1. INTRODUCTION TO REACTOR SIMULATION TOOLS: OpenSMOKE++

THERMOCHEMICAL PROCESSES FOR CARBON NEUTRAL ENERGY TRANSFORMATION

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Exercise 1 – Thermodynamic equilibrium

Syngas can be used to produce molecular hydrogen through the WGS reaction. Use the SYNGAS kinetic model together with thermodynamic properties to simulate the thermodynamic equilibrium of the syngas mixtures **a** and **b**. Assume adiabatic conditions, atmospheric pressure, an initial temperature of 500°C, at different $H_2O/(CO+CO_2)$ molar ratios (0.5, 2).

Comment about the effects of CO_2 and of H_2O/CO ratio on H_2O yield to H_2.

Mixtures:

a) Pure syngas: 100% (v/v) CO

b) Sour syngas: 98% (v/v) CO, 2% (v/v) CO_2

Exercise 1 – Thermodynamic equilibrium *(Results)*

H2O/CO = 0.5				
Status	Initial	Equilibrium		
T[K]	773.15	1016.67		
P[atm]	1	1		
rho[kg/m3]	0.38899	0.29662		
MW[kg/km	24.67833	24.74596		
H[J/kg]	-5.64E+06	-5.64E+06		
U[J/kg]	-5.90E+06	-5.98E+06		
Conv.(%)	H2O	0.00E+00	7.09E+01	
Conv.(%)	CO	0.00E+00	3.58E+01	
Element	C	2.70E-02	2.70E-02	
Element	H	2.70E-02	2.70E-02	
Element	O	4.05E-02	4.05E-02	
Mole	fractions	Initial	Equilibrium	
AR	0.00E+00	0.00E+00		
N2	0.00E+00	0.00E+00		
HE	0.00E+00	0.00E+00		H2 yield
H2	0.00E+00	2.34E-01		9.9226E+01
H	0.00E+00	1.70E-09		
O2	0.00E+00	3.50E-21		
O	0.00E+00	1.52E-20		
H2O	3.33E-01	9.74E-02		
OH	0.00E+00	2.21E-12		
H2O2	0.00E+00	1.93E-20		
HO2	0.00E+00	1.85E-24		
CO	6.67E-01	4.29E-01		
CO2	0.00E+00	2.38E-01		
HOCO	0.00E+00	3.86E-14		
CH4	0.00E+00	1.37E-03		
CH3	0.00E+00	1.78E-10		
CH2	0.00E+00	4.48E-19		

H2O/(CO+CO2) = 0.5 CO2/CO=0.02				
Status	Initial	Equilibrium		
T[K]	773.15	1012.193		
P[atm]	1	1		
rho[kg/m3]	0.39235	0.30053		
MW[kg/km	24.89165	24.9611		
H[J/kg]	-5.74E+06	-5.74E+06		
U[J/kg]	-5.99E+06	-6.07E+06		
Conv.(%)	H2O	0.00E+00	6.99E+01	
Conv.(%)	CO	0.00E+00	3.61E+01	
Conv.(%)	CO2	0.00E+00	-1.76E+03	
Element	C	2.68E-02	2.68E-02	
Element	H	2.68E-02	2.68E-02	
Element	O	4.07E-02	4.07E-02	
Mole	fractions	Initial	Equilibrium	
AR	0.00E+00	0.00E+00		
N2	0.00E+00	0.00E+00		
HE	0.00E+00	0.00E+00		H2 yield
H2	0.00E+00	2.31E-01		9.9201E+01
H	0.00E+00	1.50E-09		
O2	0.00E+00	2.97E-21		
O	0.00E+00	1.23E-20		
H2O	3.33E-01	1.01E-01		
OH	0.00E+00	1.98E-12		
H2O2	0.00E+00	1.74E-20		
HO2	0.00E+00	1.55E-24		
CO	6.53E-01	4.19E-01		
CO2	1.33E-02	2.48E-01		
HOCO	0.00E+00	3.58E-14		
CH4	0.00E+00	1.39E-03		
CH3	0.00E+00	1.62E-10		

H2O/CO = 2				
Status	Initial	Equilibrium		
T[K]	773.15	997.138		
P[atm]	1	1		
rho[kg/m3]	0.33647	0.26095		
MW[kg/km	21.34667	21.35191		
H[J/kg]	-8.52E+06	-8.52E+06		
U[J/kg]	-8.83E+06	-8.91E+06		
Conv.(%)	H2O	0.00E+00	3.60E+01	
Conv.(%)	CO	0.00E+00	7.21E+01	
Element	C	1.56E-02	1.56E-02	
Element	H	6.25E-02	6.25E-02	
Element	O	4.68E-02	4.68E-02	
Mole	fractions	Initial	Equilibrium	
AR	0.00E+00	0.00E+00		
N2	0.00E+00	0.00E+00		
HE	0.00E+00	0.00E+00		H2 yield
H2	0.00E+00	2.40E-01		9.9966E+01
H	0.00E+00	1.03E-09		
O2	0.00E+00	2.04E-20		
O	0.00E+00	2.04E-20		
H2O	6.67E-01	4.27E-01		
OH	0.00E+00	4.95E-12		
H2O2	0.00E+00	1.59E-19		
HO2	0.00E+00	1.07E-23		
CO	3.33E-01	9.32E-02		
CO2	0.00E+00	2.40E-01		
HOCO	0.00E+00	2.42E-14		
CH4	0.00E+00	1.23E-04		
CH3	0.00E+00	9.31E-12		
CH2	0.00E+00	1.30E-20		

H2O/(CO+CO2) = 2 CO2/CO=0.02				
Status	Initial	Equilibrium		
T[K]	773.15	993.142		
P[atm]	1	1		
rho[kg/m3]	0.33815	0.26331		
MW[kg/km	21.45333	21.45871		
H[J/kg]	-8.57E+06	-8.57E+06		
U[J/kg]	-8.87E+06	-8.95E+06		
Conv.(%)	H2O	0.00E+00	3.54E+01	
Conv.(%)	CO	0.00E+00	7.23E+01	
Conv.(%)	CO2	0.00E+00	-3.54E+03	
Element	C	1.55E-02	1.55E-02	
Element	H	6.22E-02	6.22E-02	
Element	O	4.69E-02	4.69E-02	
Mole	fractions	Initial	Equilibrium	
AR	0.00E+00	0.00E+00		
N2	0.00E+00	0.00E+00		
HE	0.00E+00	0.00E+00		H2 yield
H2	0.00E+00	2.36E-01		9.9965E+01
H	0.00E+00	9.16E-10		
O2	0.00E+00	1.68E-20		
O	0.00E+00	1.64E-20		
H2O	6.67E-01	4.31E-01		
OH	0.00E+00	4.39E-12		
H2O2	0.00E+00	1.39E-19		
HO2	0.00E+00	8.70E-24		
CO	3.27E-01	9.04E-02		
CO2	6.67E-03	2.43E-01		
HOCO	0.00E+00	2.19E-14		
CH4	0.00E+00	1.25E-04		
CH3	0.00E+00	8.58E-12		

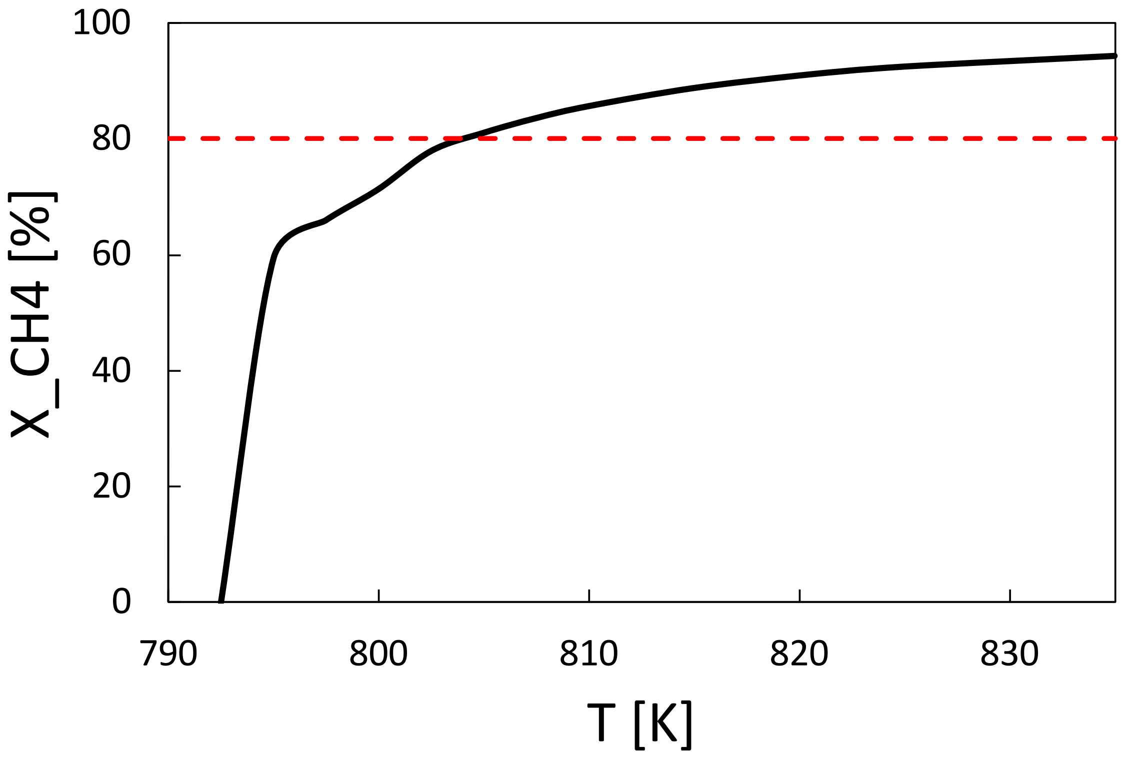
Exercise 2 – Isothermal Plug Flow Reactor

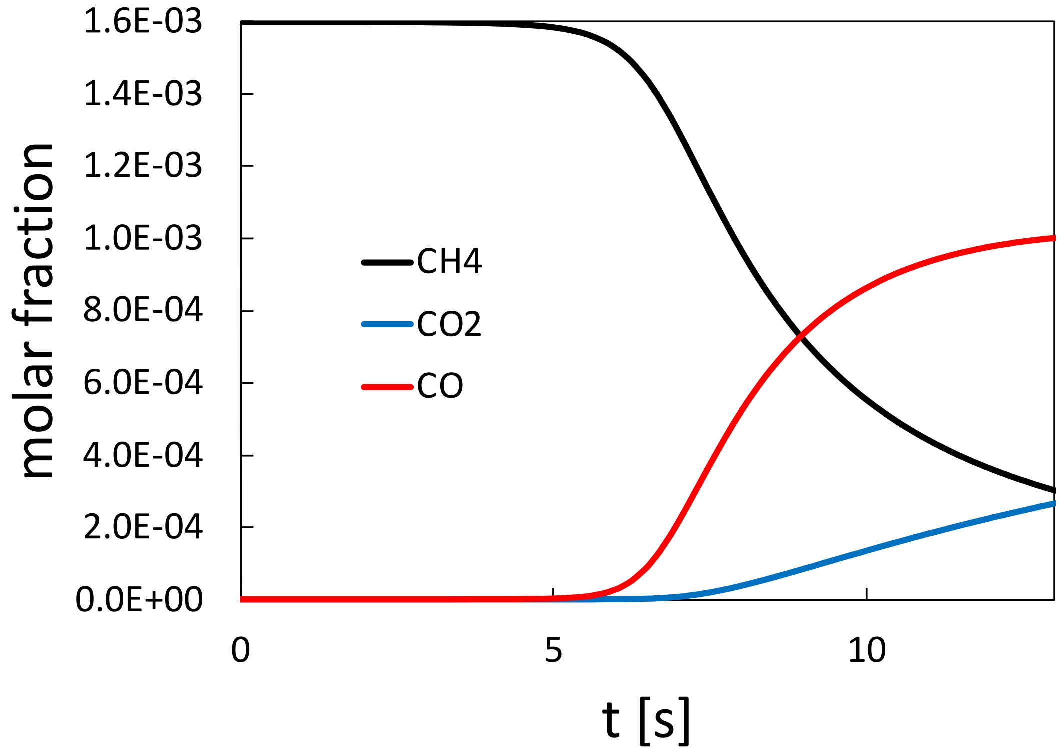
A mixture of methane, oxygen, and nitrogen is fed in a continuous reactor, operating at 100 bar. The mixture composition is: 0.16% (v/v) CH_4, 0.31% (v/v) O_2, 99.53% (v/v) N_2. The high dilution level is selected to avoid considerable temperature gradients. Assume a plug flow reactor with a length of 43 cm and a diameter of 8 mm. For residence times of 13 s, determine what is the minimum operating temperature to obtain >80% of methane conversion.

Exercise 2 – Isothermal Plug Flow Reactor *(Results)*

The minimum operating temperature ensuring the desired conversion is slighlty less than 805 K.

On the right, there is a plot of the reactant and of the produced CO_x for the reaction at 805 K as a function of the residence time.





Exercise 3 – Surface reactor

Diamond film chemical vapor deposition (CVD) is typically carried out using a methane feedstock diluted in hydrogen. The homogeneous gas-phase reactivity is activated by a metallic hot filament. The substrate is mono-hydrogenated. When a site releases the H, the main growth precursor, CH_3, can adsorb.

Assuming that only H and CH_3 are adsorbed, and that surface H are released only through abstraction, a simple detailed mechanism for diamond growth is:

$C_{,site} + H \rightarrow CH_{,site}$

$C_{,site} + CH_3 \rightarrow D + CH_{3,site}$

$CH_{3,site} + H \rightarrow CH_{2,site} + H_2$

$CH_{2,site} + H \rightarrow CH_{,site} + H_2$

$CH_{,site} + H \rightarrow C_{,site} + H_2$

Assume that the adsorbed C atom does not undergo desorption.

Exercise 3 – Surface reactor

Complete the *surface.kin* file using the following Arrhenius parameters for the different classes of reaction involved in the process.

$A = 1.0\text{E}14 \exp\left(-\frac{7300}{1.987\,T}\right)$ for the hydrogen abstractions

$A = 5\text{E}12\,T^{0.5}$ for H adsorption

$A = 1.0\text{E}11\,T^{0.5}$ for CH_3 adsorption

Simulate a 24h cycle of diamond film CVD in a mixture of 10% (v/v) of CH_4 in H_2, at 2500K and 160 torr. The reactor volume is 100 cm^3 and the substrate size is 10 cm^2.

Exercise 3 – Surface reactor *(Results)*

surface.kin

```
MATERIAL diamond-cvd

SITE/DIAMOND/   SDEN/5.22E-09/
   CH(S)      C(S,R)   CH3(S)
   CH2(S)
END

BULK
   D /3.515/
END

REACTIONS MWON

 CH(S)     + H         => C(S,R)  + H2                  1.0E14     0.0  7300.0

 C(S,R)    + H          => CH(S)                         5.E12   0.5     0.0

 C(S,R)  + CH3    => D      + CH3(S)     1.0E11  0.5  0.

 CH3(S) + H         => CH2(S)  + H2                 1.E14     0.0  7300.0

 CH2(S)  + H          => CH(S)  + H2                  1.E14     0.0  7300.0


END
```

Simulation results

Diamond mass = 1.170986e-07 kg

Surface fractions

CH(S) = 9.157414e-01

C(S,R) = 8.425864e-02

CH_3(S) = 2.555837e-42

CH_2(S) = 2.555837e-42

Gas Conversion (%) CH_4 = 100

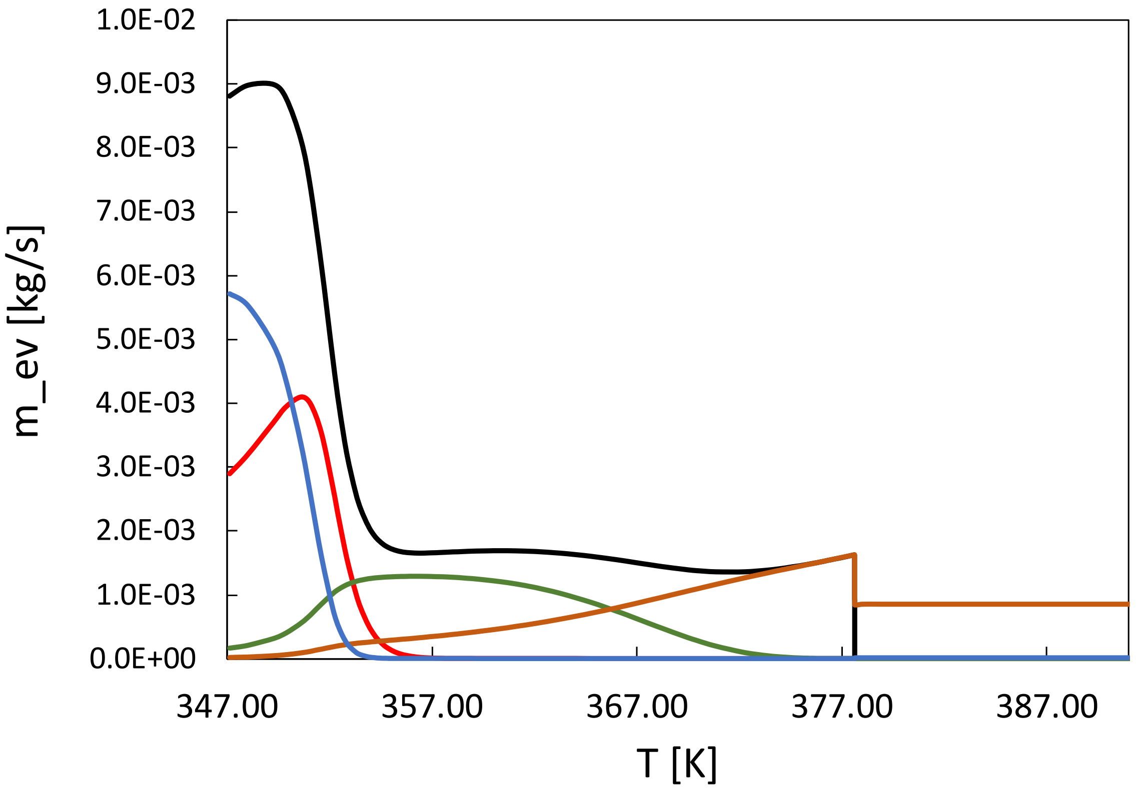
Gas Conversion (%) H_2 = -22.21

Exercise 4 – TGA

Thermogravimetric analysis is a common approach to characterize solid fuels (plastic waste, biomass, char etc.) by providing information on weight loss dynamics at well controlled conditions.

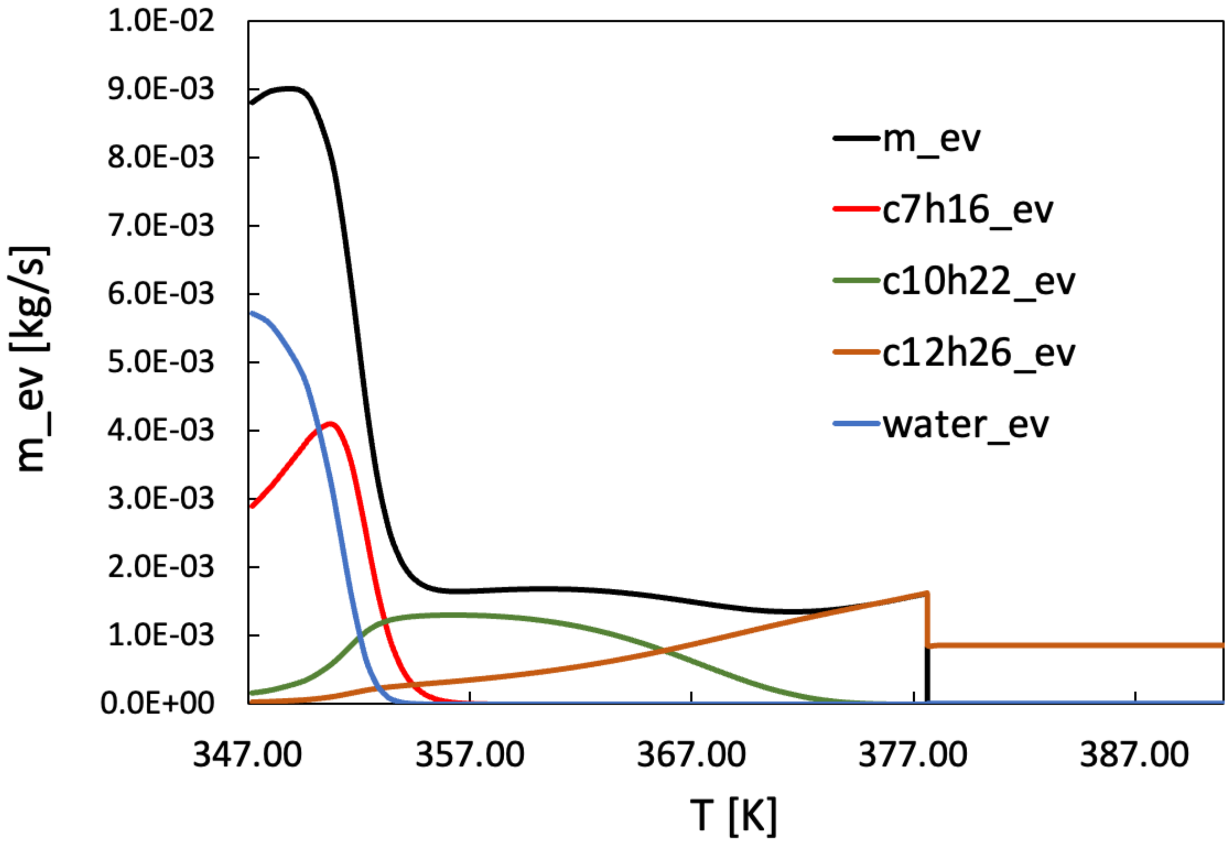
The TGA curves for an equimolar mixture of n-heptane, n-decane, n-dodecane, and water are reported below.

How does TGA curves change when an equimolar mixture containing only the heaviest and the lightest components (equal parts) is used? TGA conditions are: length 10 min, temperature linearly increasing from 347.15K to 297.15K , atmosphere of nitrogen at room temperature and atmospheric pressure.

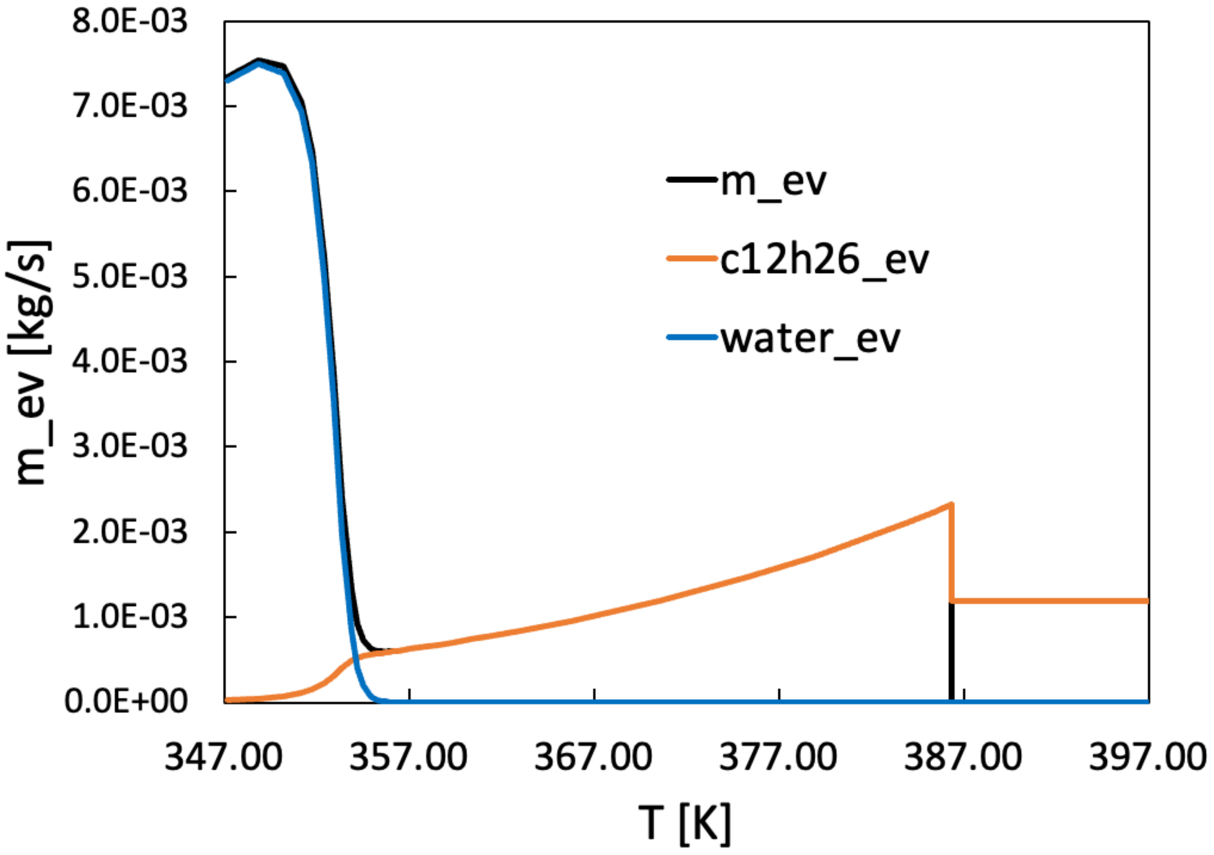


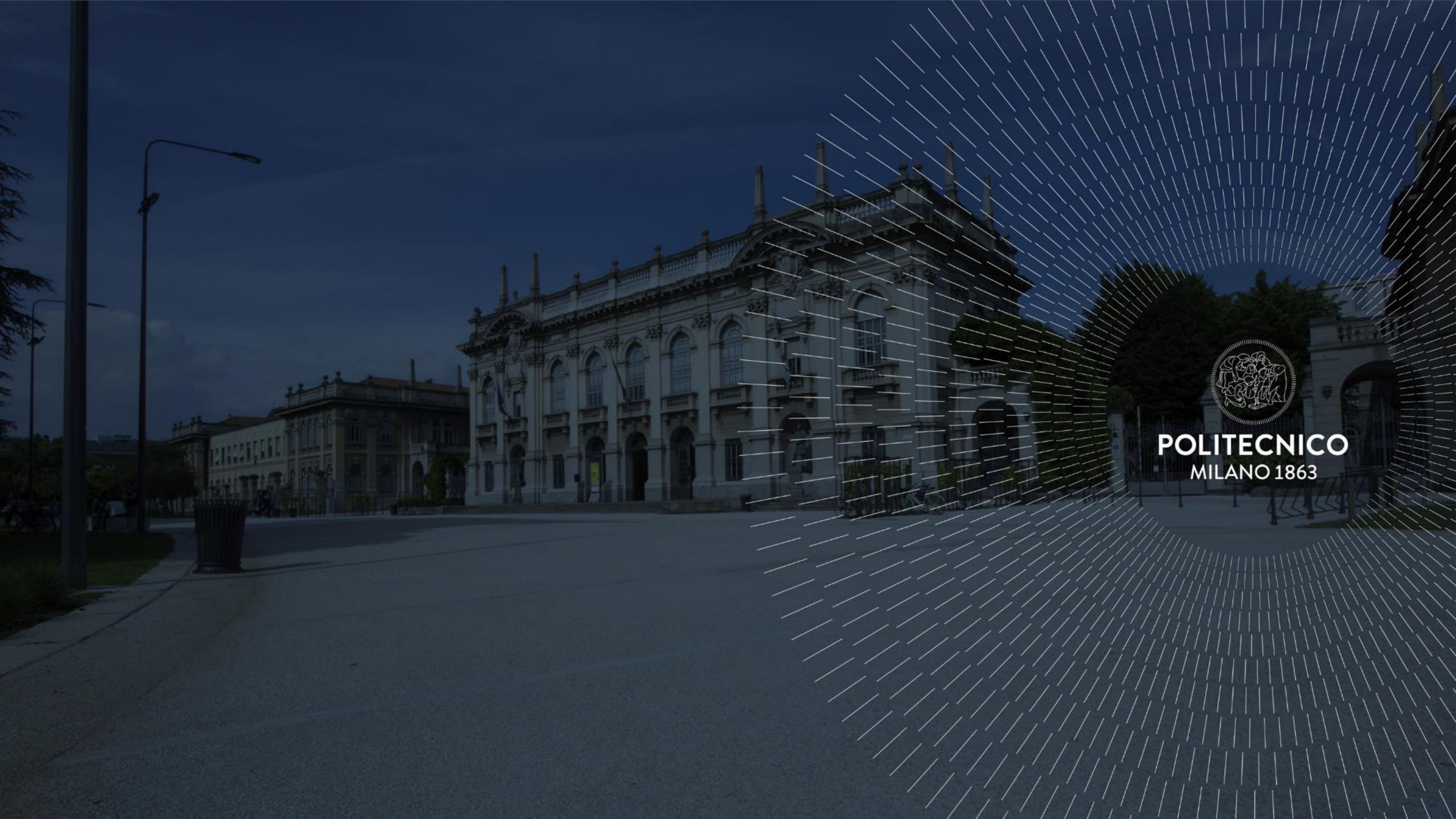
Exercise 4 – TGA *(Results)*

Case 1



Case 2

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