

SESA2023 Week 5: Combustion

This week we look at combustion processes. We will start with some fundamental concepts of combustion and chemical equations, followed by methods to calculate the heat released by combustion processes and chemical equilibrium analysis.

5.1 Learning outcomes

After completing this section you should be able to:

- Use chemical equations to describe combustion processes.
- Determine the stoichiometric air-fuel ratio for a given fuel.
- Use the equivalence ratio to determine the combustion products for a combustion process.
- Calculate the heat released in a combustion process.
- Calculate the temperature of exhaust gases in a combustion process (adiabatic flame temperature).
- Determine the equilibrium composition of exhaust gases at a specified temperature and pressure.

5.2 Introduction

The propulsion systems we have looked at so far all make use of combustion processes to add heat. Until now, we have modelled the heat addition by adding the heat of an idealized combustion process with air as the exhaust gas. In this chapter we will make a start with a more accurate description of the actual combustion process. This will involve calculating the actual change in temperature following a combustion process, and determining the exhaust gas composition.

In order to do this, we will start by looking at chemical equations for combustion processes, followed by the thermodynamic concepts of combustion and finally investigating chemical equilibrium compositions.

5.3 Combustion chemistry

5.3.1 Chemical equations

Chemical equations describe the change in molecules through a chemical reaction. We will work through the main concepts using the combustion of carbon monoxide (CO) with oxygen (O₂), which produces carbon dioxide (CO₂):



The molecules on the left hand side of the equations are called the reactants, and the molecules on the right hand side the products. In this example, the reactants are CO and O₂, and the product is CO₂.

Although molecules change in chemical reactions, the atoms are always conserved. In our example, we have 2 carbon atoms on the left hand side, and therefore we must also have 2 carbon atoms on the right hand side. Similarly, the number of molecules will change in a chemical reaction, but mass is conserved.

Instead of counting individual molecules, we rather count the number of moles (mol) or kilomoles (kmol). Because the number of moles is directly proportional to the number of molecules (1 kmol contains $6.02214076 \times 10^{26}$ molecules), nothing changes to the chemical equation written above. It does, however allow us to write it as



We usually write the amount of fuel (in this case CO) as unity (1 molecule, 1 mole, 1 kmol), and adjust the amount of oxidizer. With the number of molecules expressed as kmol, we can now also show that mass is conserved using the molar masses (M) of the molecules. Molar masses of common molecules are listed in the data book found on blackboard. Mass conservation requires that

$$M_{\text{CO}} + \frac{1}{2}M_{\text{O}_2} = M_{\text{CO}_2} \quad (5.3)$$

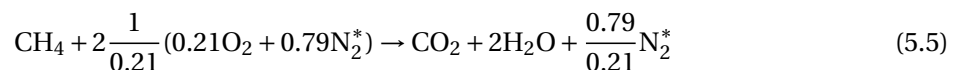
From the data book we find the molar masses $M_{\text{CO}} = 28 \text{ kg kmol}^{-1}$, $M_{\text{O}_2} = 32 \text{ kg kmol}^{-1}$ and $M_{\text{CO}_2} = 44 \text{ kg kmol}^{-1}$, so we can check that mass is indeed conserved:

$$28 \text{ kg} + 16 \text{ kg} = 44 \text{ kg}. \quad (5.4)$$

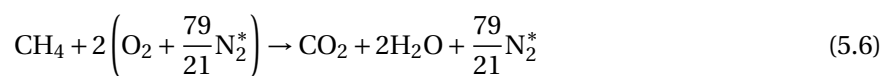
5.3.2 Combustion in air and air-fuel ratio

In the example above, we looked at a reaction of a fuel with pure oxygen. In most applications however, the fuel is mixed with air. Air is a mixture of nitrogen, oxygen, argon, and traces of other gases. Nitrogen and oxygen take up the vast majority of the air, with the other gases taking up less than 1% by volume. Because nitrogen (N_2) and the other gases don't participate in the main reaction, we commonly group them together as 'atmospheric nitrogen' (N_2^*). Atmospheric nitrogen has slightly different properties than pure nitrogen, the properties are listed in the data book.

By volume, air consists of 21.0% oxygen, and 79.0% atmospheric nitrogen. The combustion of methane (CH_4) in air, would therefore be



or



An important parameter for combustion in air is the air-fuel ratio AFR , which is the ratio of air to fuel by mass:

$$AFR = \frac{m_a}{m_f} \quad (5.7)$$

Note that this is the inverse of the fuel-air ratio f . For the reaction we just described, we can determine the air-fuel ratio using the molar masses of CH_4 , O_2 , and N_2^* :

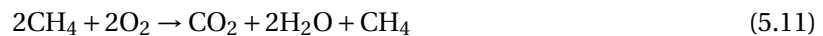
$$AFR = \frac{2 \times M_{\text{O}_2} + 2 \times \frac{79}{21} M_{\text{N}_2^*}}{M_{\text{CH}_4}} = \frac{2 \times 32 + 2 \times 3.762 \times 28.15}{16} = 17.24 \quad (5.8)$$

5.3.3 Complete combustion

When the fuel is a hydrocarbon, combustion is considered complete when the fuel is fully converted to carbon dioxide and water. We will use the combustion of methane (CH_4) as an example. The following two reactions both are examples of complete combustion:



Combustion is incomplete when either fuel is left, or components such as carbon monoxide (CO) or carbon (C) are left. Incomplete combustion can have various causes. The most trivial example is if there is not enough oxygen available, which will make complete combustion impossible, irrespective of other factors that influence the combustion process. For example:



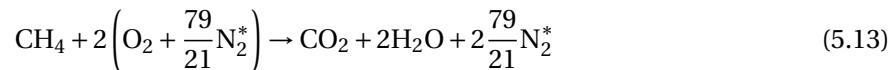
But also mixing, flow conditions, and temperature can influence the combustion, for example



where not all the oxygen was utilized because the conditions were not right for complete combustion, which resulted in the formation of soot.

5.3.4 Stoichiometric ratio and equivalence ratio

An air-fuel mixture is called stoichiometric when there is exactly enough air (or oxygen) for complete combustion. For example:



The equivalence ratio ϕ is the ratio between the stoichiometric air-fuel ratio to the actual air-fuel ratio:

$$\phi = \frac{AFR_{st}}{AFR} \quad (5.14)$$

Based on the equivalence ratio, we define three regimes for the air-fuel ratio:

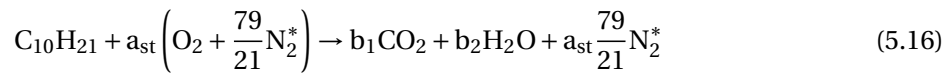
- $\phi > 1$ Fuel rich
- $\phi = 1$ Stoichiometric
- $\phi < 1$ Fuel lean

Note that although the air-fuel ratio is based on mass, the equivalence ratio is equal when based on mass or molar quantities, because it is effectively only comparing the amount of air:

$$\phi = \frac{AFR_{st}}{AFR} = \frac{\frac{m_{a,st}}{m_f}}{\frac{m_a}{m_f}} = \frac{m_{a,st}}{m_a} = \frac{n_{a,st}M_a}{n_aM_a} = \frac{n_{a,st}}{n_a} \quad (5.15)$$

5.3.5 Example: Combustion of kerosene

Write the chemical reaction for the complete combustion of kerosene ($\approx \text{C}_{10}\text{H}_{21}$) at an equivalence ratio of 0.2 in air.

Step 1: Determine the stoichiometric reaction.

Finding the unknowns using conservation of atoms:

$$\text{C: } 10 = b_1$$

$$\text{H: } 21 = 2b_2$$

$$\text{O: } 2a_{st} = 2b_1 + b_2$$

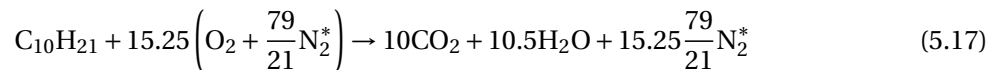
From which it follows that

$$b_1 = 10$$

$$b_2 = 10.5$$

$$a_{st} = b_1 + \frac{1}{2}b_2 = 15.25$$

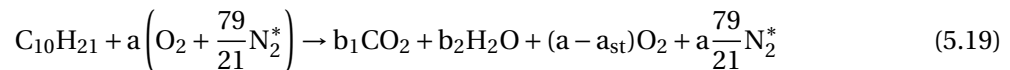
So the stoichiometric reaction would be

**Step 2: Work out the actual reaction.**

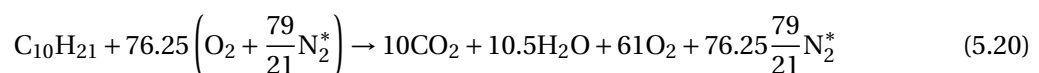
The actual amount of air follows from the equivalence ratio

$$a = \frac{a_{st}}{\phi} = \frac{15.25}{0.2} = 76.25 \quad (5.18)$$

Because we will have an excess of oxygen, we need to include this in the actual reaction, taking atom conservation into account:



which is

**5.4 Combustion thermodynamics**

The heat that is generated during a combustion process is coming from a change in the chemical energy of the gas. Burning fuel changes the chemical composition, as we've analysed in section 5.3 above. Next to generating heat, this also means that the properties of the reaction products (exhaust gas) are different from the reactants (fuel-air mixture). For example, the c_p value will change during a combustion process, which will have an influence on changes in temperature and enthalpy. Below we will provide the definitions and methods to do calculations on combustion processes, most importantly how to calculate the temperature at the outlet of an adiabatic isobaric combustor, which is also called the adiabatic flame temperature.

5.4.1 Calorific value

We will start by investigating two model combustion processes: adiabatic and isothermal combustion, both at a constant pressure. Both processes are shown schematically in figure 5.1. Writing the steady flow energy equation for the adiabatic combustion process

$$\dot{Q} - \dot{W}_x = \dot{m}(h_{out} - h_{in}) \quad (5.21)$$

with $\dot{Q} = 0$ (adiabatic) and $\dot{W}_x = 0$ (constant pressure), we find that $h_{out} = h_{in}$, so there is no enthalpy change in an adiabatic combustion process. The adiabatic process will however have a change in temperature. Although we are used to having a change in temperature accompanying a change in enthalpy ($\Delta h = c_p \Delta T$), it is not the case for adiabatic combustion. The reason is that any change in thermal energy is exactly equal to the change in chemical energy, so that together they add up to zero. In the isothermal process, all the heat that is produced by the combustion process is removed, such

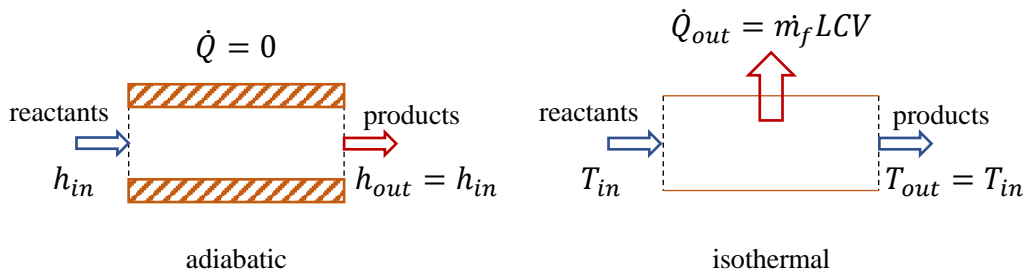


Figure 5.1: Adiabatic and isothermal combustion.

that the products leave the combustor at the same temperature as the reactants entered it. This will result in a change in enthalpy, which is equal to the change in chemical energy.

The enthalpy as a function of temperature is different for the reactants and the products, as shown in figure 5.2. Both model reactions are also shown in the figure. The vertical dashed line shows the isothermal reaction, with a reduction in enthalpy because heat is removed. The horizontal dashed line shows the adiabatic process, which results in an increase in temperature.

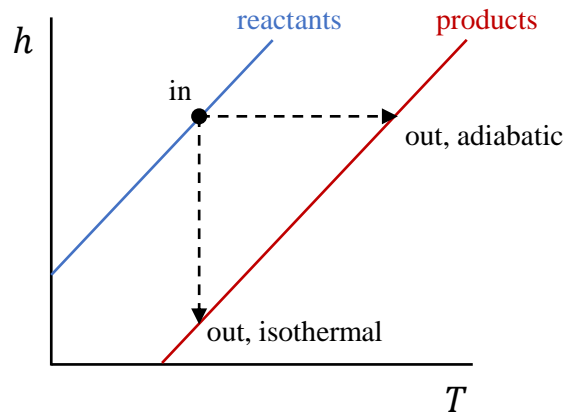


Figure 5.2: Enthalpy versus temperature for reactants and products, with the adiabatic and isothermal combustion processes indicated.

Although we are ultimately interested in the increase in temperature of an adiabatic combustion process, the calorific value of a fuel that we can find in data books is defined as the amount of heat released at constant temperature and pressure, typically at the standard values $T_0 = 298.15$ K and $p_0 = 1$ bar.

Data books further make a distinction between two variations of the calorific value: the Lower Calorific Value (LCV) and the Higher Calorific Value (HCV). The LCV corresponds to a reaction where the water in the products remains in the vapour phase, while the HCV corresponds to a scenario where the water is condensed. The condensation of water releases heat, which is why the second one is always higher. For our purposes, we will always use the Lower Calorific Value. The LCV and HCV of some standard fuels can be found in Table 1 of the databook on blackboard.

Although the pressure dependence on the calorific value is very small and can be neglected, we do need to evaluate our reactions at the constant reference temperature. The method for this will be explained next.

5.4.2 Steady flow combustion and adiabatic flame temperature

Combustion typically occurs at high pressure and high temperature. In order to use the tabulated LCV values, we will replace the combustion process by three hypothetical processes that together resemble that actual process. The actual process is adiabatic combustion in steady flow, as was indicated in figure 5.1, with no shaft work done, and no heat transfer. Figure 5.3 shows the same process (box with dashed lines), but with three sub-processes inside it. The reactants enter the process at state 1 (T_1, p_1). The first process (subscript 10) is extraction of shaft work $\dot{W}_{x,10}$ and heat rejection (negative heat addition \dot{Q}_{10}) to bring the reactants to the reference state 0, at temperature T_0 and pressure p_0 . The second process (subscript r) is combustion at constant temperature and pressure, resulting in reaction products at the reference state 0, during which more heat is rejected (negative heat addition $\dot{Q}_r = -\dot{m}LCV$). The third and last process (subscript 02) adds back the heat that was removed during the previous two processes ($\dot{Q}_{02} = -\dot{Q}_{10} - \dot{Q}_r$) such that the overall process is adiabatic, and returns the work that was extracted in the first process ($\dot{W}_{x,02} = -\dot{W}_{x,10}$) such that no net work is done during the complete process. Because the overall process is adiabatic, the outlet temperature T_2 is called the *adiabatic flame temperature*.

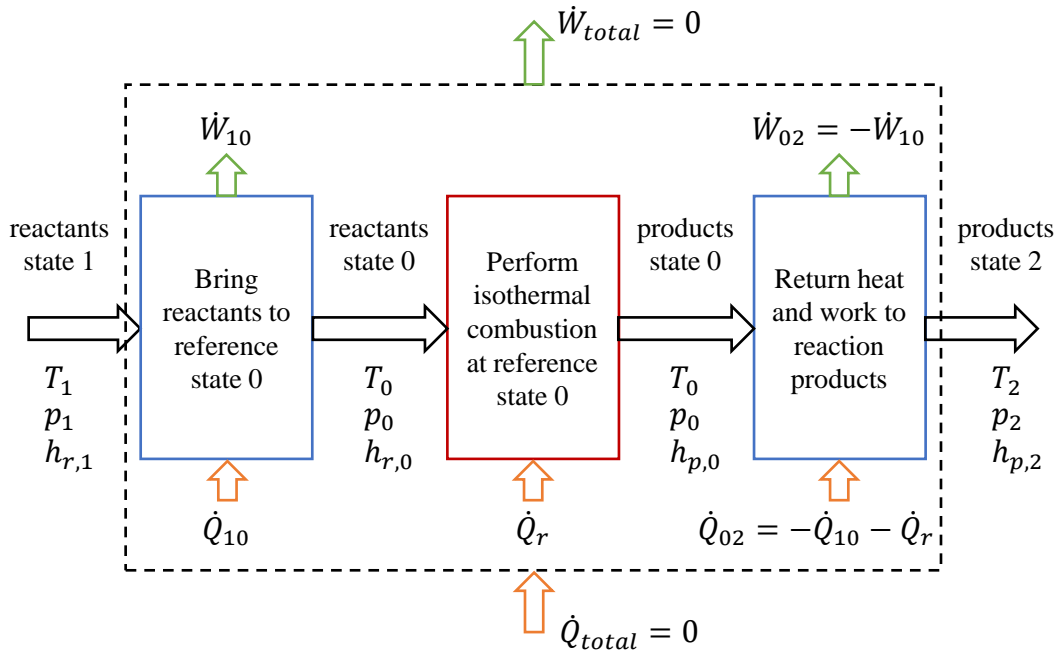


Figure 5.3: Schematic overview of the combustions process model.

Writing the steady flow energy equation for the complete process results in

$$\dot{Q} - \dot{W}_x = \sum_{\text{react}} m_i (h_{i,0} - h_{i,1}) - \dot{m}_f (LCV) + \sum_{\text{prod}} m_j (h_{j,2} - h_{j,0}) \quad (5.22)$$

with \dot{m}_f the mass flow rate of fuel, and subscripts i and j corresponding to the individual components in the reactants and products, respectively.

5.5 Chemical equilibrium

So far we have treated chemical reactions going only one way, from reactants to products. In reality, reactions will go both ways, and a dynamic equilibrium will be reached. Where the equilibrium sits depends on the temperature and the pressure.

Understanding and using chemical equilibrium is specifically important for dissociation, for example the formation of the pollutant CO instead of CO₂, which also makes combustion less efficient, and the formation of other pollutants such nitrous oxides (NO_x).

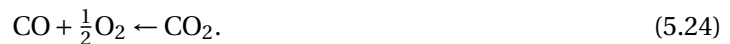
5.5.1 Le Chatelier's Principle

Le Chatelier's Principle states that "If a chemical system at equilibrium experiences a change in concentration, temperature or pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established."

For an exothermic reaction (a reaction that generates heat), this means that increasing the temperature will favour the inverse (endothermic) reaction. If we for example look at the reaction



we find in table 4 of the data book that this is an exothermic reaction. Table 4 provides the change in enthalpy per kmol at constant temperature, and referring back to figure 5.2 we see that a negative change in enthalpy corresponds to a heat-generating reaction. Therefore, an increase in temperature will favour the reverse reaction



Because both reactions will happen simultaneously, we write



Although the combustion of standard fuels will also reach an equilibrium, we can neglect the reverse reaction for them because the change in chemical energy is very large. For example the combustion of CH₄ we can safely assume to go one way. However, the products of this reaction will form a chemical equilibrium. If the reaction was fuel lean, the reaction products will contain both CO₂ and O₂, which will form an equilibrium with CO as per equation (5.25).

5.5.2 Equilibrium constants

Taking the reversible reaction (5.25), we would like to find out the equilibrium composition at a specific temperature and pressure. To calculate this, we make use of equilibrium constants, which are tabulated for common reactions. Taking a generic reaction with four species A, B, C, and D:



the partial pressures of the species are related to the equilibrium constant as

$$K^\theta = \frac{(p_c)^c (p_d)^d}{(p_a)^a (p_b)^b} \quad (5.27)$$

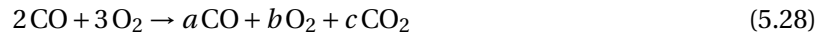
where K^θ is the equilibrium constant, which is dependent on the temperature and can be found in table 5 of the data book. Note that the values in the table are given as $\ln(K^\theta)$.

5.5.3 Chemical equilibrium example

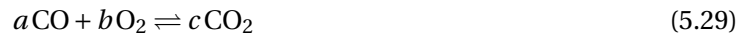
We will now determine the molar (or volumetric) composition of CO, CO₂ and O₂ at a temperature of 2600 K and pressure 3 bar, assuming we start with 2 kmol CO and 3 kmol O₂.

Step 1: write the chemical reaction

The global reaction is



with the equilibrium reaction



with a , b , and c the unknown number of kmols of each product.

Step 2: atom conservation relations

We can write down relations between our unknowns using atom conservation. This will reduce the number of unknowns:

$$\text{C: } 2 = a + c$$

$$\text{O: } 2 + 6 = a + 2b + 2c$$

We can choose any of the products (CO, O₂ or CO₂) to solve for. If we choose to solve for CO₂, then we can express a and b (the number of kmols of CO and O₂) in terms of c (the number of kmols of CO₂):

$$\text{CO: } a = 2 - c$$

$$\text{O}_2: b = 3 - \frac{1}{2}c$$

Step 3: equilibrium equation

We look in table 5 of the data book for the equilibrium constant corresponding to our equilibrium equation. We find

$$K^\theta = \frac{(p_{\text{CO}_2})(p^\theta)^{1/2}}{(p_{\text{CO}})(p_{\text{O}_2})^{1/2}} = \frac{(p_{\text{CO}_2})}{(p_{\text{CO}})(p_{\text{O}_2})^{1/2}} \quad (5.30)$$

with $\ln(K^\theta) = 2.800$, or $K^\theta = 16.445$ at a temperature of 2600 K.

Step 4: replace partial pressures with number of moles

We now replace the partial pressures with our parameters a , b , and c , using the molar fraction and the pressure $p = 3$ bar:

$$p_{\text{CO}_2} = y_{\text{CO}_2} p = \frac{c}{a + b + c} p \quad (5.31)$$

Applying the same for the other two partial pressures, and substituting in equation (5.30) results in

$$K^\theta = \frac{c}{(a)(b)^{1/2}} \left(\frac{a + b + c}{p} \right)^{1/2} \quad (5.32)$$

if we now substitute a and b using our relations $a = 2 - c$ and $b = 3 - c/2$ we get

$$K^\theta = \frac{c}{(2 - c)(3 - c/2)^{1/2}} \left(\frac{2 - c + 3 - c/2 + c}{p} \right)^{1/2} = \frac{c}{(2 - c)(3 - c/2)^{1/2}} \left(\frac{5 - c/2}{p} \right)^{1/2} \quad (5.33)$$

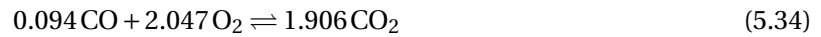
which is now an equation with c the only unknown.

Step 5: numerical solution

Solving equation (5.33) for c , and subsequently calculating a and b gives

$$\begin{aligned}c &= 1.906 \\a &= 2 - c = 0.094 \\b &= 3 - c/2 = 2.047\end{aligned}$$

So the equilibrium equation becomes



and the volumetric composition will be

$$\text{CO: } 0.094 / (0.094 + 2.047 + 1.906) = 2.3\%$$

$$\text{O}_2: 2.047 / (0.094 + 2.047 + 1.906) = 50.6\%$$

$$\text{CO}_2: 1.906 / (0.094 + 2.047 + 1.906) = 47.1\%$$