



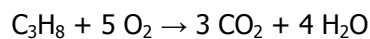
Exercises of "Fundamentals of Chemical Processes"

Prof. Gianpiero Groppi

EXERCISE 1

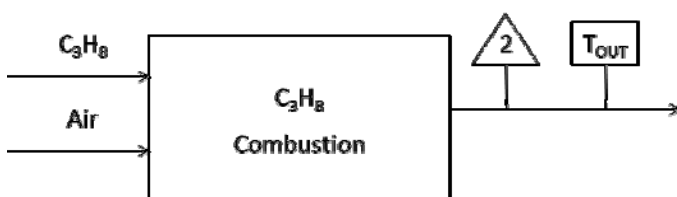
Adiabatic flame temperature for the combustion of propane

The combustion of propane with air is carried out in an adiabatic reactor:



Considering the data given below, calculate the temperature of the exhaust gas stream at the outlet of the reactor (T_{OUT}) in the following cases:

- 1) stoichiometric feed of the reactants
- 2) 30% excess air
- 3) with reference to the case with 30% excess air, assume that, due to ill-combustion, CO is present among the exhaust gases with a selectivity of 10% with respect to the moles of C converted.



Data:

<u>C₃H₈ stream:</u>	T = 25°C	P = 1 atm	$\Delta H^\circ_{\text{C}} \text{C}_3\text{H}_8 (25^\circ\text{C}) = -2043 \text{ kJ/mol}$
<u>Air stream:</u>	T = 25°C	P = 1 atm	R.H. = 60% $P_{\text{H}_2\text{O}}^{\text{SAT}}(25^\circ\text{C}) = 3.169 \text{ kPa}$
<u>Stream #2:</u>	$T_{\text{OUT}} = ?$	P = 1 atm	$\Delta H^\circ_{\text{C}} \text{CO} (25^\circ\text{C}) = -283 \text{ kJ/mol}$
<u>Hypothesis:</u>	Adiabatic reactor		

Specie	a	b	C
N ₂	3.280	5.930E-04	-4.000E+03
CO ₂	5.457	1.045E-03	-1.157E+05
H ₂ O	3.470	1.450E-03	1.210E+04
O ₂	3.639	5.060E-04	-2.270E+04
CO	3.376	5.570E-04	-3.100E+03

$$\bar{C}_{P,i} = R_{gas} \cdot \left(a_i + b_i \cdot T + \frac{c_i}{T^2} \right) \frac{J}{mol \cdot K} \quad T \text{ in } K$$

$C_{p,i}$ equation and parameters taken from J.M. Smith, H.C. Van Ness, M. M. Abbott, Introduction to Chemical Engineering Thermodynamics, 7th edition, McGraw Hill (2005).

Solution

Case 1

First, the material balance is written for each of the species involved in the reaction. Then, a basis is set for the calculation. The basis can be chosen arbitrarily. In this case, it is reasonable to choose 1 mol/s inlet propane as the basis. The amount of inlet O₂ is estimated from the reaction stoichiometry and is equal to 5 mol/s. The amount of inlet N₂ going in the reactor together with air (0.21% O₂ and 0.79% N₂ composition on molar basis) is calculated starting from the amount of O₂:

$$N_2 = 5 \cdot \frac{0.79}{0.21} = 5 \cdot 3.762 = 18.81 \text{ mol/s}$$

The amount of inlet H₂O is calculated given the relative humidity values (R.H.), as follows:

$$R.H. = \frac{P_{H_2O}}{P_{H_2O}^{Sat}(T_{Air}^in)} = \frac{P \cdot y_{H_2O}}{P_{H_2O}^{Sat}(25^\circ C)}$$

$$y_{H_2O} = H.R. \cdot \frac{P_{H_2O}^{Sat}(25^\circ C)}{P} = 0.01877$$

$$y_{H_2O} = \frac{mol_{H_2O}}{mol_{Air} + mol_{H_2O}}$$

$$mol_{H_2O} = mol_{Air} \cdot \frac{y_{H_2O}}{1 - y_{H_2O}} = 0.455$$

Knowing that the combustion occurs with complete conversion of propane, the molar gas flows at the outlet of the reactor can be calculated, solving the problem of the material balances of the reactor.

Specie	n^{in} (mol/s)	x^{in} (%)	n^{out} (mol/s)	x^{out} (%)
C_3H_8	1	3.96	0	0
O_2	5	19.79	0	0
N_2	18.81	74.45	18.81	71.62
CO_2	0	0	3	11.42
H_2O	0.455	1.80	4.455	16.96
Total	25.265	100	26.255	100

The amount of H_2O at the exit of the reactor is the sum of the H_2O fed via humidity of the inlet air and the H_2O produced by the combustion reaction. It is worthy to note that a different choice for the basis does change the absolute values of the incoming and outgoing molar flows, but does not change the composition of the mixtures.

The enthalpy balance of the reactor can be written starting from the adiabatic condition:

$$\dot{H}_{OUT} = \dot{H}_{IN}$$

The evaluation of the enthalpy fluxes requires the assumption of a reference state. The following reference state is considered:

pressure and temperature at which the fuel ΔH_C° is known, composition equal to the species entering the reactor.

In the case of propane, $\Delta H_C^\circ (25^\circ\text{C}, 1 \text{ atm}) = -2043 \text{ kJ/mol}$. Given this reference state, the enthalpy balance is written as follows:

$$\sum_{i=1}^{\text{Products}} n_i^{OUT} \cdot \int_{298K}^{T_{OUT}} \bar{C}_{P,i} \cdot dT + n_f \cdot \Delta H_C^0(298K) - \sum_{i=1}^{\text{Reactants}} n_i^{IN} \cdot \int_{298K}^{T_{IN}} \bar{C}_{P,i} \cdot dT = 0$$

In the equation, n_f is the number of moles of the fuel that are converted in the reaction. The same equation can be written using the Lower Heating Value (LHV), coherently with the gaseous state of the H_2O produced at the outlet of the reactor.

$$n_f \cdot \Delta H_C^0(298K) = -n_f \cdot LHV$$

By integrating the specific heat expression, an equation in the only unknown T_{OUT} is obtained.

$$\int_{298K}^T \bar{C}_{P,i} \cdot dT = a_i \cdot T + \frac{b_i}{2} \cdot T^2 - \frac{c_i}{T} - \left(a_i \cdot 298 + \frac{b_i}{2} \cdot 298^2 - \frac{c_i}{298} \right)$$

Going through the mathematical rearrangement, the following equation is obtained:

$$8.314 \cdot \left(93.5263 \cdot T + 1.0375 \cdot 10^{-2} \cdot T^2 + \frac{3.6843 \cdot 10^{+5}}{T} - 3.0028 \cdot 10^4 \right) - 2.043 \cdot 10^6 = 0$$

From which: $T_{OUT} = 2339.59$ K

It is possible to choose different reference states to write the enthalpy balance on the reacting system, anyway obtaining equivalent expressions. Given the following reference state:

Reference pressure P_{REF} , reference temperature T_{REF} , elementary species

the same equation previously reported can be obtained. In both cases, once the inlet and the outlet compositions are derived from the material balances, the enthalpy balance leads to one equation in one unknown variable, which is the outlet adiabatic temperature. Choosing as the reference the elementary species at reference pressure and temperature, the enthalpy equation requires to start from the definition of the molar specific enthalpy $h_i(T)$ of the individual i -th species at the generic temperature T , as follows:

$$h_i(T) = \Delta H_{F,i}(T_{REF}) + \int_{T_{REF}}^T \bar{C}_{P,i} \cdot dT$$

$$\sum_{i=1}^{Products} n_i^{OUT} \cdot h_i(T_{OUT}) = \sum_{i=1}^{Reactants} n_i^{IN} \cdot h_i(T_{IN})$$

For each specie, the values of the $\Delta H_{F,i}$ are listed in thermodynamic databases. In general, in the databases $T_{REF} = 298K$ e $P_{REF} = 1$ atm.

Case 2

In this case, the value of the excess air is given. The solving procedure does not change, a basis has to be chosen and the material balances must be written for each specie in the reaction. Choosing the same basis of Case 1 (1 mol/s of inlet propane), the O_2 in the feed is calculated starting from the reaction stoichiometry and from the definition of excess:

$$e\% = \frac{\alpha - \alpha_{stoich}}{\alpha_{stoich}} \cdot 100$$

$$e\% = \frac{mol_{O_2} - mol_{stoichO_2}}{mol_{stoich,O_2}} \cdot 100$$

$$mol_{O_2} = mol_{stoich,O_2} \cdot \left(1 + \frac{e\%}{100}\right) = 5 \cdot 1.3 = 6.5 \text{ mol / s}$$

It is worthy to note that the O₂ at the outlet amounts to:

$$mol_{O_2}^{out} = mol_{stech,O_2} \cdot \frac{e\%}{100} = 5 \cdot 0.3 = 1.5 \text{ mol / s}$$

The material balances are solved, leading to the following results:

Specie	n ⁱⁿ (mol/s)	x ⁱⁿ (%)	n ^{out} (mol/s)	x ^{out} (%)
C ₃ H ₈	1	3.07	0	0
O ₂	6.5	19.97	1.5	4.47
N ₂	24.452	75.14	24.452	72.90
CO ₂	0	0	3	8.94
H ₂ O	0.592	1.82	4.592	13.69
Total	32.544	100	33.544	100

The enthalpy balance is treated in the same way shown in Case 1. After some mathematical steps, the following solving equation is obtained:

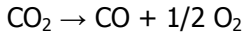
$$8.314 \cdot \left(117.967 \cdot T + 1.2526 \cdot 10^{-2} \cdot T^2 + \frac{4.2340 \cdot 10^{+5}}{T} - 3.7687 \cdot 10^4 \right) - 2.043 \cdot 10^6 = 0$$

From which: T_{OUT} = 1983.11 K

The result of Case 2 shows that the excess air acts as a thermal diluent, significantly lowering the adiabatic flame temperature of the propane combustion.

Case 3

The case of the presence of CO among the exhausts can be analyzed starting from the case with excess air. CO is produced with a selectivity of 10% with respect to the moles of atomic carbon converted. It is possible to assume that CO is formed via the thermal decomposition of CO₂, produced in stoichiometric amount from propane combustion:



Starting from the definition of selectivity:

$$S_{\text{CO}} = \frac{\text{mol}_{\text{CO}}^{\text{produced}}}{\text{mol}_{\text{C}}^{\text{reacted}}} = \frac{\text{mol}_{\text{CO}}^{\text{produced}}}{3 \cdot \text{mol}_{\text{C}_3\text{H}_8}^{\text{converted}}}$$

$$\text{mol}_{\text{CO}}^{\text{produced}} = 0.3 \text{ mol} / \text{s}$$

It is possible to estimate the outlet composition via the atomic balances for each of the atomic element introduced in the reacting system, obtaining the following set of equations:

$$C \text{ balance} : 3 \cdot n_{\text{C}_3\text{H}_8}^{\text{IN}} = n_{\text{CO}}^{\text{OUT}} + n_{\text{CO}_2}^{\text{OUT}}$$

$$O \text{ balance} : 2 \cdot n_{\text{O}_2}^{\text{IN}} + n_{\text{H}_2\text{O}}^{\text{IN}} = 3 \cdot n_{\text{C}_3\text{H}_8}^{\text{OUT}} + 2 \cdot n_{\text{O}_2}^{\text{OUT}} + n_{\text{H}_2\text{O}}^{\text{OUT}} + 2 \cdot n_{\text{CO}_2}^{\text{OUT}} + n_{\text{CO}}^{\text{OUT}}$$

$$H \text{ balance} : 8 \cdot n_{\text{C}_3\text{H}_8}^{\text{IN}} = 2 \cdot n_{\text{H}_2\text{O}}^{\text{IN}}$$

The molar flows and the molar compositions of the outlet of the reactor can be obtained:

Specie	n ⁱⁿ (mol/s)	x ⁱⁿ (%)	n ^{out} (mol/s)	x ^{out} (%)
C ₃ H ₈	1	3.07	0	0
O ₂	6.5	19.97	1.65	4.94
N ₂	24.452	75.14	24.452	73.22
CO ₂	0	0	2.7	8.09
H ₂ O	0.592	1.82	4.592	13.75
CO	0	0	0.3	0.90

As in the previous cases, for the enthalpy balance, it is convenient to assume the reference state that stems from the knowledge of the pressure and the temperature at which the ΔH[°]_C is known. In light of this, the reaction of CO₂ decomposition to produce CO subtracts a part of the heat released during the reaction. The

ΔH°_c of this decomposition reaction is the inverse of that of the reaction of CO oxidation ($\Delta H^\circ_c \text{ CO} = -283$ KJ/mol). The final form of the enthalpy balance is:

$$\sum_{i=1}^{\text{Products}} n_i^{\text{OUT}} \cdot \int_{298K}^{T_{\text{OUT}}} \bar{C}_{P,i} \cdot dT + n_f \cdot \Delta H_{C,C_3H_8}^0(298K) - n_{CO} \cdot \Delta H_{C,CO}^0(298K) - \sum_{i=1}^{\text{Reactants}} n_i^{\text{IN}} \cdot \int_{298K}^{T_{\text{IN}}} \bar{C}_{P,i} \cdot dT = 0$$

Going through the calculations, the following solving equation is obtained:

$$8.314 \cdot \left(117.8889 \cdot T + 1.2491 \cdot 10^{-2} \cdot T^2 + \frac{3.9302 \cdot 10^{+5}}{T} - 3.7559 \cdot 10^4 \right) - 2.043 \cdot 10^6 + 8.49 \cdot 10^4 = 0$$

From which $T_{\text{OUT}} = 1922.89$ K

The complete combustion dictates both the composition and the enthalpy content of the exhaust gases. The enthalpy content is given by two main contributions: a first, minor, contribution is due to the change in the sensible heat of the exhausts, which, in turn, is a consequence of the change in the composition due to the presence of CO; the second, major, contribution is associated to the decrease of the heating value, as a consequence of the ill-combustion. Nonetheless, the decrease of enthalpy associated to the formation of CO is not complete: given a 10% selectivity in the formation of CO, the decrease of the sensible heat amounts only to 5%. This effect is due to the fact that CO is a partial oxidation product, which allows to limit the energy loss.