

## 1<sup>st</sup> assignment: Flame temperature analysis and NO<sub>x</sub> emissions for different fuels and combustion conditions

**Guidelines:** Deliver excel or matlab or python or etc calculations + deliver a 5-10 page report with main results in figures for each Question and main conclusions (pdf file). By e-mail to [camsilva@fc.ul.pt](mailto:camsilva@fc.ul.pt).

**Concepts:** Adiabatic flame temperature, theoretical air, EGR percent, Diesel and Otto engine technologies of combustion

### Problem Motivation:

For a combustion process that takes place with no heat loss to the surrounding, the temperature of the products is referred to as the adiabatic flame temperature. It is found that with an increase in the adiabatic flame temperature, there is increase in NO<sub>x</sub> emissions from internal combustion engines. As we know, vehicles are a major source of air pollutants such as nitric oxides, hydrocarbons, carbon dioxide, etc., there is a growing shift in the fuels from the petroleum-based fuels such as gasoline and diesel fuel to the alternative fuels such as natural gas, ethanol, methanol, liquefied petroleum gas and hydrogen. So, in order to study NO<sub>x</sub> emissions, the change in adiabatic flame temperature values for conventional fuels in comparison to the alternative fuels with various equivalence ratios and various Exhaust Gas Recirculation (EGR) rates is studied in this module. Depending on how the process is completed, adiabatic flame temperature can be of constant volume or constant pressure type.

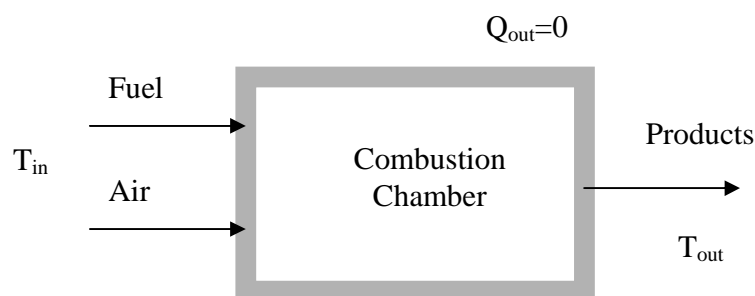
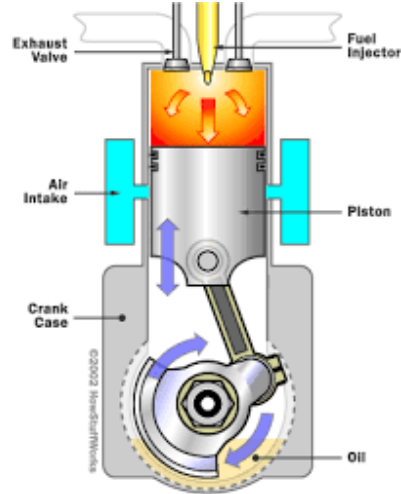
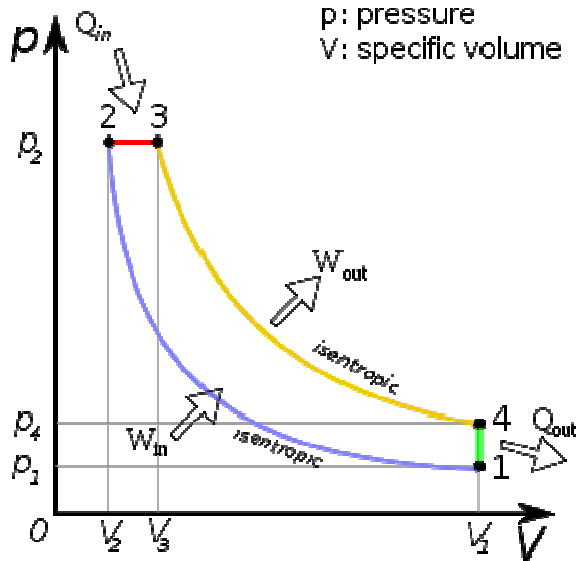
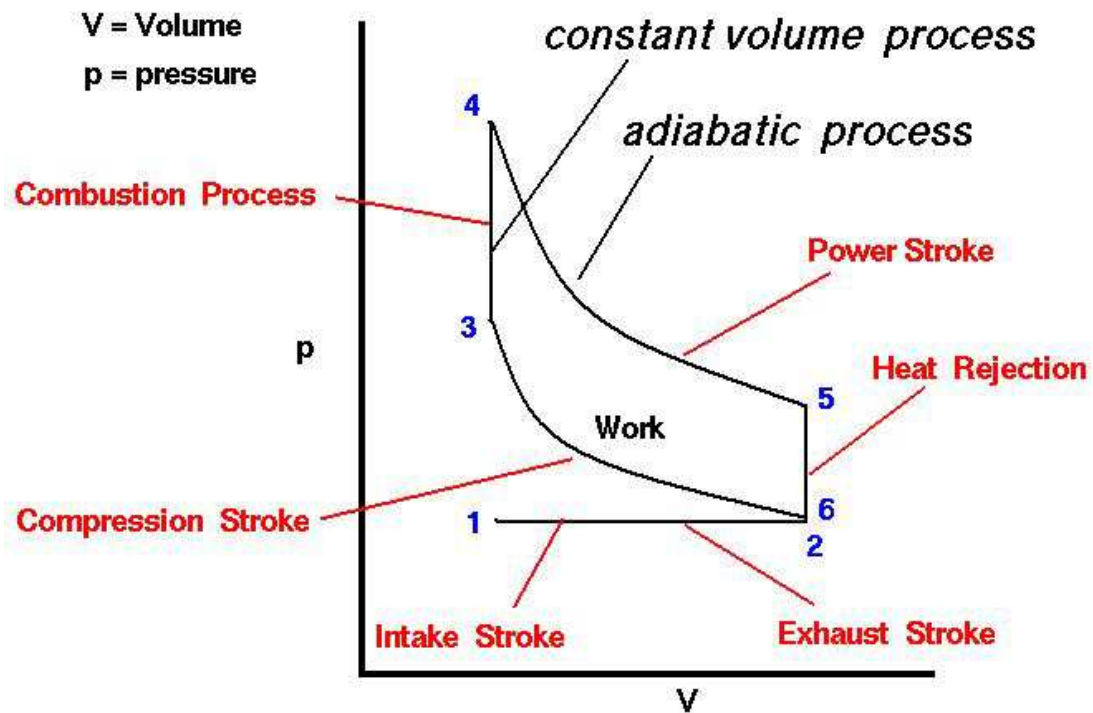


Figure 1 adiabatic combustion chamber, for adiabatic flame calculation [1]

Constant pressure combustion occurs for example in Diesel engines (see the P-v diagram), and constant volume combustion in gasoline engines (see P-v diagram).



Diesel theoretical P-v diagram  
 $Q_{in}$  from combustion 2-3



Gasoline theoretical P-v diagram  
 $Q_{in}$  from combustion 3-4

Exhaust Gas Recirculation (EGR)[2]:

Exhaust gas recirculation i.e. EGR decreases the adiabatic flame temperature and so the NO<sub>x</sub> emissions. It is the most effective technique used to reduce NO<sub>x</sub> emissions in internal combustion engines. As shown in figure 2, a fraction ( $x_1$ ) of the exhaust gases is re-circulated with the intake air into the engine. This is a technique commonly used in Diesel engines.

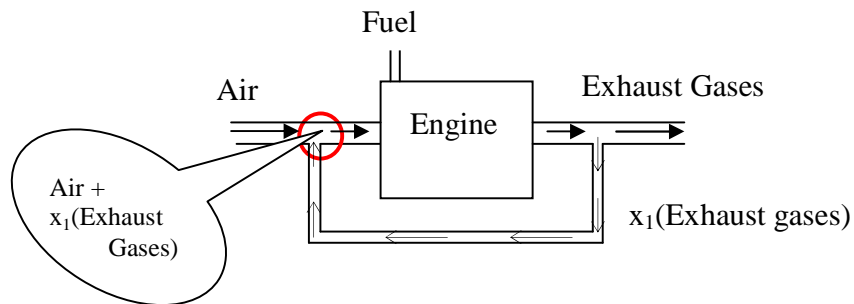
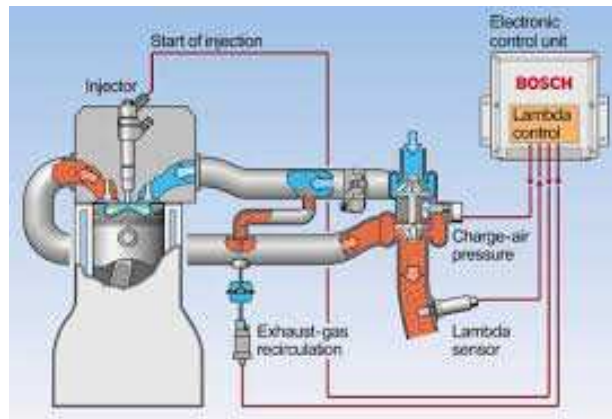


Figure 2: Exhaust Gas Re- circulation



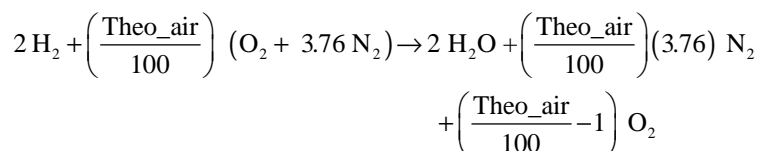
**Question # 1 (influence of different fuels, excess air, constant volume or constant pressure, dissociation and initial conditions on adiabatic flame temperature):**

- (a) Compute the adiabatic flame temperature of H<sub>2</sub>- air at constant pressure and at constant volume for 40%, 60%, 80%, 100%, 120%, 140%, 160%, 180%, 200% and 250% theoretical air (stoichiometric air). Consider that both the fuel and the air enter the combustion chamber at T<sub>in</sub> = 25 °C. Discuss the difference between the adiabatic flame temperature values at **constant pressure** and **constant volume** case as a function of lambda.
- (b) Compute the adiabatic flame temperature of gasoline- air, CH<sub>4</sub>-air and ethyl alcohol-air mixtures at **constant pressure** for 100%, 120%, 140%, 160%, 180%, 200% theoretical air. Obtain and compare a combined plot of adiabatic flame temperature vs Lambda for H<sub>2</sub>- air, CH<sub>4</sub>-air, gasoline- air and ethyl alcohol- air mixture.
- (c) Using **Cantera** [3]\*, free-open source combustion software, compute the adiabatic flame temperature and **equilibrium composition** of H<sub>2</sub>-air, CH<sub>4</sub>-air for 40, 60, 80, 100, 120, 140, 160, 180, 200 and 250 percent theoretical air. And different inlet premixed conditions: **T<sub>in</sub> ranging from 250 K to 350 K**. Mark the values you found on a) and b) for Lambda influence and compare against Cantera. Discuss the dissociation influence on adiabatic flame temperature.

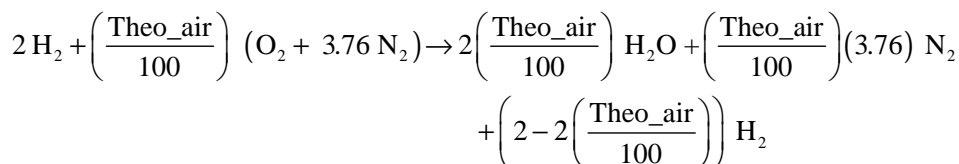
**Hints:**

- The combustion of hydrogen for two cases (i.e. for Lambda >= 1 or for Theo\_air/100 >= 100% and for lambda < 1 or for Theo\_air/100 < 100%) can be explained with the following combustion equations.

- 1) lambda >= 1 or for Theo\_air/100 >= 100%

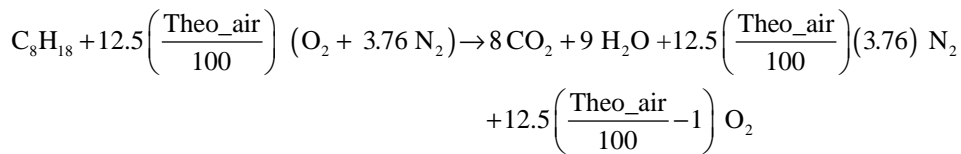


- 2) lambda < 1 or for Theo\_air/100 < 100%

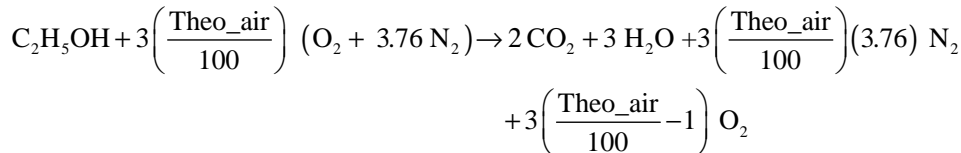


- The combustion of gasoline and ethyl alcohol for lambda >= 1 or for Theo\_air/100 >= 100% can be explained with the following combustion equations.

Gasoline



Ethyl Alcohol

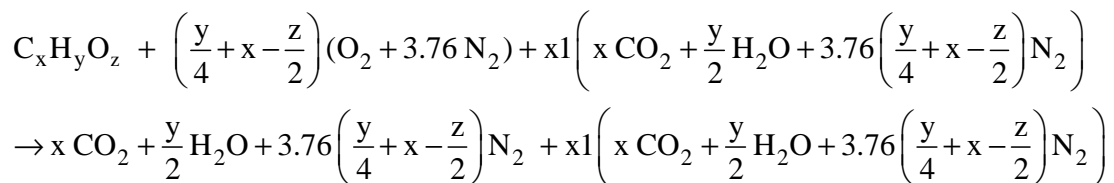


**Question # 2 (influence of different fuels, excess air, constant volume or constant pressure, dissociation and initial conditions on adiabatic flame temperature and NOx emisissions):**

- Compute the adiabatic flame temperature of the poor mixture (140% percent theoretical air) of diesel- air, and biodiesel- air at **constant volume** using 0, 5, 10, 15, 20, 25, 30% EGR percent. Assume that each fuel is burned with the stoichiometric amount of air in the combustion chamber. Obtain and compare a combined plot of adiabatic flame temperature vs EGR percent for diesel- air and biodiesel- air mixture. Assume that the recirculation does not change the air feed temperature to the exhaust.
- Is it possible to do the same calculations assuming that the recirculation change the air feed temperature to 350 K?. If so do-it.
- What engine would you guess to have higher NOx emissions? Gasoline engine working at stoichiometry (100% theoretical air) with no EGR or diesel engine working with excess air (140% theoretical air) and 20-30% EGR? Justify.
- Biodiesel blend with diesel would increase NOx emissions or not? Discuss.

**Hints:**

- Generalized equation for combustion of fuel  $C_xH_yO_z$  including EGR is given by



- EGR (fraction) and the number of moles of the exhaust gas mixture to be recirculated per mole of fuel  $C_xH_yO_z$  (x1) are related to each other by an equation,

$$x1 = \frac{\text{EGR}}{1 - \text{EGR}}$$

Diesel chemical formula:  $C_{10.8}H_{18.7}$ ; Biodiesel from sunflower:  $C_nH_{2n}O_2$  (assume it is mainly composed by Linoleic acid, C18:2).

Ideal gas phase thermodynamic properties of species involved in surrogate fuels  
Linoleic acid, C18:2 (In [4])

Species	$\Delta_f H_{298K}$	$S_{298K}$	$C_p^*(T)$						
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
N <sub>2</sub>	0.00	45.77	6.95	7.01	7.08	7.19	7.50	7.83	8.32
CH <sub>4</sub>	-17.92	44.52	8.49	9.81	11.15	12.50	15.13	17.43	21.07
C <sub>2</sub> H <sub>6</sub>	-20.29	54.85	12.59	15.76	18.67	21.31	25.80	29.37	36.24
C <sub>3</sub> H <sub>8</sub>	-24.88	64.51	17.64	22.60	26.99	30.85	37.10	41.83	49.95
C <sub>4</sub> H <sub>10</sub>	-30.23	74.12	23.36	29.69	35.31	40.25	48.24	54.24	64.51
n-C <sub>7</sub> H <sub>16</sub>	-44.96	102.01	39.81	50.57	60.02	68.25	81.49	91.28	105.73
n-C <sub>10</sub> H <sub>22</sub>	-59.81	129.96	56.05	71.35	84.71	96.29	114.75	128.16	149.00
n-C <sub>14</sub> H <sub>30</sub>	-79.62	167.35	77.94	99.18	117.69	133.68	159.11	177.51	205.99
n-C <sub>16</sub> H <sub>34</sub>	-89.49	186.10	88.88	113.06	134.14	152.35	181.27	202.13	234.41
MCYH	-36.05	81.00	32.43	44.53	55.09	64.21	78.62	88.83	103.11
PCYH	-45.40	99.73	43.36	58.44	71.56	82.89	100.78	113.48	131.56
BCYH	-50.35	109.07	48.86	65.38	79.80	92.25	111.89	125.81	145.82
Toluene	11.95	78.45	24.89	33.31	40.62	46.79	55.96	62.36	71.38
PBZ	1.91	95.61	36.28	47.53	57.18	65.38	78.03	86.74	99.77
BBZ	-3.38	104.76	42.07	54.85	65.81	75.13	89.50	99.43	114.54
OBZ	-22.83	142.37	63.65	82.30	98.39	112.12	133.48	148.40	170.97
NP	35.91	82.35	31.99	42.94	52.06	59.58	70.73	78.26	93.19
MNP	28.24	92.58	37.14	49.34	59.65	68.27	81.32	90.25	105.91
BNP	13.13	119.41	54.44	70.57	84.59	96.59	114.95	126.67	133.62
C <sub>14</sub> :0	-157.81	192.42	87.49	109.90	129.63	146.74	173.56	191.28	201.94
C <sub>15</sub> :0	-167.70	211.13	98.44	123.81	146.10	165.43	195.74	215.94	230.42
C <sub>16</sub> :0	-177.60	229.85	109.37	137.73	162.59	184.12	217.90	240.60	258.92
C <sub>18</sub> :1	-149.48	226.47	104.94	132.69	157.02	178.07	210.95	232.85	249.88
C <sub>18</sub> :2	-120.84	224.25	101.97	128.98	152.66	173.14	205.10	226.31	241.97
C <sub>18</sub> :3	-92.20	222.02	99.00	125.28	148.30	168.20	199.25	219.78	234.02
C <sub>20</sub> :0	-187.49	248.56	120.34	151.59	179.04	202.82	240.10	265.22	287.41
C <sub>20</sub> :1	-159.38	245.18	115.87	146.60	173.50	196.75	233.12	257.52	278.38
C <sub>22</sub> :0	-197.38	267.27	131.27	165.52	195.53	221.50	262.26	289.90	315.91
C <sub>22</sub> :1	-169.27	263.90	126.82	160.51	189.98	215.44	255.29	282.17	306.87

$\Delta_f H_{298K}$  is expressed in kcal mol<sup>-1</sup> and  $S_{298K}$  and  $C_p^*(T)$  are given in cal mol<sup>-1</sup> K<sup>-1</sup>.

Table H.2 Curve-Fit Coefficients for Fuel Specific Heat and Enthalpy<sup>a</sup> for Reference State of Zero Enthalpy of the Elements at 298.15 K and 1 atm:

$$\bar{c}_p \text{ (kJ/kmol} \cdot \text{K)} = 4.184(a_1 + a_2\theta + a_3\theta^2 + a_4\theta^3 + a_5\theta^{-2}),$$

$$\bar{h}^\circ \text{ (kJ/kmol)} = 4184(a_1\theta + a_2\theta^2/2 + a_3\theta^3/3 + a_4\theta^4/4 - a_5\theta^{-1} + a_6),$$

where  $\theta \equiv T \text{ (K)}/1000$

Formula	Fuel	Molecular Weight	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	$a_8^*$
CH <sub>4</sub>	Methane	16.043	-0.29149	26.327	-10.610	1.5656	0.16573	-18.331	4.300
C <sub>3</sub> H <sub>8</sub>	Propane	44.096	-1.4867	74.339	-39.065	8.0543	0.01219	-27.313	8.852
C <sub>6</sub> H <sub>14</sub>	Hexane	86.177	-20.777	210.48	-164.125	52.832	0.56635	-39.836	15.611
C <sub>8</sub> H <sub>18</sub>	Isooctane	114.230	-0.55313	181.62	-97.787	20.402	-0.03095	-60.751	20.232
CH <sub>3</sub> OH	Methanol	32.040	-2.7059	44.168	-27.501	7.2193	0.20299	-48.288	5.3375
C <sub>2</sub> H <sub>5</sub> OH	Ethanol	46.07	6.990	39.741	-11.926	0	0	-60.214	7.6135
C <sub>8,26</sub> H <sub>15,5</sub>	Gasoline	114.8	-24.078	256.63	-201.68	64.750	0.5808	-27.562	17.792
C <sub>7,76</sub> H <sub>13,1</sub>		106.4	-22.501	227.99	-177.26	56.048	0.4845	-17.578	15.232
C <sub>10,8</sub> H <sub>18,7</sub>	Diesel	148.6	-9.1063	246.97	-143.74	32.329	0.0518	-50.128	23.514

<sup>a</sup>To obtain 0 K reference state for enthalpy, add  $a_8$  to  $a_6$ .

<sup>4</sup>Source: From Heywood, J. B., *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York, 1988, by permission of McGraw-Hill, Inc.

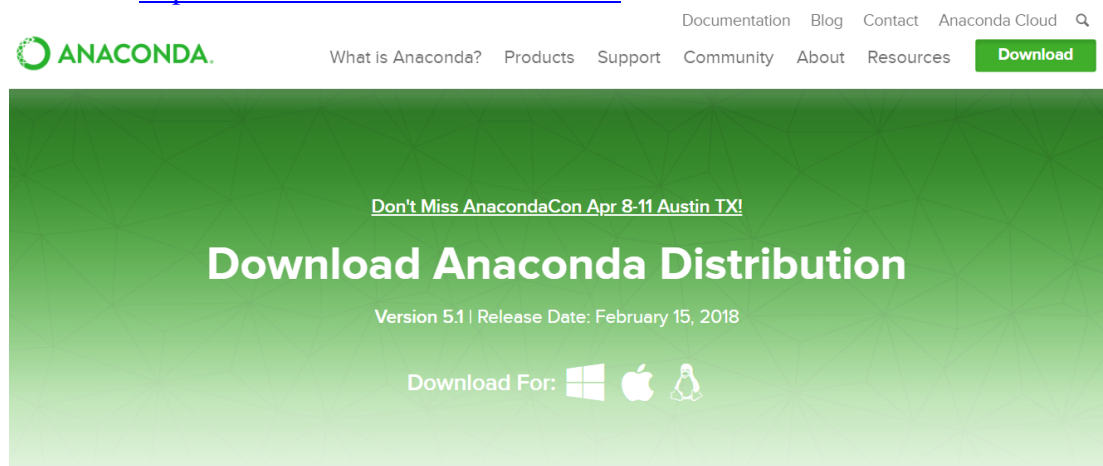
## References

- [1] Turns SR. An introduction to combustion: concepts and applications. System 2000;499:411. doi:10.1016/j.ijhydene.2008.07.121.
- [2] Heywood JB. Internal Combustion Engine Fundamentals. vol. 21. 1988.
- [3] Goodwin DG, Moffat HK, Speth RL. Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. Http://www.cantera.org 2017. doi:10.5281/zenodo.170284.
- [4] Glaude PA, Fournet R, Bounaceur R, Molière M. Adiabatic flame temperature from biofuels and fossil fuels and derived effect on NOx emissions. Fuel Process Technol 2010;91:229–35. doi:10.1016/j.fuproc.2009.10.002.

\* **Cantera freeware/open source** <http://www.cantera.org/docs/sphinx/html/index.html>

“**Anaconda** and **Miniconda** are Python distributions for which Cantera is available through the conda package manager. “

1<sup>st</sup> install: <https://www.anaconda.com/download/>



2<sup>nd</sup> **install pycharm** <https://www.jetbrains.com/pycharm/download/#section=windows>

3<sup>rd</sup> in pycharm set Conda **environment** “**combustion**”

4<sup>th</sup> Anaconda prompt:  
 activate combustion  
 conda install –c cantera cantera  
 conda install ipython matplotlib

5<sup>th</sup> copy example

[http://www.cantera.org/docs/sphinx/html/cython/examples/multiphase\\_adiabatic.html](http://www.cantera.org/docs/sphinx/html/cython/examples/multiphase_adiabatic.html)