# Tutorials of combustion and fuels 

 Power engineering
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## The content of the classes

1. Exchangeability of gases
2. Flammability limits
3. Stoichiometry of combustion processes
4. Calorimetry of combustion processes
5. Temperature of combustion processes
6. Calculations of combustion chambers

## Materials for theoretical preparation

1. Spalanie i paliwa, ed. by W. Kordylewski, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, 2008 (ed. V) or 2005 (ed. IV) (in Polish)
2. Presentations for the lecture Combustion and fuels available online at www.spalanie.pwr.wroc.pl (in English)
3. Handbook of combustion, Vol. 1-5, ed. by M. Lackner, F.Winter, A.K. Agarwal, WileyVCH Verlag GmbH \& Co. KGaA, Weinheim, 2010 (in English)

## 1. Exchangeability of gases

The gases are exchangeable with each other if they can burn properly in the same burners without the need for their change (adaptation).

The condition of exchangeability of gases is determined by Wobbe number $\left(W_{b}\right)$ :

$$
W b=\frac{Q_{s}}{\sqrt{d_{v}}}
$$

where $d_{v}$ is the relative density of gas:

$$
d_{v}=\frac{\rho_{g}}{\rho_{a i r}}
$$

and $\rho_{g}, \rho_{\text {air }}$ denote the density of gas and air.

## The condition of exchangeability of gas

Two gases are exchangeable if at the same overpressure $(\Delta \mathrm{p})$ the thermal power of a gas burner
$(\mathrm{N})$ will be the same: $\mathrm{N}_{1}=\mathrm{N}_{2}$
a) Determination:

1 - the first gas,
2 - the second gas.
$\rho_{1}, \rho_{2}\left[\mathrm{~kg} / \mathrm{m}^{3}\right]-$ density of gas 1 and 2.
$\mathrm{Q}_{\mathrm{s} 1}, \mathrm{Q}_{\mathrm{s} 2}\left[\mathrm{~J} / \mathrm{m}^{3}\right]$ - heat of combustion gas 1 and 2 (upper caloric value UCV).
$\mathrm{V}^{*}, \mathrm{~V}_{2}^{*}\left[\mathrm{~m}^{3} / \mathrm{s}\right]$ - flow rate of gas 1 and 2.
$N_{1}, N_{2}[W]$ - (the thermal power of a gas burner powered with gas 1 and 2.
b) The condition of exchangeability of gas 1 and 2: $N_{1}=N_{2}$ besides: $\Delta p=$ const
c) Justification:

$$
\mathrm{N}_{1}=\mathrm{V}_{1}^{*} \cdot \mathrm{Q}_{\mathrm{s} 1}
$$

$$
\mathrm{N}_{2}=\mathrm{V}_{2}^{*} \cdot \mathrm{Q}_{\mathrm{s} 2}
$$

Hence:

$$
\mathrm{V}_{1}^{*} \cdot \mathrm{Q}_{\mathrm{s} 1}=\mathrm{V}_{2}^{*} \cdot \mathrm{Q}_{\mathrm{s} 2} \quad-->\quad \frac{Q_{s 1}}{Q_{s 2}}=\frac{\dot{V}_{2}}{\dot{V}_{2}}
$$

Overpressure of the gas $(\Delta p)$ before the gas burner is equal to the resistance of the gas flow:
$\Delta \mathrm{p}=1 / 2 \zeta \rho_{\mathrm{g}} \mathrm{U}^{2}, \quad$ where is the velocity of the gas flow $[\mathrm{m} / \mathrm{s}]$.

For both gases:

$$
\begin{aligned}
& \Delta \mathrm{p}_{1}=1 / 2 \zeta \rho_{\mathrm{g} 1} \mathrm{U}_{1}{ }^{2}, \quad \Delta \mathrm{p}_{2}=1 / 2 \zeta \rho_{\mathrm{g} 2} \mathrm{U}_{2}{ }^{2} \\
& \Delta \mathrm{p}=\Delta \mathrm{p}_{1}=\Delta \mathrm{p}_{2} \\
& \text { that is: } \rho_{\mathrm{g} 1} \mathrm{U}_{1}{ }^{2}=\rho_{\mathrm{g} 2} \mathrm{U}_{2}{ }^{2}
\end{aligned}
$$

and next: $\quad \frac{\rho_{g 1}}{\rho_{g 2}}=\frac{U_{2}^{2}}{U_{1}^{2}}$
because: $U=\frac{\dot{V}}{F}$, therefore $\frac{\rho_{g 1}}{\rho_{g 2}}=\frac{\frac{\dot{V}_{2}^{2}}{F^{2}}}{\frac{\dot{V}_{1}^{2}}{F^{2}}}=\frac{\dot{V}_{2}^{2}}{\dot{V}_{1}^{2}}$
so:

$$
\frac{\dot{V}_{2}}{\dot{V}_{1}}=\sqrt{\frac{\rho_{g 1}}{\rho_{g 2}}}=\sqrt{\frac{\frac{\rho_{g 1}}{\frac{\rho_{p o w}}{\rho_{g 2}}}}{\rho_{\text {pow }}}}=\sqrt{\frac{d_{v 1}}{d_{v 2}}} .
$$

From the condition of equal power $\mathrm{N}_{1}=\mathrm{N}_{2}$ :

$$
\frac{Q_{s}^{1}}{Q_{s}^{2}}=\frac{\dot{V}_{2}}{\dot{V}_{2}}=\sqrt{\frac{d_{v 1}}{d_{v 2}}}
$$

So, there is:

$$
\begin{aligned}
& \frac{Q_{s}^{1}}{\sqrt{d_{v 1}}}=\frac{Q_{s}^{2}}{\sqrt{d_{v 2}}}=\frac{Q_{s}^{3}}{\sqrt{d_{v 3}}}=\ldots=\frac{Q_{s}^{n}}{\sqrt{d_{v n}}} \\
& \frac{Q_{s}}{\sqrt{d_{v}}}=\text { const }
\end{aligned}
$$

and the resulting expression is called the Wobbe number

$$
W b=\frac{Q_{s}}{\sqrt{d_{v}}} .
$$

## Density of gases

Density is the ratio of the mass ( m ) of a gas and its volume ( V )

$$
\rho=\mathrm{m} / \mathrm{V}, \quad\left[\mathrm{~kg} / \mathrm{m}^{3}\right] .
$$

Specific volume (v) is the ratio of the volume (V) of a material and its mass (m) - so it is the reciprocal of density

$$
\mathrm{v}=\mathrm{V} / \mathrm{m}, \quad\left[\mathrm{~m}^{3} / \mathrm{kg}\right]
$$

Density of a gas can be changed by modifying either the pressure or the temperature. Increasing the pressure increases the density, whereas increasing the temperature decreases it. The change can be calculated using the Clapeyron's ideal gas law:

$$
p v=R T \quad \text { or } \quad \frac{p}{\rho}=R T
$$

where: $\mathrm{p}, \mathrm{N} / \mathrm{m}^{2}$ - the absolute pressure of the gas,
$v, \mathrm{~m}^{3} / \mathrm{kg}$ - the specific volume or $\rho, \mathrm{kg} / \mathrm{m}^{3}$ - the density
$R, J /(\mathrm{kgK})$ - the individual gas constant
$\mathrm{T}, \mathrm{K}$ - the absolute temperature.

Due to this law, the following relationship can be obtained:

$$
\frac{\rho_{1}}{\rho_{2}}=\frac{p_{1}}{p_{2}} \cdot \frac{T_{2}}{T_{1}}
$$

so at a constant pressure (p)

$$
\frac{\rho_{1}}{\rho_{2}}=\frac{T_{2}}{T_{1}}
$$

and at constant temperature ( $T$ )

$$
\frac{\rho_{1}}{\rho_{2}}=\frac{p_{1}}{p_{2}} .
$$

## The task

1. Perform a sample calculation of the Wobbe number for the selected gaseous fuels.
2. Calculate the value of the Wobbe number for methane $\mathrm{CH}_{4}$.

Take for the air: $\rho_{\text {pow(200c) }}=1,164 \mathrm{~kg} / \mathrm{m}^{3}$
$\mathrm{Q}_{\mathrm{s}, \mathrm{CH} 4}=39,9 \mathrm{MJ} / \mathrm{m}^{3}$

## 2. Flammability limits

Flammability limits are the minimum (lower) and the maximum (upper) contents of fuel in the fuel/air mixture, between which flame propagation in this mixture is possible (the mixture is flammable). Flammability limits mean the same as ignition limits or explosion limits.

Table 2.1 Flammability limits of gases

| Gas | Flammability limits |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | \% gas in air |  | \% gas in oxygen |  |
|  | lower | upper | lower | upper |
| hydrogen H 2 | 4,1 | 74,2 | 4,0 | 94,0 |
| carbon monoxide CO | 12,5 | 74,2 | 15,5 | 94,0 |
| methane CH4 | 5,0 | 15,0 | 5,1 | 61,0 |
| ethane C2H6 | 3,2 | 12,5 | 3,0 | 66,0 |
| propane C 3 H 8 | 2,4 | 9,5 | 2,3 | 55,0 |
| n-buthane C 4 H 10 | 1,9 | 8,4 | 1,8 | 48,0 |
| n-pentane C 5 H 12 | 1,4 | 7,8 | - | - |
| n-hexane C 6 H 14 | 1,25 | 6,9 | - | - |
| ethylene C 4 H 10 | 3,75 | 29,6 | 2,9 | 79,9 |
| acetylene C 2 H 2 | 2,5 | 80,0 | 2,5 | 89,4 |
| benzene C 6 H 6 | 1,41 | 6,75 | 2,6 | 30,0 |
| methanol CH 3 OH | 6,72 | 36,5 | - | - |
| ethanol C 2 H 6 OH | 3,28 | 18,95 | - | - |

The flammability limit of the combustible mixture without inert components ( $\left[\mathrm{CO}_{2}\right]+\left[\mathrm{N}_{2}\right]<5 \%$ ) can be calculated from the Le Chatelier formula knowing the explosion limits of the components of the mixture:

$$
\begin{equation*}
L_{g, d}=\frac{100}{\frac{a_{1}}{L_{1(g, d)}}+\frac{a_{2}}{L_{2(g, d)}}+\ldots+\frac{a_{i}}{L_{n(g, d)}}}, \tag{2.1}
\end{equation*}
$$

where:
$L_{g d}$ - lower or upper limit of ignition, \%;
$a_{i}$ - concentration of a single, combustible component of the mixture ( $\Sigma \mathrm{a}_{\mathrm{i}}=100 \%$ ).

The flammability limit of mixtures containing the inert gases ( $\left.\left[\mathrm{CO}_{2}\right]+\left[\mathrm{N}_{2}\right]>5 \%\right)$, can be determined from the formula:

$$
\begin{equation*}
L_{\mathrm{g}, \mathrm{~d}}^{\sigma}=L_{\mathrm{g}, \mathrm{~d}} \frac{\left(1+\frac{\sigma}{1-\sigma}\right) 100}{100+L_{\mathrm{g}, \mathrm{~d}} \frac{\sigma}{1-\sigma}}, \tag{2.2}
\end{equation*}
$$

where: $\sigma=\mathrm{CO}_{2}+\mathrm{N}_{2}$.

Example 1. Calculate the lower and upper flammability limit of a gas of a given composition: $\mathrm{CO}=28 \%, \mathrm{H} 2=4 \%, \mathrm{CH} 4=1 \%, \mathrm{CO} 2=8 \%, \mathrm{~N} 2=58 \%, \mathrm{H} 2 \mathrm{O}=1 \%$.

## Solution

In the composition of the gas there are significant amounts of $\mathrm{CO} 2 \mathrm{i} 2 \mathrm{~N} 2(\mathrm{CO} 2+\mathrm{N} 2>5 \%)$. Therefore, we calculate first the lower and upper flammability limit of the gas according to the formula 2.1 and next according to the formula 2.2.

- the lower flammability limit:

$$
L_{d}=\frac{100}{\frac{C O}{L_{d C O}}+\frac{H_{2}}{L_{d H_{2}}}+\frac{C H_{4}}{L_{d C H_{4}}}}=\frac{100}{\frac{28}{12,5}+\frac{4}{5}+\frac{1}{5}}=10,2 \%
$$

$\sigma=\mathrm{CO}_{2}+\mathrm{N}_{2}=0,58+0,08=0,66$

$$
L_{\mathrm{d}}^{\sigma}=L_{\mathrm{d}} \frac{\left(1+\frac{\sigma}{1-\sigma}\right) 100}{100+L_{\mathrm{d}} \frac{\sigma}{1-\sigma}}=10,2 \frac{\left(1+\frac{0,66}{1-0,66}\right) 100}{100+10,2 \cdot \frac{0,66}{1-0,66}}=25,0 \%
$$

- the upper flammability limit:

$$
\begin{aligned}
& L_{g}=\frac{100}{\frac{C O}{L_{g C O}}+\frac{H_{2}}{L_{g H_{2}}}+\frac{C H_{4}}{L_{g C H_{4}}}}=\frac{100}{\frac{28}{74,2}+\frac{4}{74,2}+\frac{1}{15}}=66,3 \% \\
& L_{\mathrm{g}}^{\sigma}=L_{\mathrm{g}} \frac{\left(1+\frac{\sigma}{1-\sigma}\right) 100}{100+L_{\mathrm{g}} \frac{\sigma}{1-\sigma}}=66,3 \frac{\left(1+\frac{0,66}{1-0,66}\right) 100}{100+66,3 \cdot \frac{0,66}{1-0,66}}=85,3 \%
\end{aligned}
$$

Example 2. Calculate the range of the stoichiometric ratio ( $\lambda$ ) in which it is possible to burn the gas with the composition shown in Example 1

## Solution

Flammability limits were calculated previously: $L_{d}=25 \%$ i $L_{g}=85,3 \%$.
Knowing the flammability limit given by the concentration of gas $\left(\mathrm{V}_{\mathrm{g}}\right)$ in the gas/air mixture $\left(\mathrm{V}_{\mathrm{m}}\right)$ :

$$
L=\frac{V_{g}}{V_{m}} \cdot 100 \%=\frac{V_{g}}{V_{g}+V_{\text {air }}} \cdot 100 \%
$$

and the formula for the excess air ratio ( $\lambda$ )

$$
\lambda=\frac{V_{\text {air }}}{V_{\text {air }}^{t} \cdot V_{g}}, \quad \text { where } \mathrm{V}_{\text {air }}^{\mathrm{t}}-\text { unit demand for air given in } \mathrm{m}_{\text {air }}^{3} / 1 \mathrm{~m}_{\text {fuel }}^{3}
$$

we can calculate:

$$
\begin{gathered}
V_{\text {air }}=\lambda \cdot V_{\text {air }}^{t} \cdot V_{g}, \mathrm{~m}^{3} / \mathrm{s} \\
L=\frac{100 \cdot V_{g}}{V_{g}\left(1+\lambda \cdot V_{\text {air }}^{t}\right)}=\frac{100}{1+\lambda \cdot V_{\text {air }}^{t}}, \% \\
\lambda=\frac{100-L}{V_{\text {air }}^{t} \cdot L} \\
\mathrm{~V}_{\mathrm{air}}^{\mathrm{t}}=(100 / 21) \cdot[0,5(0,28+0,04)+2 \cdot 0,01]=0,857 \mathrm{~m}^{3} / \mathrm{m}^{3} \\
\lambda=\frac{100-25}{0,857 \cdot 25}=3,5 \\
\lambda=\frac{100-85,3}{0,857 \cdot 85,3}=0,2
\end{gathered}
$$

The solution - the gas is flammable within the range $0,2<\lambda<3,5$.

## 3. Stoichiometry of combustion processes

Fossil fuels are mainly compounds of carbon and hydrogen (hydrocarbons $\mathrm{C}_{\mathrm{m}} \mathrm{H}_{\mathrm{n}}$ ). The reaction of their oxidation can be expressed by an equation of stoichiometry:

$$
\begin{aligned}
& \mathrm{C}_{\mathrm{m}} \mathrm{H}_{\mathrm{n}}+(\mathrm{m}+\mathrm{n} / 4) \mathrm{O}_{2} \rightarrow \mathrm{mCO}_{2}+\mathrm{n} / 2 \mathrm{H}_{2} \mathrm{O} \\
& 1 \mathrm{~mole}+(\mathrm{m}+\mathrm{n} / 4) \mathrm{mole} \rightarrow(\mathrm{~m}+\mathrm{n} / 2) \mathrm{mole} .
\end{aligned}
$$

Therefore, for one mole of fuel there is necessary exactly: $(m+n / 4)$ moles of oxygen.
When the fuel and oxidizer content in the fuel mixture results from the equation of stoichiometry, we say that the mixture is stoichiometric.
If combustion of a stoichiometric mixture is complete, there cannot be neither fuel nor oxygen present in the flue gas.

## Example:

Burning of a stoichiometric methane mixture in air (there is no fuel or oxygen in flue gas):

$$
\mathrm{CH}_{4}+2 \mathrm{O}_{2}+7.52 \mathrm{~N}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}+7.52 \mathrm{~N}_{2} \quad \text { (where air: } 79 \% \mathrm{~N}_{2}+21 \% \mathrm{O}_{2} \text { ). }
$$

The number of moles of flue gas $N$ equals:

$$
N=1 \text { mole } \mathrm{CO}_{2}+2 \text { moles } \mathrm{H}_{2} \mathrm{O}+7.52 \text { mole } \mathrm{N}_{2}=10.52 \text { moles } .
$$

## Flue gas composition:

$\left[\mathrm{CO}_{2}\right]=1 \mathrm{~mol} \mathrm{CO} 2 / 10,52=9,5 \% \mathrm{CO}_{2}$ vol.
$\left[\mathrm{H}_{2} \mathrm{O}\right]=2$ moles $\mathrm{H}_{2} \mathrm{O} / 10,52=19 \% \mathrm{H}_{2} \mathrm{O}$ vol.
$\left[\mathrm{N}_{2}\right]=7.52$ mole $\mathrm{N}_{2} / 10,52=71,5 \% \mathrm{~N}_{2}$ vol.
Burning of a lean methane mixture in air (the content of air in the mixture is $5 \%$ larger than in the stoichiometric one):

$$
\mathrm{CH}_{4}+2.1 \mathrm{O}_{2}+7.9 \mathrm{~N}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}+0.1 \mathrm{O}_{2}+7.9 \mathrm{~N}_{2} .
$$

The number of moles of flue gas $N$ equals:

$$
N=1 \text { mole } \mathrm{CO}_{2}+2 \text { moles } \mathrm{H}_{2} \mathrm{O}+7.9 \text { mole } \mathrm{N}_{2}+0.1{\text { mole } \mathrm{O}_{2}=11 \text { moles } . ~}_{\text {. }}
$$

According to the wet (water is liquid) analysis of flue gas, the concentration of the components is as follows:
$\left[\mathrm{CO}_{2}\right]=1$ mole $\mathrm{CO}_{2} / 11=9.09 \% \mathrm{CO}_{2}$ vol.
$\left[\mathrm{H}_{2} \mathrm{O}\right]=2$ moles $\mathrm{H}_{2} \mathrm{O} / 11=18.2 \% \mathrm{H}_{2} \mathrm{O}$ vol.

$\left[\mathrm{N}_{2}\right]=7.52$ moles $\mathrm{N}_{2} / 11=71.82 \mathrm{~N}_{2}$ vol.

## Stoichiometric air

The theoretical air required to complete combustion of fuel results from the equation of stoichiometry of oxygen/fuel reaction.
Stoichiometric air means the minimum amount of air in a stoichiometric mixture.
The real combustion air depends on the assumed air excess $n$ (the equivalence ratio or the stoichiometric ratio $\lambda$ ).

$$
\begin{gathered}
\lambda=\frac{\text { Actual air }}{\text { Stoichiometric air }} \\
\lambda=\frac{21.9}{21.9-\left[\mathrm{O}_{2}\right]}
\end{gathered}
$$

The type of flame/ type of mixture:

$$
\begin{aligned}
& \lambda<1 \rightarrow \text { Rich (too much fuel) } \\
& \lambda=1 \rightarrow \text { Stoichiometric (stoichiometric content of fuel and oxygen) } \\
& \lambda>1 \rightarrow \text { Lean (too much oxidizer) }
\end{aligned}
$$

The air excess ( n ):

$$
n=\frac{\text { actual }- \text { stoichiometric air }}{\text { stoichiometric air }} .
$$

The relationship between the stoichiometric ratio $\lambda$ and the air excess $n$ :

$$
n=(\lambda-1) \cdot 100 \% .
$$

## Example:

The stoichiometric air for methane burning $\left(\mathrm{CH}_{4}\right)$ is $9.52 \mathrm{~m}^{3} / \mathrm{m}^{3}$.
Assuming:

- the rate feeding of methane $V=10 \mathrm{~m}^{3} / \mathrm{h}$
- the rate feeding of air $\quad V=110 \mathrm{~m}^{3} / \mathrm{h}$
we have: $\quad \lambda=110 / 95,2=1.16$
$n=(1.16-1.0) \cdot 100 \%=16 \%$.

Theoretical air requirement based on elementary analysis:

$$
\begin{aligned}
L_{o} & =\frac{1}{0,232}\left(\frac{8}{3} c+8 h-o+s\right), \mathrm{kg} / \mathrm{kg}_{\text {fuel }} \\
L_{o} & =3,36\left(\frac{8}{3} c+8 h-o+s\right), \mathrm{m}^{3} / \mathrm{kg}_{\text {fuel }}
\end{aligned}
$$

where: c, h, o, s - carbon, hydrogen, oxygen and sulphur content in fuel.

## 4. Calorimetry of combustion processes

Every fuel is described by two caloric parameters:

- upper caloric value: HCV [J/kg]
- lower caloric value: LCV [J/kg].

The difference between the upper and the lower caloric value results from the fact that water in flue gas is in liquid form during the determination of UCV and in gaseous form (steam) when LCV is determined.
Upper caloric value is higher than lower caloric value (UCV > LCV).

Standard lower caloric value: $\quad L C V^{a}{ }_{s t}=U C V^{a}{ }_{s t}-r \cdot\left(W^{a}+8.94 H^{a}\right)$
where:
$r$ - heat of evaporation of water at the temperature of $25^{\circ} \mathrm{C}$ corresponding to $1 \%$ of water in fuel [J/kg], r=24.42[J/kg],
$\mathrm{W}^{\text {a }}$ - moisture content in analytical sample of fuel, \%
$\mathrm{H}^{\text {a }}$ - hydrogen content in analytical sample of fuel, \%
8.94 - coefficient for water.

The caloric effect of combustion results from the oxidation reaction of a fuel due to the change of its chemical structure in the combustion process. It is calculated by subtracting the formation enthalpy of subtracts (air and fuel) from the formation enthalpy of products (flue gas).
Due to the Hess law, the caloric effect of a chemical reaction depends only on the initial and final state of the reacting system and is independent of the route of conversion.
Standard upper caloric value:

$$
\Delta \mathrm{H}=\Delta \mathrm{h}^{\text {st }}(\text { prod })-\Delta \mathrm{h}^{\text {st }}(\text { sub }) \quad(\mathrm{T}=298 \mathrm{~K}, \mathrm{p}=101.3 \mathrm{kPa})
$$

where:
sub- air and fuel, prod - flue gas

$$
\begin{aligned}
& Q= \Delta H=\sum_{i} n_{i} \cdot \Delta h_{i(\text { prod })}-\sum_{i} n_{i} \cdot \Delta h_{i(\text { sub })} \\
& \mathrm{n}_{\mathrm{i}}-\text { stoichiometric coefficients. }
\end{aligned}
$$

Table 4.1 The values of the enthalpies of formation for selected compounds

| Compound | State | $\Delta \mathrm{h}, \mathrm{kJ} / \mathrm{mol}$ |
| :---: | :---: | :---: |
| $\mathrm{O}_{2}$ | Gas | 0 |
| $\mathrm{~N}_{2}$ | Gas | 0 |
| $\mathrm{H}_{2}$ | Gas | 0 |
| C | Solid | 0 |
| O | Gas | 249,19 |
| N | Gas | 472,66 |
| H | Gas | 217,94 |
| $\mathrm{CO}_{2}$ | Gas | $-393,52$ |
| $\mathrm{H}_{2} \mathrm{O}$ | Gas | $-241,83$ |
| $\mathrm{H}_{2} \mathrm{O}$ | Liquid | $-285,84$ |
| $\mathrm{CO}^{\mathrm{CH}}$ | Gas | $-110,54$ |
| $\mathrm{C}_{4} \mathrm{H}_{2}$ | Gas | $-74,87$ |
| $\mathrm{C}_{2} \mathrm{H}_{4}$ | Gas | 227 |
| $\mathrm{C}_{2} \mathrm{H}_{6}$ | Gas | 52 |
| $\mathrm{HCl}^{\mathrm{H}_{2} \mathrm{SO}_{4}}$ | Gas | -85 |
| $\mathrm{SO}_{3}$ | Gas | -92 |
|  | Liquid | -908 |
|  | Gas | -395 |

## Example:

Evaluate UCV and LCV for hydrogen.

- hydrogen combustion reaction:

$$
2 \cdot \mathrm{H}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \cdot \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

- calculation of upper caloric value UCV, when water is liquid:

$$
\Delta H=2 \cdot \Delta H_{298 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})}^{o}-2 \cdot \Delta H_{298 \mathrm{H}_{2}(\mathrm{~g})}^{o}-\Delta H_{298 \mathrm{O}_{2}(\mathrm{~g})}^{o}
$$

$$
\Delta H=-571,68 \mathrm{~kJ} / \mathrm{mol}
$$

assuming the molar mass of hydrogen $\mathrm{M}=2 \mathrm{H}_{2}=4,04 \mathrm{~g} / \mathrm{mol}$, we obtain:

$$
U C V=\frac{\Delta H}{M}=\frac{-571,68}{4,04}=-141,5, \mathrm{MJ} / \mathrm{kg}
$$

- calculation of lower caloric value UCV, when water remains in gaseous form (steam):

$$
\begin{gathered}
2 \cdot H_{2(g)}+O_{2(g)} \rightarrow 2 \cdot H_{2} O_{(g)} \\
\Delta H=2 \cdot \Delta H_{29 \mathrm{H}_{2} O(g)}^{o}-2 \cdot \Delta H_{29 \mathrm{H}_{2}(g)}^{o}-\Delta H_{298 O_{2}(g)}^{o} \\
\Delta H=-483,66 \mathrm{~kJ} / \mathrm{mol}, \\
L C V=\frac{\Delta H}{M}=\frac{-483,66}{4,04}=-119,7, \mathrm{MJ} / \mathrm{kg} .
\end{gathered}
$$

Approximate formulas for the lower caloric value of solid and liquid fuels (Mendeleev formula)

$$
Q_{i}^{r}=339,15 \cdot C^{r}+1030 \cdot H^{r}-108,9 \cdot\left(O^{r}-S^{r}\right)-25,1 \cdot W^{r}, \mathrm{~kJ} / \mathrm{kg}
$$

where $C^{r}, H^{r}, O^{r}, S^{r}$ are weight contents of elements and $W^{r}$ - water in a fuel (\%) in raw conditions.

Approximate formulas for the lower caloric values for liquid fuels:

$$
Q_{i}^{r}=27,65+\frac{12,6 \cdot 10^{3}}{\rho_{15}}, \mathrm{MJ} / \mathrm{kg}
$$

and

$$
Q_{i}^{r}=\frac{54230-13,5 \cdot \rho_{15}-293 \cdot S^{r}}{1000}, \mathrm{MJ} / \mathrm{kg}
$$

where $\rho_{15}$ is the density of the fuel in the temperature of $15^{\circ} \mathrm{C}\left(\mathrm{kg} / \mathrm{m}^{3}\right)$, and $S^{r}$ is the sulphur content in fuel (\%) in raw conditions.

The lower caloric values for gaseous fuels can be determined from the formula:

$$
L C V_{i}^{r}=\sum_{i=1}^{n}\left[\left(L C V_{i}^{r}\right)_{i} \cdot v_{i}\right], \mathrm{MJ} / \mathrm{m}^{3 .}
$$

## 5. Temperature of combustion processes

Temperature of combustion $T_{s}$ - can be different depending on the heat loss from flame.
Calorimetric temperature of combustion $T_{s, c}$ - the highest temperature of non-dissociated flue gas as a result of adiabatic and isobaric combustion of fuel and stoichiometric air.

Theoretical temperature of combustion $T_{s, t}$ - the highest temperature of dissociated flue gas as a result of adiabatic and isobaric combustion of fuel and not necessary stoichiometric air.

## Theoretical temperature of combustion

The theoretical temperature of combustion is calculated under constant pressure for the equation of the enthalpy balance of subtracts and products.

$$
\begin{align*}
& \mathrm{m}_{\mathrm{pp}}\left(\Delta h^{t w, s t}(p a l)+\int_{T s t}^{T p a l} c_{p}(p a l) d T\right)+m_{p o w} \int_{T s t}^{T p o w} c_{p}(p o w) d T=  \tag{5.1}\\
& m_{s p}\left(\Delta h^{t w, s t}(s p)+\int_{T s t}^{T s} c_{p}(s p) d T\right)
\end{align*}
$$

where: $m_{p p}$ - rate of fuel supply, $m_{\text {pow }}$ - rate of air supply, $m_{s p}$ - stream of flue gas.

## Simplified method of the temperature of combustion calculation

Assuming equal mean specific heat and equal initial temperature:

$$
\begin{align*}
& C_{p(\text { fuel })}=c_{p(\text { air })}=c_{p(\text { flue gas })}  \tag{5.2}\\
& T_{f}=T_{a}=T_{o} \tag{5.3}
\end{align*}
$$

we obtain:

$$
\begin{align*}
& \left(T_{c}-T_{o}\right) \cdot c_{p, f l u e ~ g a s ~} \cdot m_{\text {flue gas }}=Q_{H C V} \cdot m_{\text {fuel }}  \tag{5.4}\\
& T_{c}=T_{o}+\left(Q_{H c v} \cdot m_{\text {fuel }}\right) /\left(m_{\text {flue gas }} \cdot c_{p, f l u e ~ g a s}\right) \tag{5.5}
\end{align*}
$$

The real temperature of combustion is lower than the calorimetric temperature of combustion due to:

- heat losses from the flame,
- incomplete combustion (dissociation),
- non-total combustion.

Table 5.1. Examples of the measured temperature of combustion of selected fuels

| Fuel | Oxidizer | Fuel in mixture \% | Temperature, ${ }^{\circ} \mathrm{C}$ |
| :--- | :--- | :---: | :---: |
| Hydrogen | Air | 31,6 | 2045 |
| Hydrogen | Oxygen | 78 | 2660 |
| CO | Air | 20 | 1650 |
| Methane | Air | 10 | 1875 |
| Butane | Air | 3,2 | 1895 |
| Acetylene | Air | 9 | 2325 |
| Acetylene | Oxygen | 33 | 3007 |

## Example:

Calculate the calorimetric temperature (adiabatic, without dissociation) of combustion:


Assumption: $\quad V_{m}=100 \mathrm{~m}^{3} / \mathrm{h}$
Composition of the flammable mixture: $\quad 10 \% \mathrm{CH}_{4}+90 \%$ air
Content of components:
$\left[\mathrm{CH}_{4}\right]=0.1$
$\left[\mathrm{O}_{2}\right]=0.21 \cdot 0.9=0.189$
$\left[\mathrm{N}_{2}\right]=0.79 * 0.9=0.711$

Volumetric flow of components :
$V_{m}=100 \mathrm{~m}^{3} / \mathrm{h}$
$V_{C H 4}=0.1 \cdot 100 \mathrm{~m}^{3} / \mathrm{h}=10 \mathrm{~m}^{3} / \mathrm{h}$
$\mathrm{V}_{\mathrm{O} 2}=0.189 \cdot 100 \mathrm{~m}^{3} / \mathrm{h}=18.9 \mathrm{~m}^{3} / \mathrm{h}$
$\mathrm{V}_{\mathrm{N} 2}=0.711 \cdot 100 \mathrm{~m}^{3} / \mathrm{h}=71.1 \mathrm{~m}^{3} / \mathrm{h}$

The demand of oxygen for the combustion of methane

$$
\mathrm{V}_{\text {O2, teoret }}=2 \cdot \mathrm{~V}_{\mathrm{CH} 4}=20 \mathrm{~m}^{3} / \mathrm{h}
$$

Combustion stoichiometry

$$
\begin{gathered}
\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \\
3 \text { moles }=3 \text { moles }
\end{gathered}
$$

## Conclusions:

1. The numbers of moles of fuel mixture and flue gas are equal.
2. The volumetric flows of fuel mixture $\mathrm{V}_{\mathrm{m}}$ and of flue gas determined in the standard conditions ( $\mathrm{T}=0^{\circ} \mathrm{C}, \mathrm{p}_{\mathrm{atm}}$ ) are equal:

$$
V_{m}=V_{s .}
$$

The excess air ratio $(\lambda)$

$$
\lambda=\left(\mathrm{V}_{\text {air, real }} / \mathrm{V}_{\text {air, teoret }}\right)=\mathrm{V}_{02, \text { real }} / \mathrm{V}_{02, \text { teoret }}=\left(18.9 \mathrm{~m}^{3} / \mathrm{h}\right) /\left(20 \mathrm{~m}^{3} / \mathrm{h}\right)=0.945<1 \text { (rich mixture) }
$$

Conclusion: $\mathrm{CH}_{4}$ remains in the flu gas.
Composition of flue gas
The real (non-stoichiometric) reaction of oxidation:

$$
1 \mathrm{CH}_{4}+1.89 \mathrm{O}_{2}=0.945 \mathrm{CO}_{2}+1.89 \mathrm{H}_{2} \mathrm{O}+0.055 \mathrm{CH}_{4}
$$

The number of moles of the gases $N$ : left $=1+1.89=2.89, \quad$ right $=0.945+1.89+0.055=2.89$.
It can be calculated how much of each component $\left(\mathrm{m}^{3}\right)$ of flue gas is obtained during the combustion of $10 \mathrm{~m}^{3}$ of $\mathrm{CH}_{4}$.

$$
\begin{aligned}
& +9.45 \mathrm{~m}^{3} \mathrm{CO}_{2} \\
& +18.9 \mathrm{~m}^{3} \mathrm{H}_{2} \mathrm{O} \\
& +0.55 \mathrm{~m}^{3} \mathrm{CH}_{4}
\end{aligned}
$$

Consumption of the combustible mixture:

- $18.9 \mathrm{~m}^{3} \mathrm{O}_{2}$
- $10 \mathrm{~m}^{3} \mathrm{CH}_{4}$

Composition of the flue gas $\left(\mathrm{CH}_{4}, \mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{O}\right.$ i $\left.\mathrm{N}_{2}\right)$ :
$\mathrm{V}_{\mathrm{s}}=100 \mathrm{~m}^{3} / \mathrm{h}$ the concentration of the components:
$V_{C H 4}=0.55 \mathrm{~m}^{3} / \mathrm{h}$,
$\left[\mathrm{CH}_{4}\right]=0.0055$
$V_{\mathrm{CO} 2}=9.45 \mathrm{~m}^{3} / \mathrm{h}$,
$\left[\mathrm{CO}_{2}\right]=0.0945$
$V_{\mathrm{H} 2 \mathrm{O}}=18.9 \mathrm{~m}^{3} / \mathrm{h}$,
$\left[\mathrm{H}_{2} \mathrm{O}\right]=0.189$
$V_{N 2}=71.1 \mathrm{~m}^{3} / \mathrm{h}$,
$\left[\mathrm{N}_{2}\right]=0.711$

Specific heat of gas $\left(c_{p}\right)\left[\mathrm{kJ} /\left(\mathrm{m}^{3} \mathrm{~K}\right)\right]$ - determined in normal conditions $\left(\left(\mathrm{T}=0^{\circ} \mathrm{C}, \mathrm{p}_{\mathrm{atm}}\right)\right.$ :

$$
\begin{gathered}
\mathrm{c}_{\mathrm{p}, \mathrm{av}}\left[\mathrm{~kJ} /\left(\mathrm{m}^{3}{ }^{\circ} \mathrm{C}\right)\right]=\mathrm{c}_{\mathrm{pch} 4} \cdot\left[\mathrm{CH}_{4}\right]+\mathrm{c}_{\mathrm{pcO} 2} \cdot\left[\mathrm{CO}_{2}\right]+\mathrm{c}_{\mathrm{pH} 2 \mathrm{O}} \cdot\left[\mathrm{H}_{2} \mathrm{O}\right]+\mathrm{c}_{\mathrm{pN} 2} \cdot\left[\mathrm{~N}_{2}\right]= \\
2.826 \cdot 0.0055+2.45 \cdot 0.0945+2.026 \cdot 0.189+1.5 \cdot 0.711=1.695 \mathrm{~kJ} /\left(\mathrm{m}^{3}{ }^{\circ} \mathrm{C}\right)
\end{gathered}
$$

$\mathrm{C}_{\mathrm{p}, \mathrm{av}}$ - average specific heat of gas ( T from 0 to $\mathrm{T}_{\mathrm{s}}{ }^{\circ} \mathrm{C}$ )
To calculate the $\mathrm{c}_{\mathrm{p}, \dot{\mathrm{s}}}$, values were taken for the temperature of $2500^{\circ} \mathrm{C}$.

The combustion temperature (flue gas)

$$
\begin{gathered}
\mathrm{T}_{\mathrm{s}}=\mathrm{T}_{\mathrm{o}}+\mathrm{LCV} \cdot \mathrm{~V}_{\mathrm{CH} 4} /\left(\mathrm{V}_{\mathrm{s}} \mathrm{c}_{\mathrm{p}, \mathrm{av}}\right), \quad \mathrm{T}_{\mathrm{o}}=0^{\circ} \mathrm{C} \\
\mathrm{~T}_{\mathrm{s}}=\mathrm{LCV} \cdot \mathrm{~V}_{\mathrm{m}} /\left(\mathrm{V}_{\mathrm{s}} \cdot \mathrm{c}_{\mathrm{p}, \mathrm{av}}\right)=\left(35330 \mathrm{~kJ} / \mathrm{m}^{3} \cdot 9.45 \mathrm{~m}^{3} / \mathrm{h}\right) /\left(100 \mathrm{~m}^{3} / \mathrm{h} \cdot 1.695 \mathrm{~kJ} /\left(\mathrm{m}^{3}{ }^{\circ} \mathrm{C}\right)\right)
\end{gathered}
$$

The lower calorific value (LCV = $35330 \mathrm{~kJ} / \mathrm{m}^{3}$ ) was assumed for methane, because the water in the flue gas is gaseous (steam).

The flow rate of burnt methane $\mathrm{V}_{\text {CH4 }}=\mathrm{V}_{\text {CH4pal }}-\mathrm{V}_{\text {CH4spal }}=10-0,55=9.45 \mathrm{~m}^{3} / \mathrm{h}$

$$
\mathrm{T}_{\mathrm{s}}=1969.7^{\circ} \mathrm{C}
$$

The measured temperature: (see the table 5.1): $\mathrm{T}_{\mathrm{s}}=1875^{\circ} \mathrm{C}$.
The relative error is $\Delta T / T_{s} \cdot 100 \%=(1969.7-1875) /(1875+273.15)=94.7 / 2148.15=4.41 \%$.

Note 1: To calculate the relative error, the temperature difference is divided by the absolute temperature.
Note 2: The calculations are iterative. This is the first approximation - the second approximation is obtained when the average specific heat of flue gas components will be taken for the calculated temperature $1970^{\circ} \mathrm{C}$, and so on.

Note 3: The dissociation of $\mathrm{H}_{2} \mathrm{O}$ i CO 2 was not included in the calculations.

## 6. Calculations of combustion chambers

The initial dimensions of the combustion chamber are determined on the basis of the unit volumetric heat load of the combustion chamber:

$$
\begin{equation*}
\mathrm{q}_{\mathrm{v}}=\mathrm{B} \cdot \mathrm{LCV} / \mathrm{V}_{\mathrm{ch}}, \quad \mathrm{~kW} / \mathrm{m}^{3} \tag{6.1}
\end{equation*}
$$

where: B - fuel flow rate, $\mathrm{kg} / \mathrm{s}$ or $\mathrm{m}^{3} / \mathrm{s}$
LCV - lower caloric value, $\mathrm{kJ} / \mathrm{kg}$ or $\mathrm{kJ} / \mathrm{m}^{3}$
$V_{k}$-combustion chamber volume, $m^{3}$.

The following equation describes the unit heat load of cross-section area:

$$
\begin{equation*}
\mathrm{q}_{\mathrm{F}}=\mathrm{B} \cdot \mathrm{LCV} / \mathrm{F}_{\mathrm{ch}}, \quad \mathrm{~kW} / \mathrm{m}^{2} \tag{6.2}
\end{equation*}
$$

where: $F_{c h}$ - cross-section area of the combustion chamber, $\mathrm{m}^{2 .}$
The approximate height of the chamber: $\mathrm{h}=\mathrm{V}_{\mathrm{k}} / \mathrm{F}_{\mathrm{k}}, \mathrm{m}$.

For stoker-fired boilers the combustion chamber size depends on the grate size and it is calculated from this formula:

$$
\begin{equation*}
F_{G}=B \cdot L C V / q_{G}, m^{2} \tag{6.3}
\end{equation*}
$$

where: $F_{G}$ - the grate area, $\mathrm{m}^{2}$
$\mathrm{q}_{\mathrm{G}}$ - acceptable unit heat load of the grate, $\mathrm{kW} / \mathrm{m}^{2}$

In the case of the initial design of steam boilers combustion chambers, usually the following values of the unit heat load are taken:

- boilers with a mechanical stoker

$$
q_{v}=250-300
$$

$\mathrm{kW} / \mathrm{m}^{3}$

$$
\mathrm{q}_{\mathrm{F}}=1000-2000 \mathrm{~kW} / \mathrm{m}^{2}
$$

- pulverized boilers:
$\mathrm{q}_{\mathrm{v}}=150-250 \mathrm{~kW} / \mathrm{m}^{3}$
$\mathrm{q}_{\mathrm{F}}=2000-4000 \mathrm{~kW} / \mathrm{m}^{2}$
- heavy oil or natural gas boilers:

$$
\mathrm{q}_{\mathrm{v}}=300-350 \mathrm{~kW} / \mathrm{m}^{3} .
$$

According to other sources, for the dry-slag pulverized coal furnace the following values of the unit volumetric heat load can be assumed:

- for coals
$\mathrm{q}_{\mathrm{v}}=200-230 \mathrm{~kW} / \mathrm{m}^{3}$,
- for lignites
$\mathrm{q}_{\mathrm{v}}=150-180 \mathrm{~kW} / \mathrm{m}^{3}$,
- for oil and natural gas
$q_{v}=280-350 \mathrm{~kW} / \mathrm{m}^{3}$.

The unit heat load of cross-sectional area of the combustion chamber is assumed within the range:

- for the dry-slag pulverized coal boilers depending on the heat capacity:

$$
\begin{array}{ll}
\text { - up to } 50 \mathrm{~kg} / \mathrm{s} & \mathrm{q}_{\mathrm{F}}=2300-2900 \mathrm{~kW} / \mathrm{m}^{2} \\
\text { - up to } 100 \mathrm{~kg} / \mathrm{s} & \mathrm{q}_{\mathrm{F}}=2900-3500 \mathrm{~kW} / \mathrm{m}^{2} \\
\text { - up to } 180 \mathrm{~kg} / \mathrm{s} & \mathrm{q}_{\mathrm{F}}=3500-4100 \mathrm{~kW} / \mathrm{m}^{2} \\
\text { - above } 180 \mathrm{~kg} / \mathrm{s} & \mathrm{q}_{\mathrm{F}}=4100-4700 \mathrm{~kW} / \mathrm{m}^{2} \\
\text { ght oil and natural gas boilers } & \mathrm{q}_{\mathrm{F}}=3500-6000 \mathrm{~kW} / \mathrm{m}^{2}
\end{array}
$$

Note: The loss of incomplete combustion can be considered:

$$
\begin{equation*}
\mathrm{B}_{\mathrm{cal}}=\mathrm{B} \cdot\left(1-\mathrm{S}_{\mathrm{n}} / 100\right) \tag{6.4}
\end{equation*}
$$

where: $\mathrm{S}_{\mathrm{n}}$ - the loss of incomplete combustion, \% (the loss associated with the participation of the combustible particles in ash and slag).

## Example 1:

Determine the size of the combustion chamber of a pulverized coal fired boiler for combustion $8 \mathrm{t} / \mathrm{h}$ of hard coal with LCV $=22500 \mathrm{~kJ} / \mathrm{kg}$.

## Solution

- The volume of combustion chamber ( $\mathrm{q}_{\mathrm{v}}=250 \mathrm{~kW} / \mathrm{m}^{3}$ ):

$$
V_{c h}=B \cdot L C V / q_{v}=8000 \cdot 22500 /(3600 \cdot 250)=200 \mathrm{~m}^{3}
$$

- Cross-section area of combustion chamber ( $\mathrm{q}_{\mathrm{F}}=2000 \mathrm{~kW} / \mathrm{m}^{2}$ ):

$$
\mathrm{F}_{\mathrm{ch}}=\mathrm{B} \cdot \mathrm{LCV} / \mathrm{q}_{\mathrm{F}}=8000 \cdot 22500 /(3600 \cdot 2000)=25 \mathrm{~m}^{2}
$$

- Height of the chamber: $\mathrm{h}=\mathrm{V}_{\mathrm{ch}} / \mathrm{F}_{\mathrm{ch}}=200 / 25=8 \mathrm{~m}$


## Example 2:

The steam boiler is fired with coal ( $C^{r}=65 \%, H^{r}=6 \%, S^{r}=5 \%, N^{r}=4 \%, O^{r}=10 \%, W^{r}=10 \%$ ). The efficiency of the boiler is $\eta=0.78$. Steam parameters: $m_{s}=1150 \mathrm{Mg} / \mathrm{h}, \mathrm{p}_{\mathrm{s}}=13 \mathrm{Mpa}, \mathrm{t}_{\mathrm{s}}=560^{\circ} \mathrm{C}$, the temperature of supply water $\mathrm{t}_{\mathrm{w}}=80^{\circ} \mathrm{C}$. Calculate the mass flow of burnt coal.

## Solution:

The lower caloric value of coal: $\mathrm{LCV}=339.15 \cdot \mathrm{C}+1030 \cdot \mathrm{H}-108.9(\mathrm{O}-\mathrm{S})-25.1 \cdot \mathrm{~W}=21311 \mathrm{~kJ} / \mathrm{kg}$
From the $\mathrm{i}-\mathrm{s}$ graph (for $\mathrm{p}=13 \mathrm{MPa}$ and $\mathrm{T}=833 \mathrm{~K}$ ) $\rightarrow \mathrm{i}_{\mathrm{s}}=3510 \mathrm{~kJ} / \mathrm{kg}$
From the tables (for $\mathrm{t}_{\mathrm{w}}=80^{\circ} \mathrm{C}$ ) $\rightarrow \mathrm{i}_{\mathrm{w}}=258.8 \mathrm{~kJ} / \mathrm{kg}$
$\eta=\frac{m_{p} \cdot\left(i_{p}-i_{w}\right)}{B \cdot L C V}, \quad B=\frac{m_{p} \cdot\left(i_{p}-i_{w}\right)}{\eta \cdot L C V}$
$B=\frac{1150 \frac{\mathrm{t}}{\mathrm{h}} \cdot(3510-258,8) \frac{\mathrm{kJ}}{\mathrm{kg}}}{0,78 \cdot 21311 \frac{\mathrm{~kJ}}{\mathrm{~kg}}}=225 \frac{\mathrm{t}}{\mathrm{h}}$
For the pulverized boiler we assume: $q_{v}=200 \mathrm{~kW} / \mathrm{m}^{3}, \mathrm{q}_{\mathrm{F}}=4500 \mathrm{~kW} / \mathrm{m}^{3}$.
The volume of the combustion chamber:

$$
V_{c h}=B \cdot L C V / q_{v}=225000 \cdot 21311 /(3600 \cdot 200)=6660 \mathrm{~m}^{3 .}
$$

The cross-section area of the combustion chamber:

$$
F_{c h}=B \cdot L C V / q_{F}=225000 \cdot 21311 /(3600 \cdot 4500)=296 \mathrm{~m}^{2}
$$

The height of the combustion chamber:

$$
\mathrm{h}=\mathrm{V}_{\mathrm{k}} / \mathrm{F}_{\mathrm{k}}=6660 / 296=22,5 \mathrm{~m}
$$

