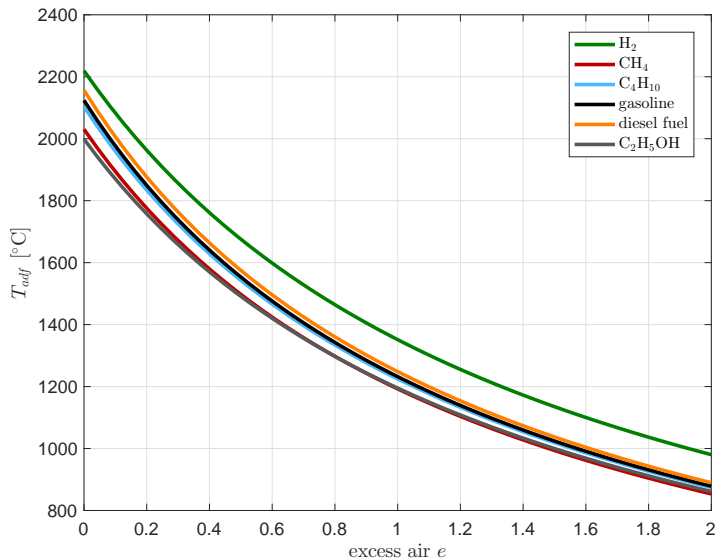
If $T_a = T_0$:

$$T_{adf} = T_0 + \frac{1}{[c_{p_g}]_{T_0}} \frac{Q_{LHV}}{\alpha + 1}$$

$$T_{adf} = T_0 + \frac{1}{[c_{p_g}]_{T_0}} \frac{Q_{LHV}}{\alpha_{st} + 1} \frac{\alpha_{st} + 1}{\alpha + 1} \approx T_0 + \frac{Q_{LHV}/(\alpha_{st} + 1)}{[c_{p_g}]_{T_0}} \frac{1}{1 + e}$$

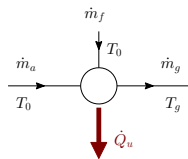
The most important parameter in the determination of the adiabatic flame temperature is the percent excess air e used in combustion (which indeed is used to control T_{adf}).

Adiabatic flame temperature



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Heat generator efficiency



Neglecting heat losses the energy balance is:

$$\dot{m}_f Q_{LHV} = \dot{Q}_u + \dot{m}_g c_{pg} (T_g - T_0)$$

Efficiency is by definition:

$$\eta = \frac{\dot{Q}_u}{\dot{m}_f Q_{LHV}}$$

It is possible to express the efficiency in an indirect form using the energy balance:

$$\eta = 1 - \frac{\dot{m}_g c_{pg} (T_g - T_0)}{\dot{m}_f Q_{LHV}}$$

$$\eta = 1 - \frac{c_{pg} (T_g - T_0)}{Q_{LHV} / (\alpha + 1)}$$

$$\eta = 1 - \frac{[c_{pg}]_{T_0}^{T_g}}{[c_{pg}]_{T_0}^{T_{adf}}} \frac{T_g - T_0}{T_{adf} - T_0}$$

Heat generator efficiency

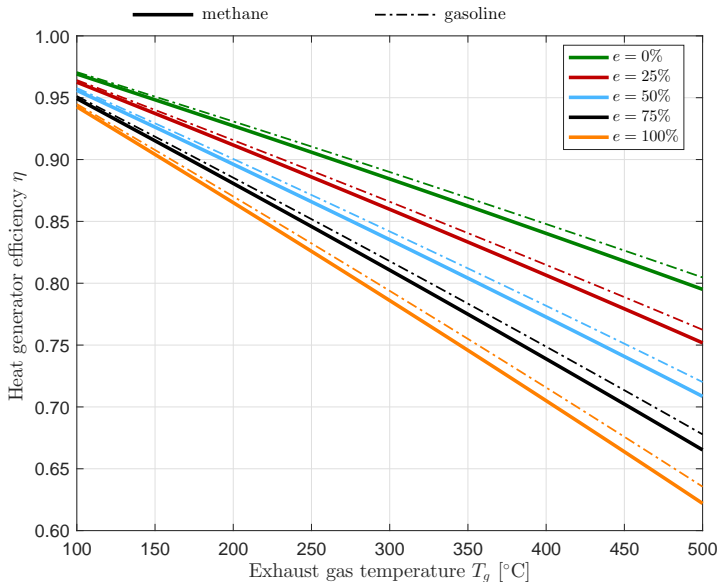
$$\eta = 1 - \frac{c_{pg}(T_g - T_0)}{Q_{LHV}/(\alpha_{st} + 1)} \frac{(\alpha + 1)}{(\alpha_{st} + 1)} \approx 1 - \frac{c_{pg}(T_g - T_0)}{Q_{LHV}/(\alpha_{st} + 1)} (1 + e)$$

The efficiency of a heat generator is mainly affected by:

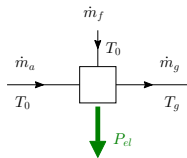
- **exhaust gas temperature** T_g , which defines the “quality” of heat rejection into the environment
- **excess air** e , which defines the “quantity” of hot gas released into the environment

The type of fuel is less important because the quantity $Q_{LHV}/(\alpha_{st} + 1)$, which is the heating value per unit of mass of combustion products, does not change significantly for different fossil fuels (it is in the range 2.6–2.9 MJ/kg for fossil fuels).

Heat generator efficiency



Specific CO₂ emissions



Specific CO₂ emissions are defined as the mass of CO₂ emitted by a thermoelectric power plant over a certain period of time relative to the electric energy produced in the same period (or, analogously, in terms of CO₂ mass flow rate and electric power produced):

$$\epsilon_{\text{CO}_2} = \frac{\dot{m}_{\text{CO}_2, \text{g}}}{P_{\text{el}}} = \frac{m_{\text{CO}_2, \text{g}}}{E_{\text{el}}}$$

CO₂ mass flow rate depends on fuel composition:

$$\dot{m}_{\text{CO}_2, \text{g}} = \frac{11}{3} x_{\text{C}, \text{f}} \dot{m}_{\text{f}}$$

Specific CO₂ emissions

Electric power output depends on power plant's global efficiency:

$$P_{el} = \eta_g \dot{m}_f Q_{LHV}$$

Specific emissions are thus given by:

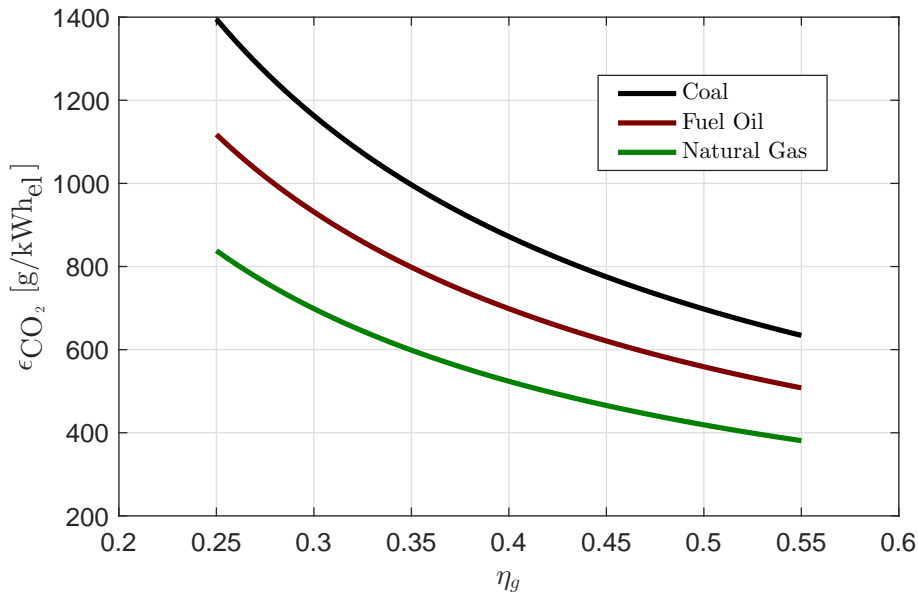
$$\epsilon_{CO_2} = \frac{\frac{11}{3} x_{C,f}}{\eta_g Q_{LHV}}$$

Specific CO₂ emissions depend on a property of the fuel ($\epsilon_{CO_2,f}$) and on power plant's global efficiency:

$$\epsilon_{CO_2,f} = \frac{\frac{11}{3} x_{C,f}}{Q_{LHV}}$$

$$\boxed{\epsilon_{CO_2} = \frac{\epsilon_{CO_2,f}}{\eta_g}}$$

Specific CO₂ emissions



- 1 Introduction
- 2 Heating value
- 3 Combustion stoichiometry
- 4 Properties of combustion products
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- 7 Properties of selected fuels**

Solid fuels

	Ultimate analysis [kg/kg _f]						<i>HHV</i>	<i>LHV</i>	α_{st}	$\frac{Q_{LHV}}{\alpha_{st}+1}$	€CO _{2,f}
	C	H	O+N	S	H ₂ O	ash					
Anthracite	84,5%	2,0%	3,5%	1,0%	3,0%	6,0%	31,5	31,0	10,4	2,72	99,9
Bituminous coal	76,0%	5,0%	8,0%	1,0%	3,0%	7,0%	31,1	29,9	10,2	2,67	93,2
Coke	85,0%	1,0%	3,0%	1,0%	2,5%	7,5%	30,5	30,2	10,1	2,72	103,2
Coal [‡]	66,5%	3,8%	7,1%	0,5%	8,0%	14,2%	26,2	25,2	8,79	2,57	96,8
Lignite	55,0%	4,5%	16,0%	2,0%	10,0%	12,5%	22,2	20,9	7,42	2,48	96,5
Peat	34,0%	5,5%	24,5%	1,0%	25,0%	10,0%	14,2	12,3	4,85	2,10	101,4
Wood	37,0%	4,5%	32,0%	0,5%	25,0%	1,0%	13,8	10,7	4,60	1,91	126,8

Heating values in MJ/kg; Fuel specific CO₂ emissions (€CO_{2,f}) in g/MJ.

Reference values; actual fuel properties strongly depend on fuel's origin.

[‡] "Douglas Premium"

Liquid fuels

	Elemental composition [kg/kg _f]				ρ	HHV	LHV	α_{st}	$\frac{QLHV}{\alpha_{st}+1}$	$\epsilon_{CO_2,f}$
	C	H	O+N	S						
Gasoline	85,5%	14,4%	-	0,1%	740	47,2	44,0	14,8	2,78	71,3
Kerosene	86,3%	13,6%	-	0,1%	790	46,5	43,5	14,6	2,79	72,7
Diesel fuel	86,3%	12,7%	0,3%	0,7%	880	45,7	42,9	14,3	2,80	73,8
Fuel oil	87,0%	11,0%	1,0%	1,0%	950	43,5	41,1	13,8	2,78	77,6
Vegetable oil	77,2%	12,0%	10,7%	0,1%	910	41,2	38,5	12,7	2,81	73,5
Methanol	37,5%	12,6%	49,9%	-	792	22,6	19,9	6,51	2,65	69,1
Ethanol	52,1%	13,1%	34,8%	-	789	29,7	26,8	9,01	2,68	71,3

Density at 15 °C; Heating values in MJ/kg; Fuel specific CO₂ emissions ($\epsilon_{CO_2,f}$) in g/MJ.

Reference values; actual fuel properties strongly depend on fuel's origin.

Gaseous fuels

	Molar composition [mol/mol _f], [m ³ /m ³ _f]								ρ_n
	H ₂	CO	CO ₂	N ₂	CH ₄	H ₂ O	O ₂	other	
Natural gas	-	-	0,6%	0,8%	89,0%	-	-	9,6%	0,81
Coal gas	47,0%	7,0%	2,0%	5,0%	35,0%	-	1,0%	3,0%	0,55
Water gas	50,0%	38,0%	4,0%	4,0%	-	2,0%	-	2,0%	0,70
H ₂	100%	-	-	-	-	-	-	-	0,09
CO	-	100%	-	-	-	-	-	-	1,25
CH ₄	-	-	-	-	100%	-	-	-	0,72
C ₂ H ₆	-	-	-	-	-	-	-	100%	2,02
C ₃ H ₈	-	-	-	-	-	-	-	100%	2,70

	HHV	LHV	α_{st}	$\frac{QLHV}{\alpha_{st}+1}$	€CO _{2,f}
Natural gas	53,2	48,1	16,7	2,87	56,7
Coal gas	40,5	35,1	12,2	2,66	30,6
Water gas	17,4	15,8	4,60	2,82	98,7
H ₂	141,8	120,0	34,5	3,38	0,0
CO	10,1	10,1	2,48	2,90	155,6
CH ₄	55,5	50,0	17,3	2,73	55,0
C ₂ H ₆	51,9	47,5	16,2	2,76	51,8
C ₃ H ₈	50,3	46,4	15,8	2,76	64,7

Density at normal conditions ρ_n in kg/m³_n; Heating values in MJ/kg; Fuel specific CO₂ emissions in g/MJ.
Reference values; actual fuel properties strongly depend on fuel's origin.