

COMBUSTION AND EMISSION STUDY: MODELLING FUELS AND NO_x

POWERTRAIN AND SUSTAINABILITY

SUPERVISION

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1 INTRODUCTION

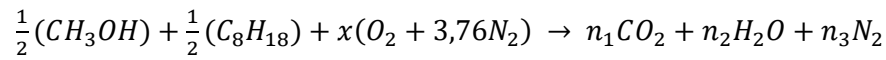
The following assessment was developed for the module of Powertrain and Sustainability of the third year – level 6 of the Motorcycle Engineering Degree.

The aim of the presented work is to demonstrate a comprehensive and thorough knowledge of the chemical process behind a combustion with different fuel blends.

An emissions model to allow the calculation of NO_x levels and the study of the effects of adding E.G.R. will be developed through theoretical methods lectured in classes and some other known models, e.g Zeldovich model.

Success will be measured by how accurate and cohesive the results are, allowing to study the chemical products of different fuel reactions and the emission levels of those reactions.

2 STUDY OF A BLEND MIXTURE WITH A MOLAR COMPOSITION OF 50% ISOCTANE AND 50% OF METHANOL

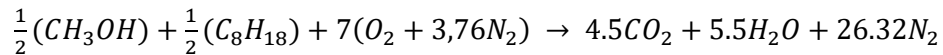


$$n_1 = \frac{1}{2} * 1 + \frac{1}{2} * 8 = 4.5$$

$$n_2 = \frac{1}{2} \left(\frac{1}{2} * 4 + \frac{1}{2} * 18 \right) = 5.5$$

$$x = \frac{1}{2} (4.5 * 2 + 5.5 * 1 - 0.5) = 7$$

$$n_3 = 7.25 * 3.76 = 27.26$$



2.1 Calculate the mass percentages of methanol and isooctane in this blend

Element	Atomic Mass Number
C	12
H	1
O	16
N	14

$$\text{Mass of } \frac{1}{2} \text{ kmol of methanol} = \frac{1}{2} (12 + 3 * 1 + 16 + 1) = 16 \text{ Kg}$$

$$\text{Mass of } \frac{1}{2} \text{ kmol of isooctane} = \frac{1}{2} (8 * 12 + 18 * 1) = 57 \text{ Kg}$$

$$\text{Percentage of methanol} = \frac{16}{(16 + 57)} * 100 = 21.92 \%$$

$$\text{Percentage of isooctane} = \frac{57}{(16 + 57)} * 100 = 78.08 \%$$

The results above mean that with a molar composition of 50% methanol and 50% isooctane, for each 1kg of methanol burned, 3.56kg (57/16*1) of isooctane are also burned.

2.2 Calculation of the Air/Fuel mass ratio for stoichiometric combustion in air

$$\text{AFR by mass} = \frac{\text{Air mass}}{\text{Fuel mass}} = \frac{7 \cdot (2 \cdot 16 + 3.76 \cdot 2 \cdot 14)}{1/2 \cdot ((12 + 3 + 16 + 1) + (8 \cdot 12 + 18 \cdot 1))} = 13.16$$

The Air/Fuel Ratio (AFR) by mass, ratio of the air mass to the fuel mass of the blend being analysed is 13.16. For comparison reasons, AFR from different fuels are presented below:

- AFR by mass Isooctane = 15.05;
- AFR by mass Methanol = 6.435;
- AFR by mass Diesel = 14.94;

2.3 Calculation of the lower heating value of the blend in MJ/kg (from the enthalpy of formations of the fuel blend and products)

For constant pressure (P):

$$dH = dU + PdV = dQ$$

The heat going in or out of the reaction is equal to change in the enthalpy value.

Substance	Combustion Reaction	Enthalpy of Combustion $\Delta H_c^\circ \left(\frac{\text{kJ}}{\text{mol}} \text{ at } 25^\circ\text{C} \right)$
carbon	$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$	-393.5
hydrogen	$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$	-285.8
magnesium	$\text{Mg}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{MgO}(s)$	-601.6
sulfur	$\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$	-296.8
carbon monoxide	$\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$	-283.0
methane	$\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$	-890.8
acetylene	$\text{C}_2\text{H}_2(g) + \frac{5}{2}\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(l)$	-1301.1
ethanol	$\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 3\text{H}_2\text{O}(l)$	-1366.8
methanol	$\text{CH}_3\text{OH}(l) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$	-726.1
isooctane	$\text{C}_8\text{H}_{18}(l) + \frac{25}{2}\text{O}_2(g) \longrightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l)$	-5461

Table 1. Examples of Enthalpies of Combustion

From the table above, Table 1, for our fuel blend, it is shown that the Δh_f^0 for iso-octane and methanol is:

- $\Delta h_f^0 \text{ isooctane} = -259.2 \text{ kJ/mol (or MJ/kmol)}$
- $\Delta h_f^0 \text{ methanol} = -201.5 \text{ kJ/mol (or MJ/kmol)}$

Formula	Fuel	M (kg/kmol)	T _b (°C)	c _{pg} ^a (kJ/kg·K)	T _{ig} (°C)	HHV (MJ/kg)	LHV (MJ/kg)	h _{fg} ^b (kJ/kg)	AFRs	T _f (K) ^c	Δh _f ⁰ (kJ/mol)	RON ^d	MON ^e
CH ₄	Methane	16.04	-161	2.21	537	55.536	50.048	510	17.2	2,226	-74.4	120	120
C ₂ H ₂	Acetylene	26.04	-84	1.60	305	49.923	48.225	—	13.2	2,540	8.7	50	50
C ₂ H ₄	Ethylene	28.05	-104	1.54	490	50.312	47.132	—	14.7	2,380	52.4	—	—
C ₂ H ₆	Ethane	30.07	-89	1.75	472	51.902	47.611	489	16.1	2,370	-83.8	115	99
C ₃ H ₈	Propane	44.10	-42	1.62	470	50.322	46.330	432	15.7	2,334	-104.7	112	97
C ₄ H ₁₀	n-Butane	58.12	-0.5	1.64	365	49.511	45.725	386	15.5	2,270	-146.6	94	90
C ₄ H ₁₀	iso-Butane	58.12	-12	1.62	460	49.363	45.577	366	15.5	2,310	-153.5	102	98
C ₅ H ₁₂	n-Pentane	72.15	36	1.62	284	49.003	45.343	357	15.3	2,270	-173.5	62	63
C ₅ H ₁₂	iso-Pentane	72.15	28	1.60	420	48.909	45.249	342	15.3	2,310	-178.5	93	90
C ₆ H ₁₄	n-Hexane	86.18	69	1.62	233	48.674	45.099	335	15.2	2,271	-198.7	25	26
C ₆ H ₁₄	iso-Hexane	86.18	50	1.58	421	48.454	44.879	305	15.2	2,300	-207.4	104	94
C ₇ H ₁₆	n-Heptane	100.20	99	1.61	215	48.438	44.925	317	15.2	2,273	-224.2	0	0
C ₈ H ₁₈	n-Octane	114.23	126	1.61	206	48.254	44.786	301	15.1	2,275	-250.1	20	17
C ₈ H ₁₈	iso-Octane	114.23	114	1.59	418	48.119	44.651	283	15.1	2,300	-259.2	100	100
C ₉ H ₂₀	n-Nonane	128.6	151	1.61	—	48.119	44.688	295	15.1	2,274	-274.7	—	—
C ₁₀ H ₂₂	n-Decane	142.28	174	1.61	210	48.002	44.599	277	15.1	2,278	-300.9	-41	-38
C ₁₀ H ₂₂	iso-Decane	142.28	171	1.61	—	48.565	44.413	—	15.1	2,340	—	113	92
C ₁₂ H ₂₆	n-Dodecane	170.33	216	1.61	204	47.838	44.574	256	15.0	2,276	-350.9	-88	-90
CH ₃ O	Methanol	32.04	65	1.37	385	22.663	19.915	1,099	6.5	2,183	-201.5	106	92
C ₂ H ₅ O	Ethanol	46.07	78	1.42	365	29.668	26.803	836	9.0	2,144	-235.1	107	89
H ₂	Hydrogen	2.02	-253	14.47	400	141.72	119.96	451	34.3	2,345	0	—	—

^aGas phase specific heat evaluated at 25°C

^bHeat of vaporization at 1 atm

^cEstimated equilibrium flame temperature

^dResearch octane number

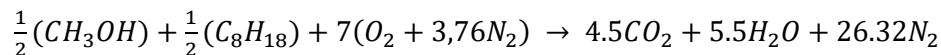
^eMotoring octane number

Table 2. Properties of Fuels

From Table 2:

- $\Delta h_f^0 \text{ CO}_2 = -393.5 \text{ kJ/mol}$;
- $\Delta h_f^0 \text{ H}_2\text{O (gas)} = -241.8 \text{ kJ/mol}$
- $\Delta h_f^0 \text{ H}_2\text{O (liquid)} = -285.8 \text{ kJ/mol}$

Because,



Enthalpy needed for products

$$= \frac{201.5}{2} + \frac{259.2}{2} + 7*(0+0) = 230.35 \text{ MJ}$$

Enthalpy released from reaction

$$= (4.5*393.5) + 5.5(241.8) + 26.32*0 = 3100.7 \text{ MJ}$$

The net enthalpy, resulting from the difference in energy used for the reaction to happen and the energy released from the products, is:

$$\Delta h_f^0 \text{ Net} = 3100.7 - 230.35 = 2870.3 \text{ MJ}$$

Burning the current fuel blend, 0.5 kmol of methanol and 0.5 kmol of isooctane at constant pressure releases 2870.3 MJ of heat energy (enthalpy).

From Chapter 2.1, it is known that the fuel blend mass is 73 kg.

$$\text{LHV} = 2870.3 / 73 = 39.32 \text{ MJ/kg}$$

Result: 1kg of the fuel blend that it has been analysed releases 39.32 MJ.

2.4 Enthalpy of formation

For constant pressure (P):

$$dH = dU + PdV = dQ$$

So, enthalpy of formation (Δh_f^0) is the enthalpy change for the formation of 1 mol of a certain compound resultant from its component elements.

The values of enthalpy are dependent on the pressure of the gas elements, the temperature of the reaction and the physical states (gas, liquid, solid) of the reactants and the products.

2.5 Higher and Lower heating values

The 'Lower Heating Value'(LHV) is the term used when H₂O is a gas and the 'Higher heating Value' (HHV) is used when H₂O is a liquid.

When the H₂O in the products is a liquid, we get:

$$(4.5 \times 393.5) + (5.5 \times 285.8) + (26.32 \times 0) = 3342.7 \text{ MJ}$$

$$\Delta h_f^0 \text{ Net (H}_2\text{O liquid)} = 3342.7 - 230.35 = 3112.4 \text{ MJ}$$

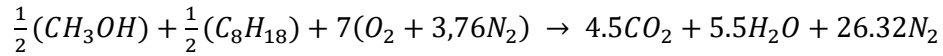
$$\text{HHV} = 3112.4 / 73 = 42.6 \text{ MJ/kg}$$

Comparing with the Lower heating value:

$$\text{LHV} = 39.32 \text{ MJ/kg}$$

$$\text{HHV} = 42.6 \text{ MJ/kg}$$

2.6 Calculation of the mass of CO₂ produced per kg of fuel burned



Mass of CO₂ in the current blend = 4.5 * (12+2*16) = 216 kg of CO₂

$$\frac{\text{Mass of } CO_2}{\text{Mass of fuel}} = \frac{216}{(16 + 57)} = 2.96$$

So, for each kg of fuel burned, 2.96 kg of CO₂ are produced.

2.7 Properties of an “Ideal” Fuel

Many different properties need to be judged and compared before deciding about an “Ideal” fuel. Ideally the best fuel would:

- Have a high Lower Heating Value to release the most amount of energy per 1kg;
- Have a high-density value to allow more liters in the same tank volume or to have a smaller tank;
- Burn at a lower temperature and produce the less amount of emissions possible, reducing CO₂ and NO_x emissions.

Emissions comparison per kg of fuel:

Diesel = 3.1Kg of CO₂

Gasoline = 3.09Kg of CO₂

Methanol = 1.375Kg of CO₂

Current blend = 2.96Kg of CO₂

Lower Heating Value comparison:

LHV isooctane = 44.4 MJ/kg

LHV methanol = 21.12 MJ/kg

LHV *current blend* = 39.32 MJ/kg

3 NOX MODEL FOR ISOCTANE RUNNING ON THE LEAN SIDE OF STOCHOMETRIC

3.1 Emissions model developed

The author developed a Matlab program able to calculate adiabatic flame temperatures, then the rise in temperature in the burned gas up to peak pressure and use the 'Zeldovich model' to obtain the NOx values.

The program developed has a main script, "Main_Menu.m", and other functions that interact with the main script to present the results expected. The function "flame_temperature.m" outputs the flame temperature for the different equivalence ratios. The function "zeldovich.m" outputs a cell array with vectors with the burned zone temperature and the NOx levels (kmols/m³) for each equivalence ratio throughout the beginning of combustion until peak power and a vector "Z_sum" with the NOx PPM per each equivalence ratio. The function "egr.m" outputs the NOx PPM at the equivalence ratio of 0.97 by adding EGR in different percentages.

By running "Main_Menu", the following menu is presented:

```
=====
COMBUSTION AND EMISSION STUDY: MODELLING FUELS AND NOX
1 - NOx Model for Isooctane running on the lean side of stoichometric
2 - The effect of adding E.G.R. on NOx PPM levels, for Fuel Equivalence Ratio = 0.97
0 - Close the program
=====
Choose an option: |
```

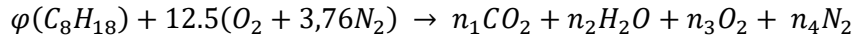
Figure 1. Menu from Matlab program

3.2 NOx PPM as a function of equivalence ratio

3.2.1 Methodology

In this chapter it was proposed to plot a graph of NOx PPM as a function of equivalence ratio on the lean side of stoichiometric, from 0.6 to 1.0.

Calculation of mols of the reactants and products with an equivalence ratio on the lean side:



$$Net\ heat\ released = \varphi * net\ heat\ released(stoch)$$

Then, using the 'Fuels Database' (McAllister, 2011) and recurring to interpolation, it is possible to obtain the flame temperature as a result of knowing the net heat released.

The burned zone temperature for each equivalence ratio from the start of combustion to peak pressure was then achieved using:

$$\frac{T_2^n}{T_1^n} = \frac{P_2^{n-1}}{P_1^{n-1}}$$

With the burned zone temperature and applying the "Zeldovich model", with a specific variation of the formula (Merker), it was possible to calculate the rate of NOx production:

$$\frac{\partial[NO]}{\partial t} = 4.7 * 10^{13} * [N_2][O_2]^{\frac{1}{2}} * \exp\left(\frac{-67837}{T}\right) kmols * m^{3^{-1}}sec^{-1}$$

As it can be observed, the NOx production rate is dependent on the burned zone temperature (T) and the concentration of oxygen (O_2) and nitrogen (N_2) molecules.

Then, to get oxygen (O_2) and nitrogen (N_2) molecules:

$$[O_2] = \frac{n_3 * \alpha}{30 * 10^{-6}}$$

$$[N_2] = \frac{n_4 * \alpha}{30 * 10^{-6}}$$

Where,

$$\alpha = \frac{6.16 * 10^{-6}}{\varphi + 12.5(1 + 3.76)}$$

The Zeldovich model can now be applied and the NOx production per each fuel equivalence ratio can be calculated.

$$\frac{\partial[NO]}{\partial t} = 4.7 * 10^{13} * [N_2][O_2]^{\frac{1}{2}} * \exp\left(\frac{-67837}{T}\right) \text{ kmols} * \text{m}^3\text{-}^1\text{sec}^{-1}$$

$$\frac{4.7 * 10^{13} * [N_2][O_2]^{\frac{1}{2}} * \exp\left(\frac{-67837}{T}\right)}{RPS} * (\text{comb chamber vol}) = \frac{\text{kmols}}{\text{g}}$$

And then, the sum of NOx from the start of combustion (soc) to peak pressure (eoc) gives the total NOx per cycle:

$$\sum_{soc}^{eoc} \left(\frac{4.7 * 10^{13} * [N_2][O_2]^{\frac{1}{2}} * \exp\left(\frac{-67837}{T}\right)}{RPS} * (\text{comb chamber vol}) \right) = \text{kmols/cycle}$$

In PPM:

$$PPM = \frac{NOx \text{ kmols/cycle}}{\text{total exhaust kmols}} * 10^6$$

Where,

$$\text{Total exhaust kmols} = \alpha (n_1 + n_2 + n_3 + n_4)$$

3.2.2 Results

Choosing option “1” of the “Main_Menu” the following information and results are presented:

Equiv Ratio	Enthalpy	CO2	H2O	O2	N2	[O2]	[N2]	alpha	Flame Temp
1.00	5065.000	8.000	9.000	0.000	47	0.00000	0.12756	1.0856e-07	2390.7
0.99	5014.350	7.920	8.910	0.125	47	0.00034	0.12758	1.0858e-07	2374.8
0.98	4963.700	7.840	8.820	0.250	47	0.00068	0.12761	1.0860e-07	2359.0
0.97	4913.050	7.760	8.730	0.375	47	0.00102	0.12763	1.0862e-07	2343.1
0.96	4862.400	7.680	8.640	0.500	47	0.00136	0.12765	1.0864e-07	2327.1
0.95	4811.750	7.600	8.550	0.625	47	0.00170	0.12767	1.0865e-07	2311.1
0.94	4761.100	7.520	8.460	0.750	47	0.00204	0.12769	1.0867e-07	2295.1
0.93	4710.450	7.440	8.370	0.875	47	0.00238	0.12771	1.0869e-07	2278.9
0.92	4659.800	7.360	8.280	1.000	47	0.00272	0.12773	1.0871e-07	2262.6
0.91	4609.150	7.280	8.190	1.125	47	0.00306	0.12775	1.0873e-07	2246.3
0.90	4558.500	7.200	8.100	1.250	47	0.00340	0.12777	1.0874e-07	2229.8
0.90	4558.500	7.200	8.100	1.250	47	0.00340	0.12777	1.0874e-07	2229.8
0.85	4305.250	6.800	7.650	1.875	47	0.00510	0.12788	1.0883e-07	2146.8
0.80	4052.000	6.400	7.200	2.500	47	0.00681	0.12799	1.0892e-07	2061.6
0.75	3798.750	6.000	6.750	3.125	47	0.00852	0.12809	1.0901e-07	1974.5
0.70	3545.500	5.600	6.300	3.750	47	0.01023	0.12820	1.0911e-07	1885.3
0.65	3292.250	5.200	5.850	4.375	47	0.01194	0.12831	1.0920e-07	1793.8
0.60	3039.000	4.800	5.400	5.000	47	0.01366	0.12841	1.0929e-07	1700.0

Table 3. Data from isooctane running on the lean side of stoichiometric

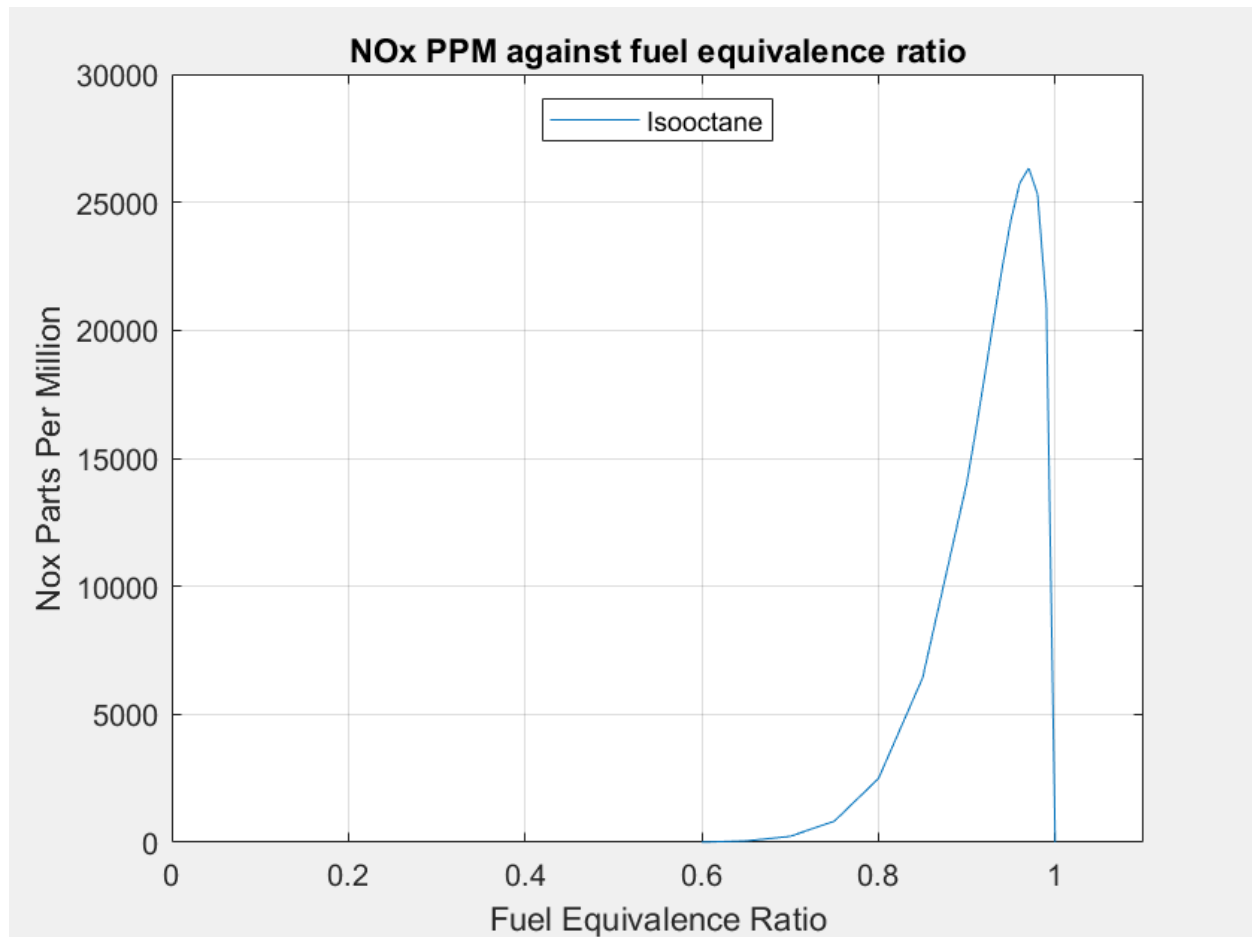


Figure 2. NOx PPM vs Fuel Equivalence Ratio

Analysing *Figure 2. NOx PPM vs Fuel Equivalence Ratio*, it is possible to observe an exponential increase of NOx production until it reaches its peak at $\phi=0.97$.

Despite the concentrations of N₂ and O₂ reduction for the highest values of fuel equivalence, the drastic increase in flame temperature and combustion temperatures means that the molecules will dissociate easily, leading to higher NOx production.

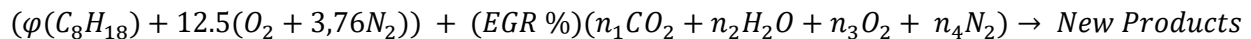
3.3 Effect of adding E.G.R. on NOx PPM levels for $\Phi = 0.97$

3.3.1 Methodology

For this chapter, it was proposed, for $\Phi = 0.97$, to calculate the effect of adding E.G.R. on NOx PPM levels assuming the same volumetric efficiency of 40% and assuming EGR levels up to 20% of the air + fuel contents.

The EGR valve (exhaust gas recirculation) is used to recirculate already burned gas back into the cylinder, where they will be burned again in the next cycle. This process will add an extra mass into the cylinder, causing the burn zone temperature to decrease, and, consequently reducing the NOx production levels.

This process will require a recalculation of the balance isooctane chemical equation, meaning that adding a percentage of EGR back into the cylinder will result in the following equation:



After the rearranged balance isooctane chemical equation, it is possible to calculate the NOx production for this new scenario, repeating the procedure already explained in chapter 3.2.1, *NOx production as a function of equivalence ratio – Methodology*.

3.3.2 Results

By choosing option “2” of the “Main_Menu”, the following results are presented:

```
EGR levels = 5%:  
NOx reduction of -56.80%, from 26331.335PPM to 11374.342PPM!  
  
EGR levels = 10%:  
NOx reduction of -82.60%, from 26331.335PPM to 4580.995PPM!  
  
EGR levels = 15%:  
NOx reduction of -92.88%, from 26331.335PPM to 1875.860PPM!  
  
EGR levels = 20%:  
NOx reduction of -97.05%, from 26331.335PPM to 776.966PPM!
```

Figure 3. Effect of EGR on NOx PPM levels

As it can be observed from Figure3, at a fuel equivalence ratio = 0.97, where the NOx levels production is at its highest, the slightest percentage of exhaust gas recirculation (EGR), e.g 5%, represents a reduction of 56.80% in the NOx PPM levels. Increasing the EGR percentage until 20% reduces the NOx emissions almost until zero (97% reduction).

4 REFERENCES

McAllister, S. (2011). *Fundamentals of Combustion Processes*. Springer Science+Business Media.

Merker, G. P. (s.d.). *Simulation Combustion*.