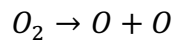


The Zeldovich Model

Dr Owen Williams – University of Wales TSD:

Oxides of nitrogen are produced during lean combustion as a result of dissociated molecules forming less stable radicals which then react with other radicals forming new molecules. At high burn zone temperatures of above 2500K nitrogen and oxygen molecules split easily into radical atoms:



The hotter the burn zone temperature, the more probable it is for molecules to break up.

The *Zeldovich mechanism* describes the formation of NO due to the dissociation of nitrogen and oxygen molecules, given by the below equations.



The first reaction in this pair is slow and hence, rate limiting; while the second is extremely fast. This means that the first equation is key in the rate of the reaction and is hence used to determine the overall reaction rates.

The model assumes that for each degree of rise in temperature and subsequent dissociation, there is enough time for equilibrium to be reached between the concentration of reactant molecules and the concentration of radicals produced.

Increased concentrations of nitrogen or oxygen molecules increases the probability of reactions happening between them; thus, the rate of NOx production is proportional to the concentrations of both nitrogen and oxygen.

Since the oxygen molecules are in equilibrium with the oxygen atoms, the concentration of oxygen atoms is proportional to the concentration of oxygen molecules:

$$[O][O] \propto [O_2]$$

$$[O] \propto \sqrt{[O_2]}$$

$$\therefore [O] \propto [O_2]^{\frac{1}{2}}$$

$$\frac{\partial[NO]}{\partial t} \propto [N_2][O_2]^{\frac{1}{2}}$$

Rate of NOx production also depends on what is known as the Arrhenius function, given by k , which calculates the temperature dependent reaction rate. It describes the proportion of molecules with enough energy to cause a reaction.

The hotter the flame temperature, the greater proportion of molecules which exceed the necessary activation energy for a reaction. The equation is given by:

$$k = Z_{AB} \exp\left(\frac{-E_A}{R_u T}\right)$$

E_A is the required energy for a reaction, with R and T being the universal gas constant and burn zone temperature respectively. Z_{AB} is known as the gas kinetic collision rate; how frequently the atoms collide to cause a reaction. Kinetic theory dictates:

$$Z_{AB} = [A][B] \sigma_{AB}^2 \left(\frac{8\pi k_B T}{\mu}\right)^{\frac{1}{2}}$$

Where σ_{AB} is the reaction cross-section, k_B is Boltzman's constant, and μ is the reduced mass of the reactants. This can be rearranged and simplified into:

$$Z_{AB} = Z'_{AB} [A][B]$$

$$Z'_{AB} = \sigma_{AB}^2 \left(\frac{8\pi k_B T}{\mu}\right)^{\frac{1}{2}}$$

In this case Z'_{AB} is assumed to be a constant $4.7 \cdot 10^{13}$, therefore this can all be combined to give an overall equation for NOx reaction rate:

$$\frac{\partial[NO]}{\partial t} = 4.7 \cdot 10^{13} * [N_2][O] \cdot \exp\left(\frac{-E_A}{RT}\right)$$

The Arrhenius form of the Zeldovich model is written as:

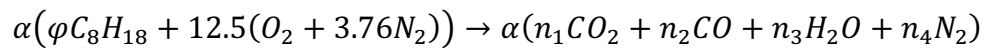
$$\frac{\partial[NO]}{\partial t} = 4.7 \cdot 10^{13} * [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-E_A}{RT}\right) \text{ kmols/m}^3/\text{sec}$$

There are a number of variations on the values to be used, based on different measured and assumed 'rate constants'. For the purposes of our work we shall use the version described by Günter P. Merker in the book 'Simulating Combustion'.

$$\frac{\partial[NO]}{\partial t} = 4.7 \cdot 10^{13} * [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-67,837}{T}\right)$$

This equation can, however, only be seen as a crude estimation, as it predicts an excessively high NO concentration due to the fact that the reverse reactions slow down the actual NO production.

Prior to calculating rate of NOx production using the Zeldovich model, you must first determine the concentrations of nitrogen and oxygen in combustion. This requires the introduction of a new variable, alpha (α), representing the actual number of kmols in the mixture. Multiplying the previous balanced chemical equation by alpha gives the correct number of kmols for one cycle of combustion.



For a 1.2L naturally-aspirated four-cylinder engine, each cylinder must have a displacement of 300cc. The volumetric efficiency at part load can be assumed to be 50%, thus enabling the calculation of the number of kmols of mixture drawn into the cylinder, n, by using the ideal gas law.

$$PV = nRT$$

It is assumed that the mixture drawn into the cylinder is at 1 Bar atmospheric pressure and at 20°C. Thus the number of kmols of mixture drawn in per cycle:

$$n = \frac{PV}{RT}$$

$$\therefore n = \frac{10^5 \times (300 \times 0.5) \cdot 10^{-6}}{8314 \times 293}$$

$$n = 6.16 \cdot 10^{-6} \text{ kmols}$$

From the balanced chemical equation, it is known that the intake of combustion mixture is made up of components of fuel and air, thus using the value just calculated for the number of kmols drawn in:

$$\alpha(\varphi C_8H_{18} + 12.5(O_2 + 3.76N_2)) = 6.16 \cdot 10^{-6} \text{ kmols}$$

$$\therefore \alpha(\varphi + 12.5(1 + 3.76)) = 6.16 \cdot 10^{-6} \text{ kmols}$$

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

Alpha changes with fuel equivalence ratio as at lower ratios there is less fuel in the mixture, thus changing the concentrations of oxygen and nitrogen.

Nitrogen and oxygen concentrations can now be calculated as their respective coefficients from the balanced chemical equation multiplied by alpha, and then divided by the combustion chamber volume. Assuming a combustion chamber volume of 30cc we get:

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

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

ϕ	Enthalpy	CO2	H2O	O2	N2	[O ₂]	[N ₂]	alpha	Flame Temp
1	5100.100	8.000	9.000	0.000	47	0.00000	0.12756	1.0856E-07	2404.2
0.99	5049.099	7.920	8.910	0.125	47	0.00034	0.12758	1.0858E-07	2388.3
0.98	4998.098	7.840	8.820	0.250	47	0.00068	0.12761	1.0860E-07	2372.4
0.97	4947.097	7.760	8.730	0.375	47	0.00102	0.12763	1.0862E-07	2356.5
0.96	4896.096	7.680	8.640	0.500	47	0.00136	0.12765	1.0864E-07	2340.4
0.95	4845.095	7.600	8.550	0.625	47	0.00170	0.12767	1.0865E-07	2324.3
0.94	4794.094	7.520	8.460	0.750	47	0.00204	0.12769	1.0867E-07	2308.1
0.93	4743.093	7.440	8.370	0.875	47	0.00238	0.12771	1.0869E-07	2291.9
0.92	4692.092	7.360	8.280	1.000	47	0.00272	0.12773	1.0871E-07	2275.5
0.91	4641.091	7.280	8.190	1.125	47	0.00306	0.12775	1.0873E-07	2259.1
0.9	4590.090	7.200	8.100	1.250	47	0.00340	0.12777	1.0874E-07	2242.6
0.85	4335.085	6.800	7.650	1.875	47	0.00510	0.12788	1.0883E-07	2159.1
0.8	4080.080	6.400	7.200	2.500	47	0.00681	0.12799	1.0892E-07	2073.6
0.75	3825.075	6.000	6.750	3.125	47	0.00852	0.12809	1.0901E-07	1986.0
0.7	3570.070	5.600	6.300	3.750	47	0.01023	0.12820	1.0911E-07	1896.3
0.65	3315.065	5.200	5.850	4.375	47	0.01194	0.12831	1.0920E-07	1804.2
0.6	3060.060	4.800	5.400	5.000	47	0.01366	0.12841	1.0929E-07	1709.6

Example table showing example alpha and example concentrations of oxygen and nitrogen

As the fuel equivalence ratio decreases, the number of free oxygens produced increases, due to there being less fuel in the mixture. This would mean that the potential for reactions between oxygen and nitrogen increases, however due to the decreasing flame temperature it is not hot enough for significant dissociation of the oxygen molecules, thus it is expected that NO_x production may decrease with phi.

Applications of the Zeldovich Model

Dr Owen Williams – University of Wales TSD:

The Zeldovich model can be applied to determine the rate of NO_x production at each respective fuel equivalence ratio.

$$\frac{\partial[NO]}{\partial t} = 4.7 \cdot 10^{13} \times [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-E_A}{RT}\right) \text{ kmols/m}^3/\text{sec}$$

Using the burn zone temperatures throughout combustion it is possible to calculate kmols of NO_x production per unit volume per second, however it is necessary to convert this into kmols per degree of crank angle. If the engine speed is assumed to be at a constant 2000 RPM, therefore:

$$2000 \cdot \frac{360}{60} = ^\circ/\text{sec}$$

$$\therefore \frac{4.7 \cdot 10^{13} \times [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-E_A}{RT}\right)}{2000 \times 6} = \frac{\text{kmols}}{m^3 \cdot ^\circ}$$

If the combustion chamber volume is 30ccs it can then be determined that kmols/[°]:

$$\frac{4.7 \cdot 10^{13} \times [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-E_A}{RT}\right)}{2000 \times 6} \times 30 \cdot 10^{-6} = \frac{\text{kmols}}{^\circ}$$

	φ	1		0.99		0.98	
θ°	P (Bar)	Temp (K)	Nox (kmols/°)	Temp (K)	Nox (kmols/°)	Temp (K)	Nox (kmols/°)
0	10	2404.20	0.000E+00	2388.30	1.676E-10	2372.40	1.960E-10
1	12	2468.74	0.000E+00	2452.41	3.521E-10	2436.09	4.138E-10
2	14	2524.66	0.000E+00	2507.96	6.498E-10	2491.27	7.668E-10
3	16	2574.12	0.000E+00	2557.10	1.093E-09	2540.07	1.294E-09
4	18	2618.55	0.000E+00	2601.24	1.714E-09	2583.92	2.036E-09
5	20	2658.95	0.000E+00	2641.36	2.547E-09	2623.78	3.034E-09
6	22	2696.03	0.000E+00	2678.20	3.626E-09	2660.37	4.329E-09
7	24	2730.33	0.000E+00	2712.27	4.985E-09	2694.22	5.963E-09
8	26	2762.27	0.000E+00	2744.00	6.657E-09	2725.73	7.979E-09
9	28	2792.17	0.000E+00	2773.71	8.675E-09	2755.24	1.042E-08
10	30	2820.30	0.000E+00	2801.65	1.107E-08	2783.00	1.332E-08
11	32	2846.88	0.000E+00	2828.05	1.388E-08	2809.22	1.672E-08
12	34	2872.06	0.000E+00	2853.07	1.713E-08	2834.08	2.066E-08
13	36	2896.02	0.000E+00	2876.86	2.085E-08	2857.71	2.518E-08
14	38	2918.86	0.000E+00	2899.55	2.508E-08	2880.25	3.032E-08
15	40	2940.69	0.000E+00	2921.24	2.983E-08	2901.79	3.612E-08

Example table of NO_x/degree with decreasing fuel equivalence ratio

Thus, the summation of NOx over the x degrees of combustion gives a total value of NOx per cycle, such that:

$$\sum_{x_{soc}}^{x_{eoc}} \left(\frac{4.7 \cdot 10^{13} \times [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-E_A}{RT}\right)}{2000 \times 6} \times 30 \cdot 10^{-6} \right) = kmols/cycle$$

The increasing pressure during combustion causes the rise in temperature, thus the dissociation of nitrogen and oxygen is more probable allowing for increased amounts of nitrogen oxides.

Stoichiometric burns do not produce any NOx in this particular model due to there being no free oxygens in the balanced chemical equation. In reality NOx is produced even at stoichiometric, however this is disregarded in this Zeldovich mechanism.

Using kmols/cycle it is possible to calculate NOx parts per million (PPM); one of the industry standards of measuring NOx production for emissions tests. PPM is the ratio of NOx produced during every cycle as a proportion of one million total exhaust gas particles. For example, a PPM value of 1000 would mean there are 1000 parts of NOx for every 1,000,000 exhaust gas parts.

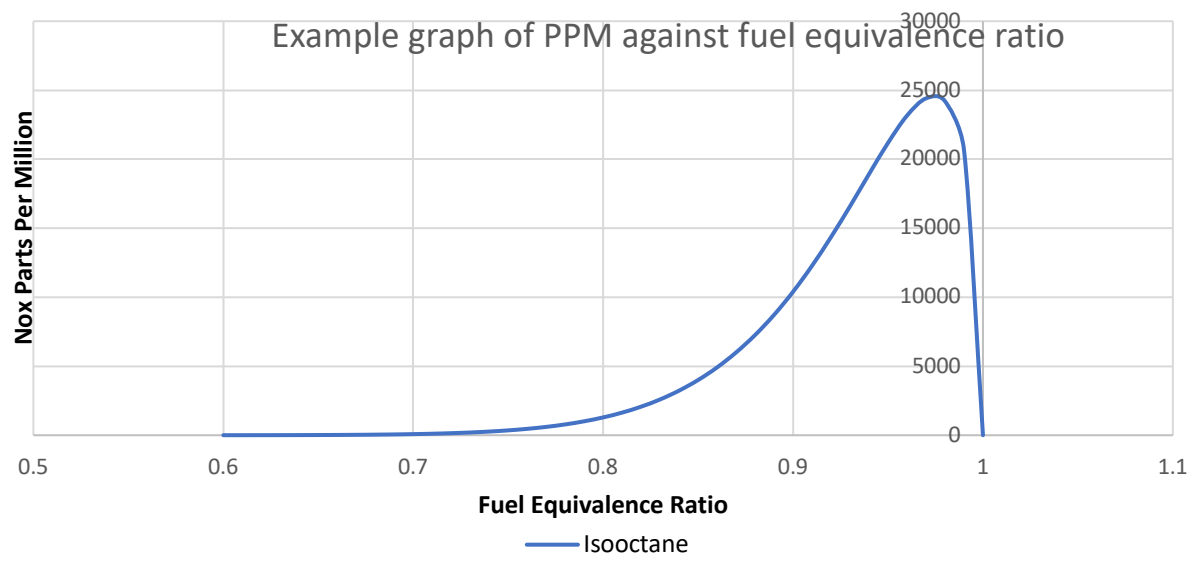
$$PPM = \frac{NOx \text{ kmols/cycle}}{\text{total exhaust kmols}} \times 10^6$$

Where,

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

The total kmols of exhaust changes with fuel equivalence ratio, since the differing amounts of fuel in the mixture has an effect on the exhaust components after burning.

At $\phi=0.97$, you'll probably find the rate of NOx production is at its highest. The high flame and burn zone temperatures, combined with increased concentrations of nitrogen and oxygen molecules leads to a higher rate of NOx production at this value. Despite there being even higher concentrations of N_2 and O_2 at the lowest values of fuel equivalence, the drastically lower combustion temperatures mean the molecules do not dissociate as easily thus leading to lower NOx production.



Example graph of PPM against fuel equivalence ratio for isooctane

Exhaust Gas Recirculation Effects

Dr Owen Williams – University of Wales TSD:

Though it is not a legal requirement to have an exhaust gas recirculation valve (EGR valve) fitted to either a petrol or diesel engine, most cars without them would fail the emissions test part of a modern MOT. As has been discovered, isooctane without any effects of EGR produces a very high amount of NOx parts per million, thus the need for a way of reducing this in order to meet emissions standards. The EGR valve works to recirculate previously burned gases back into the cylinder to be burned again in the next cycle. The recirculated gas adds extra mass to the combustion mixture and decreases the burn zone temperature following the ideal gas law, therefore reducing NOx production.

Adding EGR requires a recalculation of the balanced isooctane chemical equation, such that adding 10% of the exhaust gases back into the combustion gives the following equation:

$$\begin{aligned} & (\varphi C_8H_{18} + 12.5(O_2 + 3.76N_2)) + 0.1(n_1CO_2 + n_2H_2O + n_3O_2 + n_4N_2) \\ & \rightarrow 1.1 \times (n_1CO_2 + n_2CO + n_3H_2O + n_4N_2) \end{aligned}$$

For example, at a fuel equivalence ratio of 0.97, the right hand side of the balanced equation becomes:

$$\begin{aligned} & \rightarrow (8 \times 0.97 \times 1.1)CO_2 + (9 \times 0.97 \times 1.1)H_2O + (12.5 \times (1 - \varphi) \times 1.1)1.25O_2 + (47 \times 1.1)N_2 \\ & \therefore 1.1(0.97 \times C_8H_{18} + 12.5(O_2 + 3.76N_2)) \rightarrow 8.536CO_2 + 9.603H_2O + 0.413O_2 + 51.7N_2 \end{aligned}$$

Though exhaust gases have been added to the equation, the resultant net enthalpy is the same as when calculated without EGR due to the fact that an equal amount of exhaust components have been added to each side, thus the net heat released doesn't change.

By re-calculating new numbers of exhaust components produced with added EGR. The burn zone temperatures can be recalculated in addition to rate of NOx production over the combustion duration, and thus plot NOx/cycle against fuel equivalence ratio can be produced.

Since we have assumed a volumetric efficiency of the engine. For consistency's sake it is ok to assume that for EGR in this type of model, the volumetric efficiency can remain the same, with enough space to compensate for added exhaust gases in the mixture.

If the volumetric efficiency was 50% *with* the added EGR gases it would require the recalculation of the alpha values such that the summation of the volume of mixture drawn in and exhaust gases added has an overall volume 50% of the cylinder volume. Thus, retaining the alpha values from the previously calculated model without EGR allows the calculation of new concentrations of nitrogen and oxygen with increasing levels of exhaust gas recirculation.

		5% EGR									
ϕ	Enthalpy	CO2	H2O	O2	N2	[O2]	[N2]	alpha	Exhaust	Flame Temp	PPM
1	5100.100	8.400	9.450	0.000	49.35	0.00000	0.13394	1.0856E-07	7.2955E-06	2313.9	0.000
0.99	5049.099	8.316	9.356	0.131	49.35	0.00036	0.13396	1.0858E-07	7.2916E-06	2298.7	8621.074
0.98	4998.098	8.232	9.261	0.263	49.35	0.00071	0.13399	1.0860E-07	7.2877E-06	2283.5	10350.228
0.97	4947.097	8.148	9.167	0.394	49.35	0.00107	0.13401	1.0862E-07	7.2837E-06	2268.2	10720.244
0.96	4896.096	8.064	9.072	0.525	49.35	0.00143	0.13403	1.0864E-07	7.2798E-06	2252.9	10444.834
0.95	4845.095	7.980	8.978	0.656	49.35	0.00178	0.13405	1.0865E-07	7.2759E-06	2237.4	9808.300
0.94	4794.094	7.896	8.883	0.788	49.35	0.00214	0.13407	1.0867E-07	7.2720E-06	2221.9	9002.687
0.93	4743.093	7.812	8.789	0.919	49.35	0.00250	0.13410	1.0869E-07	7.2680E-06	2206.4	8127.593
0.92	4692.092	7.728	8.694	1.050	49.35	0.00285	0.13412	1.0871E-07	7.2641E-06	2190.7	7226.858
0.91	4641.091	7.644	8.600	1.181	49.35	0.00321	0.13414	1.0873E-07	7.2602E-06	2175.0	6358.737
0.9	4590.090	7.560	8.505	1.313	49.35	0.00357	0.13416	1.0874E-07	7.2562E-06	2159.2	5538.508
0.85	4335.085	7.140	8.033	1.969	49.35	0.00536	0.13427	1.0883E-07	7.2365E-06	2079.2	2470.045
0.8	4080.080	6.720	7.560	2.625	49.35	0.00715	0.13439	1.0892E-07	7.2168E-06	1997.3	932.938
0.75	3825.075	6.300	7.088	3.281	49.35	0.00894	0.13450	1.0901E-07	7.1970E-06	1913.4	300.851
0.7	3570.070	5.880	6.615	3.938	49.35	0.01074	0.13461	1.0911E-07	7.1772E-06	1827.4	81.918
0.65	3315.065	5.460	6.143	4.594	49.35	0.01254	0.13472	1.0920E-07	7.1574E-06	1739.2	18.415
0.6	3060.060	5.040	5.670	5.250	49.35	0.01434	0.13483	1.0929E-07	7.1375E-06	1648.6	3.300

Example table of calculated figures for isoctane with 5% added EGR

Shown above is an example table of calculated results for NOx PPM with the addition of 5% exhaust gases recycled back into the cylinder. This causes an increase in nitrogen and oxygen concentrations of just under 5%, and an average flame temperature decrease of 3.7%.

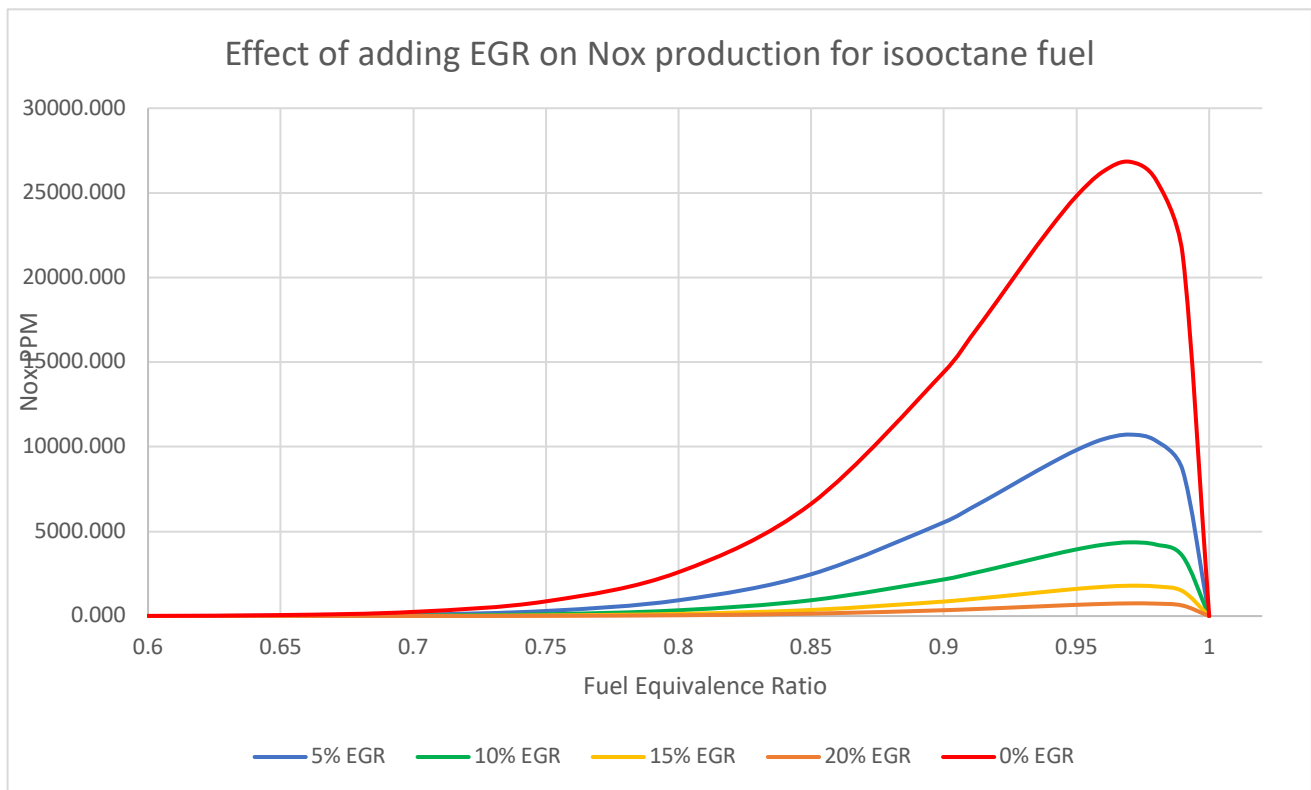
This combination of variables leads to a 60% reduction of produced NOx parts per million with just 5% added EGR.

$$\frac{\text{Average PPM @ 0 EGR} - \text{Average PPM @ 5\% EGR}}{\text{Average PPM @ 0 EGR}} \times 100 = 60.7\%$$

Regardless of the increased concentrations, if the temperature is reduced there are a lower proportion of molecules with significant activation energy to react and create NOx.

As the level of EGR increases up to 10%, the comparative maximum burn zone temperature at the end of combustion drops again from approximately 2850K to approximately 2750K, another 100°K difference resulting in an additional almost 60% drop in NOx PPM.

EGR levels up to 15 and 20% follow a similar trend, with the temperatures decreasing across all fuel equivalence ratios as the EGR level increases, reducing the NOx production by roughly 60% with each 5% increase in EGR.



Shown above is a plot of the produced NOx with increasing fuel equivalence ratio for EGR levels up to 20%. The more EGR you add, the more the NOx emissions reduce, this is why many car manufacturers include an EGR system in order to comply with Euro VI emission regulations.

Fuels containing alcohol such as methanol and ethanol have a different chemical makeup than isooctane and thus produce different amounts of NOx. Methanol and a blend of isooctane and methanol emit less NOx per engine cycle than isooctane itself and would be a benefit in terms of reducing exhaust emissions.

The Zeldovich mechanism can only be applied to lean burn scenarios, though it is known that NOx is still produced in fuel-rich mixtures. Since many engines tend to run on the rich side of stoichiometric for increased power output, the lean-only model is not a full representation of an engine NOx model. We will look at some of the other methods for NOx modelling and other emission modelling next.