Chapter 25
Combustion

25.1 Fuels

Combustion describes the exothermic reaction between a fuel and an oxidizer, most often oxygen from air. Normally, the reactive equilibrium lies almost completely on the product side (∼99.99%,), so that for computations it can be assumed that all fuel is consumed, as long as enough oxygen is present. However, by the Le Chatelier principle, the reaction will be less complete when the product temperature is high: in very hot combustion one might have to account for the law of mass action.

Many fuels are hydrocarbons, C_xH_y, of different compositions. Of these, the best known are methane (natural gas) CH_4, propane C_3H_8, n-octane C_8H_{18}, n-dodecane $C_{12}H_{26}$, and hydrogen H_2. Octane is the main ingredient in gasoline which is a mixture of various hydrocarbons. Similarly, Diesel fuel is a mixture of heavier hydrocarbons such as dodecane. Other fuels contain additional elements as well, e.g. methyl alcohol CH_3OH, ethyl alcohol C_2H_5OH, or coal which is mainly carbon (C) and other elements (S, O, H, N, ash) in varying amounts.

The basic reactions occurring are the formation of water and carbon dioxide

$$\mathrm{C}_x\mathrm{H}_y + \left(x + \frac{y}{4}\right)\mathrm{O}_2 \rightarrow x\mathrm{CO}_2 + \frac{y}{2}\mathrm{H}_2\mathrm{O}\ . \tag{25.1}$$

In the above, $\left(x + \frac{y}{4}\right)$ is the stoichiometric amount of oxygen required to fully oxidize a hydrocarbon fuel. With the equation written for one mole of fuel, the stoichiometric coefficients are $\gamma_{\mathrm{C}_x\mathrm{H}_y} = -1$, $\gamma_{\mathrm{O}_2} = -\left(x + \frac{y}{4}\right)$, $\gamma_{\mathrm{CO}_2} = x$, $\gamma_{\mathrm{H}_2\mathrm{O}} = \frac{y}{2}$.

In case that not enough oxygen is present, the combustion is incomplete, and some carbon monoxide is formed,

$$\mathrm{C}_x\mathrm{H}_y + \left(x + \frac{y}{4} - \frac{z}{2}\right)\mathrm{O}_2 \rightarrow (x - z)\,\mathrm{CO}_2 + \frac{y}{2}\mathrm{H}_2\mathrm{O} + z\mathrm{CO}\ . \tag{25.2}$$

H. Struchtrup, *Thermodynamics and Energy Conversion*,
DOI: 10.1007/978-3-662-43715-5_25,

Carbon monoxide is an odorless and highly toxic gas that is a fuel itself ($CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$). Combustion processes take place in many reaction steps, which involve the splitting of larger molecules into smaller units, and the formation of new species. The formation of H_2O and CO is relatively fast, while the formation of CO_2 is slow, hence CO is formed first, and then reacts to CO_2 later.

25.2 Combustion Air

Most combustion processes use air as an oxidizer, which is freely available for most applications, e.g., stationary power plants or air breathing engines for cars and airplanes. Rockets fly at high altitudes or in space where the oxygen density is low or zero and thus they must bring their oxidizer along. To reduce payload, rocket engines are fed with fuel and pure oxygen, or with solid oxidizer-fuel compounds, e.g., ammonium perchlorate and aluminium powder.

For combustion with air, the oxygen is accompanied by the other components of air. Since oxygen and nitrogen are the two main ingredients, in combustion analysis one normally ignores the other components, and considers air as a mixture of oxygen and nitrogen with $X_{\mathrm{O}_2} = 0.21$ and $X_{\mathrm{N}_2} = 0.79$. Thus, in dry air for one mole of oxygen $\frac{1}{X_{\mathrm{O}_2}} = 4.76$ moles of air are required, that is each mole of oxygen is accompanied by 3.76 moles of nitrogen.

Due to the presence of nitrogen, nitrogen oxides (NO_x) may form in the combustion processes which are toxic. Since the amounts are small, the formation of NO_x will be ignored below, but due to the toxicity the formation of NO_x must be monitored, and suppressed, in practice.

The amount of oxygen that is required for complete combustion of a fuel is known as the stoichiometric amount, the corresponding amount of air is denoted as *stoichiometric air* or as *theoretical air*. For the general hydrocarbon reaction (25.1) the stoichiometric air is $\left[4.76\left(x + \frac{y}{4}\right)\right]$ moles of air per mole of fuel. Often the air amount is given as *percent of theoretical air*, for instance 150% of theoretical air corresponds to $\left[7.14\left(x + \frac{y}{4}\right)\right]$ moles of air per mole of fuel, or to 50% of *excess air*.

25.3 Example: Mole and Mass Flow Balances

As an example we consider the combustion of a mass flow $\dot{m}_{\mathrm{F}} = 5\frac{\mathrm{kg}}{\mathrm{h}}$ of octane (C_8H_{18}) with 150% theoretical air. We ask for the mass flow of air required, and the mass flows of the products. Since chemical balances concern mole numbers rather than masses, we first determine the mole flow of fuel as ($M_{\mathrm{C}_8\mathrm{H}_{18}} = 114\frac{\mathrm{kg}}{\mathrm{kmol}}$)

$$\dot{n}_{\mathrm{F}} = \frac{\dot{m}_{\mathrm{F}}}{M_{\mathrm{C}_8\mathrm{H}_{18}}} = 0.0122\frac{\mathrm{mol}}{\mathrm{s}} .$$

The required amount of air, and the resulting amount of product, is determined by writing a chemical equation for all involved components as

$$C_8H_{18} + 1.5a\,(O_2 + 3.76N_2) \to 0.5aO_2 + bCO_2 + cH_2O + dN_2\ .$$

Here, a is the amount of oxygen required for the stoichiometric combustion per mole of fuel, the factor 1.5 on the left accounts for 150% of theoretical air. The first term on the right is the unused portion of oxygen, which is total oxygen coming in ($1.5a$) minus the stoichiometric amount (a). The numbers a, b, c, d must be determined from balancing the elements C, H, O and N, on both sides of the equation. This gives

$$8 = b\ \ ,\ \ 18 = 2c\ \ ,\ \ 1.5a \times 2 = 0.5a \times 2 + 2b + c\ \ ,\ \ 1.5a \times 3.76 \times 2 = 2d\ ,$$

so that

$$a = 12.5\ \ ,\ \ b = 8\ \ ,\ \ c = 9\ \ ,\ \ d = 70.5\ .$$

The resulting mole flows entering the combustion process are

$$\begin{aligned}
\dot{n}_{O_2} &= 1.5a\,\dot{n}_F = 0.229\frac{\text{mol}}{\text{s}}\ ,\\
\dot{n}_{N_2} &= d\,\dot{n}_F = 0.86\frac{\text{mol}}{\text{s}}\ ,\\
\dot{n}_{\text{air}} &= \dot{n}_{O_2} + \dot{n}_{N_2} = 1.089\frac{\text{mol}}{\text{s}}\ ,
\end{aligned}$$

and the outgoing flows are

$$\begin{aligned}
\dot{n}_{CO_2} &= b\,\dot{n}_{\text{F}} = 0.098\frac{\text{mol}}{\text{s}}\ ,\\
\dot{n}_{H_2O} &= c\,\dot{n}_{\text{F}} = 0.110\frac{\text{mol}}{\text{s}}\ ,\\
\dot{n}_{O_2} &= 0.5a\,\dot{n}_{\text{F}} = 0.076\frac{\text{mol}}{\text{s}}\ ,\\
\dot{n}_{N_2} &= d\,\dot{n}_{\text{F}} = 0.86\frac{\text{mol}}{\text{s}}\ .
\end{aligned}$$

The mass flows of incoming air and outgoing carbon dioxide and water are ($M_{\text{air}} = 29\frac{\text{kg}}{\text{kmol}}$, $M_{CO_2} = 44\frac{\text{kg}}{\text{kmol}}$, $M_{H_2O} = 18\frac{\text{kg}}{\text{kmol}}$)

$$\begin{aligned}
\dot{m}_{\text{air}} &= M_{\text{air}}\dot{n}_{\text{air}} = 31.58\frac{\text{g}}{\text{s}} = 113.7\frac{\text{kg}}{\text{h}}\\
\dot{m}_{CO_2} &= M_{CO_2}\dot{n}_{CO_2} = 4.31\frac{\text{g}}{\text{s}} = 15.5\frac{\text{kg}}{\text{h}}\\
\dot{m}_{H_2O} &= M_{H_2O}\dot{n}_{H_2O} = 1.98\frac{\text{g}}{\text{s}} = 7.13\frac{\text{kg}}{\text{h}}
\end{aligned}$$

The mass-based air-fuel ratio is

$$AF = \frac{\dot{m}_{\mathrm{air}}}{\dot{m}_{\mathrm{F}}} = \frac{M_{\mathrm{air}}}{M_{\mathrm{F}}}\frac{\dot{n}_{\mathrm{air}}}{\dot{n}_{\mathrm{F}}} = \frac{M_{\mathrm{air}}}{M_{\mathrm{F}}} 1.5a\,(1+3.76) = 22.7\;.$$

One litre of octane ($\rho_{C_8H_{18}} = 0.703\frac{\mathrm{kg}}{\mathrm{litre}}$) has the mass $m_{\mathrm{F}} = 703\,\mathrm{g}$ which corresponds to the mole number $n_{\mathrm{F}} = 6.17\,\mathrm{mol}$. Thus, the amount of CO_2 produced in combustion of 1 litre of octane is $n_{CO_2} = b n_{\mathrm{F}} = 49.3\,\mathrm{mol}$ that is $m_{CO_2} = M_{CO_2} n_{CO_2} = 2.17\,\mathrm{kg}$ of CO_2 per litre of fuel. A car with a gas mileage of $14\frac{\mathrm{litres}}{100\,\mathrm{km}}$ travelling at $50\frac{\mathrm{km}}{\mathrm{h}}$ requires approximately $5\frac{\mathrm{kg}}{\mathrm{h}}$ of octane and expels 15.5 kg of carbon dioxide per hour.

25.4 Example: Exhaust Water

For the analysis of combustion processes it is important to know whether some of the product water is liquid. Liquid water can lead to corrosion in the system, and should be avoided; it will form when the temperature of the combustion product sinks below the dewpoint of the product. For the analysis, the moisture content of the incoming combustion air must be considered as well to obtain accurate results.

We study this by means of an example. Fuel gas with a volumetric analysis of 60% CH_4 and 40% H_2 is burnt with moist air at temperature 20 °C and relative humidity $\phi = 0.7$ with 60% excess air; the pressure is 1 bar. We ask for the dew point temperature of the combustion product.

The mole fraction of water in the incoming air is

$$X_{H_2O} = \frac{p_{\mathrm{v}}}{p} = \phi\frac{p_{\mathrm{sat}}\,(20\,^{\circ}\mathrm{C})}{p} = 0.0164\;,$$

so that each mole of oxygen is accompanied by $X_{H_2O}/X_{O_2} = 0.079$ moles of water.[1] Then, the overall mole balance for the combustion per mole of fuel reads

$$\begin{aligned} &0.6CH_4 + 0.4H_2 + 1.6a\,(O_2 + 3.76N_2 + 0.079H_2O) \\ &\qquad\qquad\qquad\qquad \to 0.6aO_2 + bCO_2 + cH_2O + dN_2\;, \end{aligned}$$

which yields, from balancing elements (C, H, O, N),

$$\begin{aligned} 0.6 = b \quad , \quad 0.6\times 4 + 0.4\times 2 + 1.6a\times 0.079\times 2 = 2c\;, \\ 1.6a\,(2+0.079) = 0.6a\times 2 + 2b + c \quad , \quad 12.032a = 2d\;, \end{aligned}$$

with the solution

$$a = 1.4 \quad , \quad b = 0.6 \quad , \quad c = 1.78 \quad , \quad d = 8.42\;.$$

---

[1] The calculation is as follows: Mole fraction of water is $X_{H_2O} = \frac{n_{H_2O}}{n_{O_2}+n_{N_2}+n_{H_2O}}$; with $n_{N_2} = 3.76 n_{O_2}$ follows $\frac{n_{H_2O}}{n_{O_2}} = \frac{X_{H_2O}}{X_{O_2}} = \frac{4.76}{\frac{1}{X_{H_2O}}-1}$.

The mole fraction of water in the product is

$$X_{\mathrm{H_2O}}^{prod} = \frac{c}{0.6a + b + c + d} = 0.153 \, .$$

Thus, the partial pressure of the vapor in the product is $p_\mathrm{v} = 0.153\,\mathrm{bar}$ which corresponds to a dewpoint temperature $T_\mathrm{d} = T_\mathrm{sat}\left(p_\mathrm{v}\right) = 54.4\,^\circ\mathrm{C}$.

When the reaction product is cooled below the dewpoint, c_liq moles of water per mole of fuel will condense, while the remaining $c_\mathrm{vap} = c - c_\mathrm{liq}$ moles per mole of fuel will be in the vapor phase. When the product temperature is $25\,^\circ\mathrm{C}$, the partial pressure of the vapor in the gas phase is $p_\mathrm{v} = p_{sat}\left(25\,^\circ\mathrm{C}\right) = 3.169\,\mathrm{kPa}$, and the mole fraction of the vapor is

$$X_{\mathrm{H_2O}} = \frac{p_\mathrm{v}}{p} = \frac{c_\mathrm{vap}}{0.6a + b + c_\mathrm{vap} + d} \, ,$$

so that

$$c_\mathrm{vap} = \frac{0.6a + b + d}{\frac{p}{p_\mathrm{v}} - 1} = 0.323 \quad \text{and} \quad c_\mathrm{liq} = 1.452 \, .$$

Thus, for each mole of fuel there will be 1.452 mol of liquid water in the system, which have to be removed.

25.5 First and Second Law for Combustion Systems

The goal of combustion is to produce heat, either for heating purposes or for conversion into work in heat engines. Since the changes in chemical energy are reflected in the proper values for enthalpies (23.20) and entropies (23.22), the first and second law for a combustion system have the usual form (9.9, 9.10),

$$\frac{dE}{dt} + \sum_{\alpha,out} \dot{m}_\alpha \left(h_\alpha + \frac{1}{2}\mathcal{V}_\alpha^2 + g z_\alpha \right) - \sum_{\alpha,in} \dot{m}_\alpha \left(h_\alpha + \frac{1}{2}\mathcal{V}_\alpha^2 + g z_\alpha \right) = \dot{Q} - \dot{W} \, , \tag{25.3}$$

$$\frac{dS}{dt} - \sum_k \frac{\dot{Q}_k}{T_k} + \sum_{\alpha,out} \dot{m}_\alpha s_\alpha - \sum_{\alpha,in} \dot{m}_\alpha s_\alpha = \dot{S}_{gen} \geq 0 \, . \tag{25.4}$$

We shall consider mainly open systems, e.g., combustion chambers, at steady state and ignore kinetic and potential energies, so that, now written with mole flows instead of mass flows, and with molar enthalpy and entropy, the first and second law read

$$\sum_{\alpha,out}\dot{n}_\alpha\bar{h}_\alpha-\sum_{\alpha,in}\dot{n}_\alpha\bar{h}_\alpha=\dot{Q}-\dot{W}\ , \tag{25.5}$$

$$\sum_{\alpha,out}\dot{n}_\alpha\bar{s}_\alpha-\sum_{\alpha,in}\dot{n}_\alpha\bar{s}_\alpha-\sum_k\frac{\dot{Q}_k}{T_k}=\dot{S}_{gen}\geq 0\ . \tag{25.6}$$

The mole flows $\dot{n}_\alpha$ must be determined by analysis of the combustion process as shown in the previous sections.

25.6 Adiabatic Flame Temperature

If the combustion system is adiabatic, and no power is exchanged, the first law for isobaric combustion reduces to

$$\sum_{\alpha,out}\dot{n}_\alpha\bar{h}_\alpha\left(T_f\right)=\sum_{\alpha,in}\dot{n}_\alpha\bar{h}_\alpha\left(T_{in}\right)\ . \tag{25.7}$$

The temperature T_f of the combustion product is the adiabatic flame temperature.

25.7 Example: Adiabatic Flame Temperature

As an example, we compute the adiabatic flame temperature for the combustion process studied in Section 25.3, when the incoming fuel and airstreams are at reference temperature and pressure, $T_{in}=T_0$, $p=p_0$. Then, the enthalpies for the incoming streams are

$$\begin{aligned}\bar{h}_{\mathrm{F}}\left(T_{in}\right)&=\bar{h}^0_{f,\mathrm{C_8H_{18}}}=-249.95\frac{\mathrm{kJ}}{\mathrm{mol}}\ ,\\ \bar{h}_{\mathrm{O_2}}\left(T_{in}\right)&=\bar{h}^0_{f,\mathrm{O_2}}=0\ ,\ \ \bar{h}_{\mathrm{N_2}}\left(T_{in}\right)=\bar{h}^0_{f,\mathrm{N_2}}=0\ .\end{aligned}$$

After division by $\dot{n}_F$, and with the results of Sec. 25.3, the energy balance (25.7) becomes

$$b\bar{h}_{\mathrm{CO_2}}\left(T_f\right)+0.5a\bar{h}_{\mathrm{O_2}}\left(T_f\right)+c\bar{h}_{\mathrm{H_2O}}\left(T_f\right)+d\bar{h}_{\mathrm{N_2}}\left(T_f\right)=\bar{h}_{\mathrm{F}}\left(T_{in},p\right)\ .$$

When written with tabulated enthalpy values $\tilde{h}_\alpha\left(T\right)$ instead, this gives, by means of (23.20),

$$\begin{aligned}&b\tilde{h}_{\mathrm{CO_2}}\left(T_f\right)+0.5a\tilde{h}_{\mathrm{O_2}}\left(T_f\right)+c\tilde{h}_{\mathrm{H_2O}}\left(T_f\right)+d\tilde{h}_{\mathrm{N_2}}\left(T_f\right)\\ &\qquad=\bar{h}^0_{f,\mathrm{C_8H_{18}}}+b\left[\tilde{h}_{\mathrm{CO_2}}\left(T_0\right)-\bar{h}^0_{f,\mathrm{CO_2}}\right]\\ &\qquad+0.5a\left[\tilde{h}_{\mathrm{O_2}}\left(T_0\right)\right]+c\left[\tilde{h}_{\mathrm{H_2O}}\left(T_0\right)-\bar{h}^0_{f,\mathrm{H_2O}}\right]+d\left[\tilde{h}_{\mathrm{N_2}}\left(T_0\right)\right]\ .\end{aligned}$$

Here we used that the products are ideal gases, so that the enthalpies depend only on temperature. From the tables we find the values

$$\bar{h}^0_{f,\mathrm{CO}_2} = -393.52\frac{\mathrm{kJ}}{\mathrm{mol}} \quad , \quad \bar{h}^0_{f,\mathrm{H}_2\mathrm{O}} = -241.82\frac{\mathrm{kJ}}{\mathrm{mol}}$$

and

$$\begin{aligned} \tilde{h}_{\mathrm{CO}_2}(T_0,p_0) &= 9.624\frac{\mathrm{kJ}}{\mathrm{mol}} \quad , \quad \tilde{h}_{\mathrm{O}_2}(T_0,p_0) = 8.903\frac{\mathrm{kJ}}{\mathrm{mol}} \ , \\ \tilde{h}_{\mathrm{H}_2\mathrm{O}}(T_0,p_0) &= 9.783\frac{\mathrm{kJ}}{\mathrm{mol}} \quad , \quad \tilde{h}_{\mathrm{N}_2}(T_0,p_0) = 8.672\frac{\mathrm{kJ}}{\mathrm{mol}} \ , \end{aligned}$$

so that,

$$\begin{aligned} H(T_f) := 8\tilde{h}_{\mathrm{CO}_2}(T_f) + 6.25\tilde{h}_{\mathrm{O}_2}(T_f) + 9\tilde{h}_{\mathrm{H}_2\mathrm{O}}(T_f) + 70.5\tilde{h}_{\mathrm{N}_2}(T_f) \\ = 5906.65\frac{\mathrm{kJ}}{\mathrm{mol}} \ . \end{aligned}$$

The flame temperature must be determined by trial and error from tabulated data. We find $H(1800\,\mathrm{K}) = 5810.9\frac{\mathrm{kJ}}{\mathrm{mol}}$ and $H(1850\,\mathrm{K}) = 5994.6\frac{\mathrm{kJ}}{\mathrm{mol}}$. Linear interpolation between these values gives the flame temperature as $T_f = 1826\,\mathrm{K}$.

25.8 Closed System Combustion

For a combustion process in a closed system, the integrated first law gives (kinetic and potential energies ignored)

$$U_2 - U_1 = Q_{12} - W_{12} \ . \tag{25.8}$$

As for enthalpies, the internal energies must be taken with respect to proper reference data, and the best way to ensure this is to determine them from enthalpies.

For ideal mixtures, which exhibit neither enthalpy nor volume of mixing, we have

$$U_1 = \sum_{\alpha,\,\mathrm{react}} n_\alpha \bar{u}_\alpha = \sum_{\alpha,\,\mathrm{react}} n_\alpha \left[\bar{h}_\alpha(T_1,p_1) - p_1\bar{v}_\alpha(T_1,p_1)\right] \ , \tag{25.9}$$

$$U_2 = \sum_{\alpha,\,\mathrm{prod}} n_\alpha \bar{u}_\alpha = \sum_{\alpha,\,\mathrm{prod}} n_\alpha \left[\bar{h}_\alpha(T_2,p_2) - p_2\bar{v}_\alpha(T_2,p_2)\right] \ . \tag{25.10}$$

Here, $\bar{v}_\alpha(T,p)$ is the mole volume of α alone at (T,p) (Amagat model). Application of the ideal gas laws $p\bar{v} = \bar{R}T$, $\bar{h} = \bar{h}(T)$, gives

$$U_1 = \sum_{\mathrm{react}} n_\alpha \left(\bar{h}_\alpha(T_1) - \bar{R}T_1\right) \ , \quad U_2 = \sum_{\mathrm{prod}} n_\alpha \left(\bar{h}_\alpha(T_2) - \bar{R}T_2\right) \ . \tag{25.11}$$

25.9 Example: Closed System Combustion

As an example we consider the isochoric and adiabatic combustion of $n_{\mathrm{CH}_4} = 1\,\mathrm{mol}$ of methane with $n_{\mathrm{O}_2} = 9\,\mathrm{mol}$ of oxygen $\left(X^1_{\mathrm{CH}_4} = 0.1, X^1_{\mathrm{O}_2} = 0.9\right)$ in a closed container, the initial temperature is $T_1 = 25°C$ and the initial pressure is $p_1 = 10\,\mathrm{atm}$. Reactants and products are considered as ideal gases.

The chemical equation for this reaction is

$$\mathrm{CH}_4 + 9\mathrm{O}_2 = \mathrm{CO}_2 + 2\mathrm{H}_2\mathrm{O} + 7\mathrm{O}_2\ ,$$

which implies $n_{\mathrm{CO}_2} = 1\,\mathrm{mol}$, $n_{\mathrm{H}_2\mathrm{O}} = 2\,\mathrm{mol}$, $n_{\mathrm{O}_2} = 7\,\mathrm{mol}$. The final temperature must be determined from the first law, which reduces to $U_2 = U_1$. With $\bar{h}^0_{f,\mathrm{CH}_4} = -74.85\frac{\mathrm{kJ}}{\mathrm{mol}}$ and $\bar{h}^0_{f,\mathrm{O}_2} = 0$, we find

$$U_1 = n_{\mathrm{CH}_4}\left(\bar{h}_{\mathrm{CH}_4}(T_1) - \bar{R}T_1\right) + n_{\mathrm{O}_2}\left(\bar{h}_{\mathrm{O}_2}(T_1) - \bar{R}T_1\right) = -99.64\,\mathrm{kJ}\ .$$

The final energy is given by

$$\begin{aligned} U_2 = n_{\mathrm{CO}_2}\left(\bar{h}_{\mathrm{CO}_2}(T_2) - \bar{R}T_2\right) + n_{\mathrm{H}_2\mathrm{O}}\left(\bar{h}_{\mathrm{H}_2\mathrm{O}}(T_2) - \bar{R}T_1\right) \\ + n_{\mathrm{O}_2}\left(\bar{h}_{\mathrm{O}_2}(T_2) - \bar{R}T_2\right)\ . \end{aligned}$$

Again we must use trial and error to determine the final temperature. We find $U_2(T = 2800\,\mathrm{K}) = -107.6\,\mathrm{kJ}$ and $U_2(T = 2900\,\mathrm{K}) = -70.98\,\mathrm{kJ}$ so that, from $U_2 = U_1$ we find by linear interpolation, $T_2 = 2822\,\mathrm{K}$.

The total number of moles stays constant over the process, and the ideal gas equation gives the final pressure

$$p_2 = p_1\frac{T_2}{T_1} = 9.464\,p_1 = 94.64\,\mathrm{atm}\ .$$

The partial pressures are obtained from the mole ratios, $X_\alpha = \frac{p_\alpha}{p} = \frac{n_\alpha}{n}$ as

$$\begin{aligned} &p^1_{\mathrm{CH}_4} = 1\,\mathrm{atm}\quad,\quad p^1_{\mathrm{O}_2} = 9\,\mathrm{atm}\quad,\quad p^2_{\mathrm{CO}_2} = 9.464\,\mathrm{atm}\ ,\\ &p^2_{\mathrm{H}_2\mathrm{O}} = 18.93\,\mathrm{atm}\quad,\quad p^2_{\mathrm{O}_2} = 66.25\,\mathrm{atm}\ . \end{aligned}$$

25.10 Entropy Generation in Closed System Combustion

In a combustion process, the entropy changes due to temperature and compositions change. and are affected by the different entropies of formation $\bar{s}^0_{f,\alpha}$ of the various constituents. One will expect entropy generation in combustion, since combustion processes cannot be controlled once started. As always, the generation of entropy is related to a work loss.

The computation of the entropy changes in steady state combustion in open systems will be seen in Sec. 25.12. Here we have a look at the entropy generation in closed system combustion, for the process described in the preceding section.

Since the process is adiabatic, the second law can be integrated to

$$S_2 - S_1 = S_{gen} \geq 0 \tag{25.12}$$

where $S_{gen} = \int_{t=0}^{t_f} \dot{S}_{gen} dt$ is the overall entropy generated over the duration of the process. We obtain

$$S_1 = \sum_{\text{reactants}} n_\alpha \bar{s}_\alpha \left(T_1, p_\alpha^1\right) \quad , \quad S_2 = \sum_{\text{products}} n_\alpha \bar{s}_\alpha \left(T_2, p_\alpha^2\right) \ , \tag{25.13}$$

where the entropies must be evaluated as

$$\bar{s}_\alpha \left(T, p_\alpha\right) = \bar{s}_\alpha^0 \left(T, p_0\right) - \bar{R} \ln \frac{p_\alpha}{p_0} \tag{25.14}$$

with the partial pressures $p_\alpha = X_\alpha p$.

The $\bar{s}_\alpha^0 \left(T, p_0\right)$ are tabulated, and we find from the tables (with some interpolation)

$$\begin{aligned} \bar{s}_{\mathrm{CH}_4} \left(T_1, p_0\right) &= 186.16 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \quad , \quad \bar{s}_{\mathrm{O}_2} \left(T_1, p_0\right) = 205.04 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \ , \\ \bar{s}_{\mathrm{CO}_2} \left(T_2, p_0\right) &= 331.09 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \quad , \quad \bar{s}_{\mathrm{H}_2\mathrm{O}} \left(T_2, p_0\right) = 283.19 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \ , \\ \bar{s}_{\mathrm{O}_2} \left(T_2, p_0\right) &= 282.08 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \ . \end{aligned}$$

Then we have

$$S_1 = 2.032 \frac{\mathrm{kJ}}{\mathrm{K}} \quad , \quad S_2 = 2.872 \frac{\mathrm{kJ}}{\mathrm{K}} \quad \text{and} \quad S_{gen} = 0.841 \frac{\mathrm{kJ}}{\mathrm{K}} \ .$$

25.11 Work Potential of a Fuel

As we have seen in the last section, combustion processes are accompanied by entropy generation. Combustion is irreversible, and work potential is lost to the irreversibility. In order to quantify the work loss, we ask how much work one could obtain from a fuel in a reversible process.

Figure 25.1 shows the mass and energy flows of a fuel consuming power plant: fuel and oxidizer enter the plant at reference conditions (T_0, p_0) and are processed inside the plant, which produces the net power $\dot{W}_{\text{net}}$ and rejects the heat $\left|\dot{Q}_{\text{out}}\right|$. The reaction products leave the plant through the exhaust, and we assume that they are in thermal and mechanical equilibrium with the outer environment, i.e., they are at (T_0, p_0) as well. This guarantees that most work available from the exhaust with respect to the environment is harvested. Note that, in principle, some work could be obtained by reversible

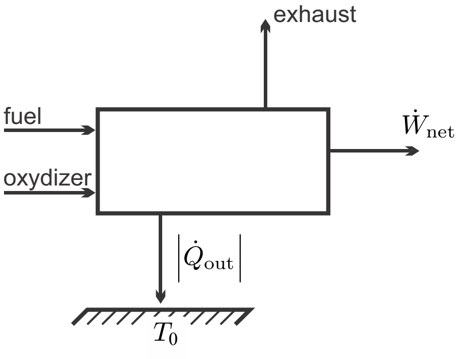

Fig. 25.1 Mass and energy flows for a fuel consuming power plant

mixing of the exhaust and the atmosphere. If the exhaust is just ejected into the environment, the mixing process is irreversible with an associated work loss; this loss will not be quantified.

Since nothing is said about the processes inside the plant, this set-up is applicable to a wide array of systems, in particular to all combustion based heat engines, that is Otto, Diesel, Brayton, Rankine cycles, and their variants, and to electrochemical power devices, i.e., fuel cells.

Elimination of the heat rejected into the environment between (25.5) and (25.6) gives the net work of the plant as

$$\dot{W}_{\rm net} = -T_0 \dot{S}_{gen} + \sum_{\substack{\text{reactants}\\ \text{at } T_0, p_0}} \dot{n}_\alpha \left(\bar{h}_\alpha - T_0 \bar{s}_\alpha \right) - \sum_{\substack{\text{products}\\ \text{at } T_0, p_0}} \dot{n}_\alpha \left(\bar{h}_\alpha - T_0 \bar{s}_\alpha \right) \ . \tag{25.15}$$

All irreversible processes occurring inside the plant, e.g., combustion, heat transfer over finite temperature differences, or friction losses in turbines, contribute to the entropy generation $\dot{S}_{gen}$, and thus diminishes the net work output of the plant.

We evaluate (25.15) for the stoichiometric combustion of a fuel with pure oxygen, with the chemical equation

$$\left|\gamma_{\rm fuel}\right| \text{fuel} + \left|\gamma_{O_2}\right| \text{O}_2 = \gamma_{\rm CO_2} \text{CO}_2 + \gamma_{\rm H_2O} \text{H}_2\text{O} \ . \tag{25.16}$$

We choose $\gamma_{\rm fuel} = -1$, and thus the mole flow of oxygen entering is $\dot{n}_{\rm O_2} = \left|\gamma_{\rm O_2}\right| \dot{n}_{\rm fuel}$ and the mole flows of the products, carbon dioxide and water, are $\dot{n}_{\rm CO_2} = \gamma_{\rm CO_2} \dot{n}_{\rm fuel}$ and $\dot{n}_{\rm H_2O} = \gamma_{\rm H_2O} \dot{n}_{\rm fuel}$.

Since all flows are entering and leaving at atmospheric conditions (T_0, p_0), we have $\bar{h}_\alpha (T_0, p_0) - T_0 \bar{s}_\alpha (T_0, p_0, X_\alpha) = \bar{g}_\alpha (T_0, p_0) + \bar{R} T_0 \ln X_\alpha$, where we have assumed ideal mixtures; as always $\bar{g}_\alpha (T_0, p_0)$ is the Gibbs free energy of α alone at standard conditions.

For this case, (25.15) can be written as

$$\dot{W}_{\text{net}} = -T_0\dot{S}_{gen} - \dot{n}_{\text{fuel}}\Delta\bar{g}_R\left(T_0, p_0\right) - \dot{n}_{\text{fuel}}\bar{R}T_0 \ln\left(X_{CO_2}^{\gamma_{CO_2}} X_{H_2O}^{\gamma_{H_2O}}\right) \ . \quad (25.17)$$

The last term is the entropy of mixing of the products. Since fuel and oxidizer enter the system separately, there is no mixing term for the reactants.

The first term—which is always negative—is the work lost to the irreversible processes inside the system, and the last term is the work that could be obtained by reversible mixing of the combustion products CO_2 and H_2O. The second term—which is positive, since for a fuel $\Delta\bar{g}_R < 0$—is just the Gibbs free energy of reaction, which is the dominant contribution to the work potential of a fuel. The maximum work obtainable from the fuel in a reversible process results from setting $\dot{S}_{gen} = 0$.

In case that the combustion products (CO_2, H_2O) leave the plant in separate streams at (T_0, p_0) the mixing term vanishes (last term in (25.17)), and the maximum work that can be extracted per mole of fuel in a reversible process is just the Gibbs free energy of the reaction,

$$w_{\text{fuel}}^{\text{rev}} = \frac{\dot{W}_{\text{net}}}{\dot{n}_{\text{fuel}}} = -\Delta\bar{g}_R\left(T_0, p_0\right) \ . \quad (25.18)$$

Additional work could be obtained by mixing the exhaust streams reversibly (last term in (25.17)), and by reversible mixing of the exhaust with the environmental air. The exhaust is in thermal (T_0) and mechanical (p_0) equilibrium with the environment, but not in chemical equilibrium $(\bar{\mu}_{\alpha,0})$. For combustion with (excess) air, additional mixing terms arise due to the presence of N_2 and excess O_2; these will be studied in the next section.

The question arises whether the maximum work obtainable from a fuel can be obtained from actual engineering devices. The answer is no, obviously, since all realistic processes are somewhat irreversible. It is, however, important to understand and quantify the different causes for irreversible losses, since only this understanding can lead to the design of better devices, with smaller losses.

In a classical combustion power plant losses are due to combustion, heat transfer, irreversible mixing, and friction. We shall study the relative importance of these in an extended example in the next section.

In fuel cells the flow of electrons is controlled, and thus combustion losses do not occur, but there are other causes for irreversible losses. Fuel cells and the losses within will be discussed in Chapter 26.

25.12 Example: Work Losses in a CH_4 Fired Steam Power Plant

The work produced in a combustion power plant differs significantly from the work available from the fuel, due to entropy generation within the system. In the present section we study and compare the contributions to work loss from all elements of a combustion driven Rankine cycle, where we consider different amounts of excess air. Figure 25.2 shows a simplified picture of the energy and mass flows in the considered system; neither reheat nor regeneration are considered. Fuel and air enter the plant at (T_0, p_0), the fuel is burned at constant pressure in the combustion chamber so that the flame temperature is T_2, and then the hot flue gas passes the steam generator that delivers heat to the Rankine cycle. The exhaust leaves the plant at (T_3, p_0).

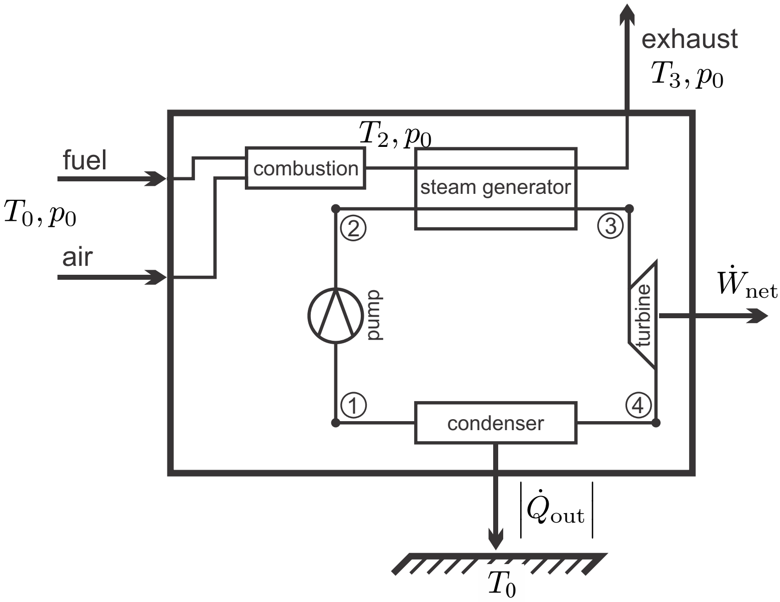

Fig. 25.2 A combustion steam power plant

For simplicity we consider the fuel to be methane (CH_4). The heat of reaction and the Gibbs free energy of reaction for the combustion of CH_4 are (at T_0, p_0, product water is vapor)

$$\Delta\bar{h}_R = -802.31\frac{\text{kJ}}{\text{mol}} \quad , \quad \Delta\bar{g}_R = -800.89\frac{\text{kJ}}{\text{mol}} \, .$$

The combustion equation reads

$$\mathrm{CH_4} + 2\,(1+x)\,(\mathrm{O_2} + 3.76\mathrm{N_2}) \longrightarrow \mathrm{CO_2} + 2\mathrm{H_2O} + 2x\mathrm{O_2} + 2\,(1+x)\,3.76\mathrm{N_2}\ ,$$

where x is the excess air in percent.

The corresponding incoming and outgoing mole flows are, expressed as multiples of the fuel flow $\dot{n}_\mathrm{F}$,

$$\begin{aligned}&\text{inflows:}\\ &\qquad \text{fuel} : \dot{n}_\mathrm{F}\ ,\\ &\qquad \mathrm{O_2}\ : \dot{n}_{\mathrm{O_2}} = 2\,(1+x)\,\dot{n}_\mathrm{F}\ ,\\ &\qquad \mathrm{N_2}\ : \dot{n}_{\mathrm{N_2}} = 7.52\,(1+x)\,\dot{n}_\mathrm{F}\ ,\end{aligned}$$

$$\begin{aligned}&\text{outflows:}\\ &\qquad \mathrm{CO_2} : \dot{n}_{\mathrm{CO_2}} = \dot{n}_\mathrm{F}\ ,\\ &\qquad \mathrm{H_2O} : \dot{n}_{\mathrm{H_2O}} = 2\dot{n}_\mathrm{F}\ ,\\ &\qquad \mathrm{O_2}\ : \dot{n}_{\mathrm{O_2}} = 2x\dot{n}_\mathrm{F}\ ,\\ &\qquad \mathrm{N_2}\ : \dot{n}_{\mathrm{N_2}} = 7.52\,(1+x)\,\dot{n}_\mathrm{F}\ .\end{aligned}$$

The mole fractions in the outflow are

$$X_{\mathrm{CO_2}} = \frac{1}{10.52+9.52x}\ ,\quad X_{\mathrm{H_2O}} = \frac{2}{10.52+9.52x}\ ,$$
$$X_{\mathrm{O_2}} = \frac{2x}{10.52+9.52x}\ ,\quad X_{\mathrm{N_2}} = \frac{7.52\,(1+x)}{10.52+9.52x}\ .$$

The amount of excess air, x, follows from the first law for a given value of the flame temperature T_2, for which we consider three different values,

$$T_2 = \{1000\,\mathrm{K},\ 1600\,\mathrm{K},\ 2200\,\mathrm{K}\}\ .$$

The first law for adiabatic combustion reads

$$\sum_{in} \dot{n}_\alpha \bar{h}_\alpha\,(T_0) = \sum_{out} \dot{n}_\alpha \bar{h}_\alpha\,(T_2)\ ,$$

which yields (with $\bar{h}^0_{f,\mathrm{O_2}} = \bar{h}^0_{f,\mathrm{N_2}} = 0$)

$$x = \frac{\bar{h}^0_\mathrm{F} - \bar{h}_{\mathrm{CO_2}}\,(T_2) - 2\bar{h}_{\mathrm{H_2O}}\,(T_2) - 7.52\bar{h}_{\mathrm{N_2}}\,(T_2)}{2\bar{h}_{\mathrm{O_2}}\,(T_2) + 7.52\bar{h}_{\mathrm{N_2}}\,(T_2)}\ ,$$

and thus, for the three chosen values of the flame temperature,

$$x = \{2.684,\ 0.776,\ 0.091\}\ .$$

Next we ask for the maximum amount of work that could be obtained from the fuel with the given amounts of excess air, i.e., in a reversible process with exhaust at T_0, p_0. For fully reversible operation (25.15) reduces to

$$\dot{W}_{\max} = \sum_{in} \dot{n}_\alpha \left(\bar{h}_\alpha - T_0 \bar{s}_\alpha\right) - \sum_{out} \dot{n}_\alpha \left(\bar{h}_\alpha - T_0 \bar{s}_\alpha\right) \ ,$$

where the appropriate values of enthalpies and entropies must be inserted.

Since the gas mixture is always at p_0, the entropies are $\bar{s}_\alpha (T, p_0, X_\alpha) = \bar{s}^0_\alpha (T) - \bar{R} \ln X_\alpha$. One has to be careful with the choice of the mole fractions for the inflow: since the fuel enters the plant unmixed with the air, which is a mixture of oxygen and nitrogen, the entropies for the incoming flows are

$$\bar{s}_{\mathrm{F}} = \bar{s}^0_{\mathrm{F}} (T_0) \quad , \quad \bar{s}_{\mathrm{O}_2} = \bar{s}^0_{\mathrm{O}_2} (T_0) - \bar{R} \ln X^{\mathrm{air}}_{\mathrm{O}_2} \quad , \quad \bar{s}_{N_2} = \bar{s}^0_{\mathrm{N}_2} (T_0) - \bar{R} \ln X^{\mathrm{air}}_{\mathrm{N}_2}$$

with $X^{\mathrm{air}}_{\mathrm{O}_2} = 0.21$, $X^{\mathrm{air}}_{\mathrm{N}_2} = 0.79$. For the computation of reversible work, the exhaust temperature is T_0, while the mole fractions of the products are given above in terms of the amount of excess air.

Using tabulated data for $\bar{s}^0_\alpha (T)$ and $\bar{h}_{\mathrm{CO}_2} (T)$, the following values for the maximum work per mole of fuel are found:

$$\frac{\dot{W}_{\max}}{\dot{n}_{\mathrm{F}}} = \left\{ 822.9 \frac{\mathrm{kJ}}{\mathrm{mol}},\ 816.5 \frac{\mathrm{kJ}}{\mathrm{mol}},\ 810.8 \frac{\mathrm{kJ}}{\mathrm{mol}} \right\} \ .$$

More work could be obtained for larger amounts of excess air. Part of the reversible work is related to reversible mixing of the products, and this contribution is larger for larger amounts of excess air.

Now we proceed with the evaluation of the actual process, which is irreversible.

The combustion chamber is adiabatic, and exchanges no work with the surroundings. The entropy generation in the combustion process follows from applying the second law between inlet and combustion chamber exit as

$$\dot{S}^{\mathrm{comb}}_{gen} = \sum_{out,2} \dot{n}_\alpha \bar{s}_\alpha - \sum_{in} \dot{n}_\alpha \bar{s}_\alpha \ .$$

The corresponding power loss is $T_0 \dot{S}^{\mathrm{comb}}_{gen}$ and we compute the ratio between the loss and the maximum work as

$$\frac{T_0 \dot{S}^{\mathrm{comb}}_{gen}}{\dot{W}_{\max}} = \{51.9\%,\ 38.3\%,\ 30.5\%\} \ .$$

Thus, depending on the flame temperature (or the amount of excess air), a large amount of the work that is available from the fuel is lost to the irreversibility of the combustion process. The loss is larger for lower flame temperature, since the hotter flow has increased work potential (or exergy): heat at higher temperature is more valuable. A closer look shows that only a small part of this loss (2.67%, 1.91%, 1.23%) can be attributed to mixing loss.

After the combustion chamber, the hot flue gas enters the heat exchanger where the heat $\dot{Q}_{\mathrm{SE}}$ is withdrawn from the gas and transferred to the steam engine. The heat exchange follows from the first law for the gas as

$$\dot{Q}_{\mathrm{SE}} = \sum_2 \dot{n}_\alpha \bar{h}_\alpha - \sum_3 \dot{n}_\alpha \bar{h}_\alpha \,.$$

To determine the values, we need to specify the exhaust temperature, and we assume an exhaust temperature of 400 K (127 °C). Depending on the flame temperature, we find the following amounts of heat transmitted to the steam cycle (per mole of fuel):

$$\frac{\dot{Q}_{\mathrm{SE}}}{\dot{n}_{\mathrm{F}}} = \left\{692.7\frac{\mathrm{kJ}}{\mathrm{mol}},\ 746.9\frac{\mathrm{kJ}}{\mathrm{mol}},\ 766.3\frac{\mathrm{kJ}}{\mathrm{mol}}\right\} .$$

Since some thermal energy leaves with the exhaust, the heat transmitted lies below the available heat of reaction, $\Delta\bar{h}_R$. Since the total mass flow is higher at high excess air (low flame temperature), more heat (13.6% $\Delta\bar{h}_R$) is lost than in the case for lower amounts of excess air (6.9%, 4.5%).

For the further calculation we have to specify the details of the steam engine. We choose a standard Rankine cycle operating at condenser temperature of $T_c = 40\,°\mathrm{C}$, turbine inlet conditions are $T_T = 550\,°\mathrm{C}$, $p_T = 80\,\mathrm{bar}$; pump and turbine have isentropic efficiencies of 80% and 85%, respectively. The corresponding specific enthalpies and entropies of the vapor stream are (the subscripts refer to the the encircled numbers in Fig. 25.2)

$$\begin{array}{ll}
h_1 = 167.6\frac{\mathrm{kJ}}{\mathrm{kg}} & ,\ s_1 = 0.5725\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\ , \\
h_{2s} = 175.6\frac{\mathrm{kJ}}{\mathrm{kg}} & ,\ s_{2s} = 0.5724\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\ , \\
h_2 = 177.7\frac{\mathrm{kJ}}{\mathrm{kg}} & ,\ s_2 = 0.5792\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\ , \\
h_3 = 3521\frac{\mathrm{kJ}}{\mathrm{kg}} & ,\ s_3 = 6.878\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\ ,
\end{array}$$

$$\begin{array}{ll}
h_{4s} = 2142\frac{\mathrm{kJ}}{\mathrm{kg}} & ,\ s_4 = 6.878\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\ , \\
h_4 = 2348\frac{\mathrm{kJ}}{\mathrm{kg}} & ,\ s_4 = 7.488\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\ .
\end{array}$$

The thermal efficiency of the steam cycle is

$$\eta = \frac{h_1 - h_2 + h_3 - h_4}{h_3 - h_2} = 34.8\%$$

for irreversible operation, and $\eta_{rev} = 41.0\%$ when pump and turbines are reversible (states $2s$, $4s$ instead of states 2, 4).

The energy balance for the heat exchanger gives the mass flow of steam per mole of fuel as

$$\frac{\dot{m}_{\mathrm{steam}}}{\dot{n}_{\mathrm{F}}} = \frac{\dot{Q}_{\mathrm{SE}}}{\dot{n}_{\mathrm{F}}\left(h_3 - h_2\right)} \,.$$

The entropy generated in the heat exchanger, which is adiabatic to the outside, is computed from the entropy flows as

$$\dot{S}_{gen}^{\mathrm{HE}} = \sum_{3} \dot{n}_\alpha \bar{s}_\alpha - \sum_{2} \dot{n}_\alpha \bar{s}_\alpha + \dot{m}_{\mathrm{steam}} \left(s_3 - s_2 \right) \ .$$

The relative amounts of work lost are

$$\frac{T_0 \dot{S}_{gen}^{\mathrm{HE}}}{\dot{W}_{\max}} = \{9.33\%,\ 20.7\%,\ 27.5\%\} \ .$$

Entropy generation in heat transfer is larger when the temperature difference between the flows is large. Since the temperatures for the steam cycle are fixed, there are higher heat transfer losses for larger flame temperature. The heat transfer loss could be reduced by using a heat engine that operates at higher maximum temperature. This would reduce heat transfer losses, and increase the thermal efficiency.

Another source of irreversibility is the thermal equilibration of the hot exhaust (state 3) with the atmosphere,

$$\dot{S}_{gen}^{\mathrm{exhaust}} = \sum_{\text{exhaust at } T_0} \frac{\dot{n}_\alpha}{T_0} \left(\bar{h}_\alpha - T_0 \bar{s}_\alpha \right) - \sum_{3} \frac{\dot{n}_\alpha}{T_0} \left(\bar{h}_\alpha - T_0 \bar{s}_\alpha \right) \ .$$

The relative contributions of the exhaust loss are

$$\frac{T_0 \dot{S}_{gen}^{\mathrm{exhaust}}}{\dot{W}_{\max}} = \{1.85\%,\ 0.95\%,\ 0.62\%\} \ .$$

The condenser contributes to work loss, due to the temperature difference between the condensing steam and the environment. The entropy generation for this process is

$$\dot{S}_{gen}^{\mathrm{cond}} = \left| \dot{Q}_C \right| \left(\frac{1}{T_0} - \frac{1}{T_C} \right) = (1 - \eta)\, \dot{Q}_{\mathrm{SE}} \left(\frac{1}{T_0} - \frac{1}{T_C} \right) \ ,$$

and this corresponds to the relative work loss

$$\frac{T_0 \dot{S}_{gen}^{\mathrm{cond}}}{\dot{W}_{\max}} = \{7.62\%,\ 8.28\%,\ 8.56\%\} \ .$$

Finally, we determine the actual power delivered by the power plant relative to the maximum work

$$\frac{\dot{W}_{\mathrm{SE}}}{\dot{W}_{\max}} = \frac{\eta \dot{Q}_{\mathrm{SE}}}{\dot{W}_{\max}} = \{29.3\%,\ 31.8\%,\ 32.9\%\} \ .$$

The efficiency of the power plant with respect to the heat available from combustion is

$$\frac{\dot{W}_{\mathrm{SE}}}{\dot{n}_{\mathrm{F}} \Delta \bar{h}_R} = \{30.0\%,\ 32.4\%,\ 33.2\%\} \ .$$

The actual work delivered and the various losses add up to the maximum work,

$$\dot{W}_{\max} = \dot{W}_{\mathrm{SE}} + T_0 \left(\dot{S}_{gen}^{\mathrm{comb}} + \dot{S}_{gen}^{\mathrm{HE}} + \dot{S}_{gen}^{\mathrm{exhaust}} + \dot{S}_{gen}^{\mathrm{cond}} \right) \ .$$

The above analysis gives insight into the relative importance of the different entropy generating processes.

For this standard steam cycle it becomes evident that more than 60% of the available work are lost in combustion and heat transfer ($T_0 \dot{S}_{gen}^{\mathrm{comb}} + T_0 \dot{S}_{gen}^{\mathrm{HE}}$). The heat transfer loss is reduced when the flame temperature is smaller, and more excess air is used, but this also increases the combustion loss.

For the low exhaust temperature chosen, the exhaust loss ($T_0 \dot{S}_{gen}^{\mathrm{exhaust}}$) is relatively small, but still amounts to up to 6% of the work produced ($\dot{W}_{\mathrm{SE}}$). Obviously this contribution will increase when the exhaust is hotter. While we did not explicitly account for regeneration of the exhaust, which might be used for preheating of the combustion air, see Sec. 12.1, it is clear that a regenerator will reduce the final exhaust temperature, T_3. When the exhaust temperature is lowered to 350 K, the exhaust loss is $\{0.51\%,\ 0.27\%,\ 0.18\%\}$ of $\dot{W}_{\max}$, and the overall efficiency is increased, so that $\dot{W}_{\mathrm{SE}}/\dot{W}_{\max} = \{31.6\%,\ 33.0\%,\ 33.7\%\}$.

Due to the large amount of heat transferred, the condenser loss ($T_0 \dot{S}_{gen}^{\mathrm{cond}}$) is relatively large. While the temperature difference between environment and condenser ($T_c - T_0 = 15\,^\circ\mathrm{C}$) cannot be reduced further, this contribution to the irreversible losses will become smaller when a more efficient heat cycle (reheat and regeneration) is used, where more of the incoming heat is converted to work, and less heat is rejected in the condenser.

The entropy generation in turbine and pump is

$$\dot{S}_{gen}^{\mathrm{irr}} = \dot{m}_{\mathrm{steam}} \left(s_2 - s_1 + s_4 - s_3 \right) \ ,$$

which relates to the relative work loss

$$\frac{T_0 \dot{S}_{gen}^{\mathrm{irr}}}{\dot{W}_{\max}} = \{5.36\%,\ 5.40\%,\ 5.44\%\} \ .$$

This loss is already included in the above calculation. Improved turbine and pump increase the thermal efficiency and thus increase the net work, and reduce the heat rejection—and thus the entropy generation—in the condenser. Indeed, for reversible operation of the steam cycle (use of h_{2s}, h_{4s} instead of h_2, h_4, $\eta = \eta_{\mathrm{rev}} = 41\%$), the relative condenser loss reduces to $\{2.40\%,\ 2.61\%,\ 2.70\%\}$,while the relative amount of power produced, $\dot{W}_{\mathrm{SE}}/\dot{W}_{\max}$, increases to $\{34.5\%,\ 37.5\%,\ 38.7\%\}$.

In summary, most of the heat available from the fuel, $\Delta \bar{h}_R$, is supplied to the steam cycle, and converted to work with the thermal efficiency of that cycle. Improving the thermal efficiency of the cycle leads to better conversion of the thermal energy of the hot combustion gas. Modern combined cycle power plants, in which high temperatures are reached, have a thermal efficiency of close to 60%.

It must be noted, though, that the combustion process and the subsequent heat transfer process are accompanied by a substantial work loss, due to irreversible combustion and heat transfer. The combustion irreversibility is due to the uncontrolled reorganization of the molecules in the reaction, which involves movement of electrons. In fuel cells the paths of the electrons are controlled, and combustion entropy is avoided. Thus they promise to harvest larger portions of the theoretically available work. However, also in fuel cells irreversible processes occur, which reduce their efficiencies, see Chapter 26.

Problems

25.1. Combustion Analysis

One kmol of ethane (C_2H_6) is burned with an unknown amount of air. An analysis of the combustion products reveals that the combustion is complete, and there are 3 kmol of free O_2 in the products. Determine the air-fuel ratio and the percentage of theoretical air.

25.2. Combustion Analysis

Octane (C_8H_{18}) is burned with dry air. The mole fractions of the products on a dry basis are 9.21 percent CO_2, 0.61 percent CO, 7.06 percent O_2, and 83.12 percent N_2.

Determine the air–fuel ratio and the percentage of theoretical air used.

25.3. Dewpoint Temperature

In a closed system, 3 kg of C_4H_{10} (butane) is burned with 75 kg of saturated moist air at 30 °C, 90 kPa. Determine the air-fuel ratio and the dewpoint temperature of the combustion product when the products are at 0.5 bar.

25.4. Dewpoint Temperature

A mass flow of $5\frac{\mathrm{kg}}{\mathrm{s}}$ of $C_{12}H_{26}$ (dodecane) is burned with a mass flow of $150\frac{\mathrm{kg}}{\mathrm{s}}$ of moist air at 30 °C, 90 kPa with relative humidity of 80%. Determine the relative amount of excess air, and the dewpoint temperature of the combustion product when the products are at 0.7 bar.

25.5. Combustion of Liquid Fuel Mixture

A liquid mixture of 90 mol octane (C_8H_{18}) and 10 mol ethyl alcohol (C_2H_5OH) at 25 °C, 1 atm is burned isobarically at 150% theoretical air with dry air at 25 °C. Heat is transferred to the surroundings and the final product temperature is 25 °C.

1. Determine the mole numbers of the combustion products.
2. Determine the amount of liquid water in the product.
3. Determine the heat transferred to the surroundings.

25.6. Incomplete Combustion

When hydrocarbon fuels are burnt with less than theoretical air, the products may contain carbon monoxide, carbon (as soot) and hydrogen. When there is only little deficiency of oxygen, all hydrogen in the fuel will form water, but some carbon monoxide will exist. This is due to reaction kinetics: water and carbon monoxide are formed earlier in the combustion process, while carbon dioxide is formed later from the reaction between CO and O_2.

Benzene gas, C_6H_6 at 25 °C is burned in a steady flow process with 95% of theoretical air that enters at 25 °C as well. The products leave at 1000 K. Determine the mole fraction of CO in the product and the heat transfer from the combustion chamber.

25.7. Soot Formation

2 mole of propylene gas (C_3H_6) react with 6 moles of oxygen gas (O_2) to form a mixture of water (H_2O), carbon dioxide (CO_2), carbon monoxide (CO) and soot (i.e., pure carbon, C). Determine the mole numbers of the products.

25.8. Non-adiabatic Flame Temperature of Acetylene

Acetylene gas (C_2H_2) at 25 °C is burned with 30% excess air at 27 °C, combustion is complete. The combustion chamber loses 75 kJ of heat per mole of fuel. Determine the temperature of the combustion products.

25.9. Adiabatic Combustion of Methanol

Liquid methanol (CH_3OH) at 25 °C is burned adiabatically with excess air that enters the combustion chamber at a temperature of 47 °C, combustion is complete. The temperature of the combustion products is 1500 K. Determine the relative amount of excess air.

25.10. Combustion

Liquid Ethanol (C_2H_5OH) at 25 °C, 1 atm is burned isobarically with 50% excess air (dry air) at 25 °C. Heat is transferred to the surroundings and the final product temperature is 600 K.

1. Determine the mole fractions of the combustion products.
2. Determine the heat transferred to the surroundings for a mass flow of ethanol of 15 kg/ h.

25.11. Combustion of Dodecane

Dodecane ($C_{12}H_{26}$) is burned adiabatically with 150% excess air.

Determine the balanced reaction equation and compute the upper heating value.

25.12. Combustion of Ethane

Consider the combustion of ethane (C_2H_6) with 100% of excess air at a pressure of 1.74 bar. Consider the air as dry air.

1. Set up the chemical equation.
2. Compute the higher and the lower heating value.

3. Compute the dewpoint of the combustion products.
4. Compute the heat of reaction at the dewpoint.

25.13. Combustion of Diesel Fuel

Diesel fuel (modelled as dodecane, $C_{12}H_{26}$, enthalpy of formation at 25 °C: $\bar{h}_f^0 = -291.01\frac{\text{kJ}}{\text{mol}}$) is burned in an adiabatic steady-flow combustion chamber with 50% excess air. Fuel and air enter at 25 °C. The hot combustion gas flows through an heat exchanger where heat is transferred to an environment at 750 K, the combustion gas leaves the heat exchanger at 800 K. Assume complete combustion and determine the required mass flow rate of diesel fuel to supply heat at a rate of 3000 kW. Compute the production of entropy in the combustion chamber and in the heat exchanger.

25.14. Combustion: Heat and Entropy Generation

In a technical process, a mass flow of $2\frac{\text{kg}}{\text{s}}$ of liquid ethyl alcohol C_2H_5OH is burned with 50% excess air; both incoming flows are at standard conditions (1 bar, 25 °C). The exhaust leaves at 500 K. Determine the heat provided by this process, and the entropy generation rate, assuming that the heat is received at 500 K.

25.15. Isochoric Combustion

Consider the adiabatic combustion of methyl alcohol vapor CH_3OH with the stoichiometric amount of air in an 0.8 litre combustion chamber. Initially, the mixture is at 25 °C and 98 kPa.

Determine the maximum pressure that can occur in the combustion chamber if the combustion takes place at constant volume.

25.16. Combustion Analysis

An equimolar mixture of carbon monoxide (CO) and methane (CH_4) is burned with 200% theoretical air (dry air). The mole flow of fuel is $2\frac{\text{kmol}}{\text{s}}$. Fuel stream and air enter the combustor at 25 °C, 1 atm, and the reactants leave at 127 °C. Determine:

1. The air fuel ratio on per mass basis.
2. The dew point of the products.
3. The heat transfer out of the combustion chamber.
4. Entropy generation and work loss.
5. The work to isothermally separate the CO_2 from the exhaust gas.

25.17. Combustion: Ammonia as a Fuel

By means of catalysts, gaseous ammonia (NH_3) reacts with oxygen (O_2) to water (H_2O) and molecular nitrogen (N_2). Consider the oxidation of ammonia with with 200% excess air (dry) at a pressure of 3 bar.

1. Set up the combustion equation.
2. Determine the dewpoint of the combustion products.
3. Determine the heat of reaction per mole of NH_3 at 25 °C for the cases that all product water is liquid, or all water is vapor, respectively.

25.18. Combustion Plant: Heat and Entropy Generation

In a technical process, a mass flow of $20\frac{\mathrm{g}}{\mathrm{s}}$ of liquid ethyl alcohol C_2H_5OH is burned with 100% excess air; both incoming flows are at standard conditions (1 bar, 25 °C). The process produces a power of 300 kW, and the exhaust leaves the plant at standard conditions.

1. Determine the heat rejection rate of the plant.
2. Determine the entropy generation rate, assuming that the plant rejects waste heat into the environment at 25 °C.

Hint: start with a good sketch.