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Combustion and Emission Study:
Modelling Fuels & NO_x.

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1 Introduction

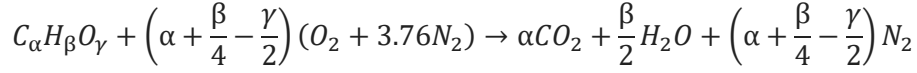
This investigation has been carried out because the automotive industry is advancing. This is causing an interest in fuel development which has real life effects, such as the E5 fuel which is sold at the majority of fuel stations throughout UK. The E5 fuel blend has become so common because it is believed to be more eco-friendly, since 5% of it contains alcohol (ethanol) which is a renewable resource, as it can be produced from plants by the means of fermentation and distillation. Author believed it to be of great importance to investigate the effects on the fuel characteristics and the NO_x emissions.

Therefore, in this document author explains and utilizes the fuel blend model from section 2 and NO_x production model from section 3, to investigate the effects of the introduction of alcohol to iso-Octane species from the fuel characteristics perspective, as well as the effects on the NO_x production.

2 Fuel Composition Model

2.1 Governing Equations

Author has based the chemical balance equations on Equation 1. Author believes the mistake of the lack of “3.76” on the product side for N_2 to be a typo.



Equation 1: global equation for a generic reaction of hydrocarbon fuel with air (Wolk, 2014)

Author has included additional parameters such as:

- φ – equivalence ratio
- δ – ratio between N_2 and O_2
- Egr – EGR amount
- ΣEXH – sum of combusted species
- CO – carbon monoxide product in rich combustion
- O_2 – oxygen product in lean combustion
- ε – total carbon associated mass
- f – total oxygen mass – oxygen in other species

As such, author has created the following equations:

$$\begin{aligned} & \varphi(C_\alpha H_\beta O_\gamma) + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) (O_2 + \delta N_2) + Egr \Sigma EXH \\ & \rightarrow (\varepsilon - \varphi\alpha)CO_2 + (2\varphi\alpha - \varepsilon)CO + \frac{\varphi\beta}{2} H_2O + \delta \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) N_2 + Egr \Sigma EXH \end{aligned}$$

Equation 2: Chemistry Balance for Rich Combustion

$$\begin{aligned} & \varphi(C_\alpha H_\beta O_\gamma) + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) (O_2 + \delta N_2) + Egr \Sigma EXH \\ & \rightarrow \varphi\alpha CO_2 + \frac{\varphi\beta}{2} H_2O + fO_2 + \delta \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) N_2 + Egr \Sigma EXH \end{aligned}$$

Equation 3: Chemistry Balance for Lean Combustion

Where:

$$\varepsilon = \gamma\varphi + 2\left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) - \frac{\varphi\beta}{2}$$

Equation 4: epsilon part of Chemistry Balance for Rich Combustion

$$f = \frac{\left(\phi \gamma + 2 \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2} \right) \right) - 2\phi\alpha - \frac{\phi\beta}{2}}{2}$$

Equation 5: digamma part of Chemistry Balance for Lean Combustion

Author has put the governing equations in this form to allow easy automatic calculations to be carried out for variety of scenarios.

The reason for two different equations which are dependent on the fuel air fraction is due to the 'ideal combustion' assumptions which greatly reduce the combustion mechanism. This has been done so that the calculations are easy to compute and most importantly they yield definite results that don't require cyclic computation or more than one forward reaction rate equation.

2.2 Fuel Blend Method

Fuel Blend			
Fuel Type	iso-Octane	n-Decane	Ethanol
Fuel Quality	1.00	0.00	0.00
Carbon (kmol)	8.0	0.0	0.0
Hydrogen (kmol)	18.0	0.0	0.0
Oxygen (kmol)	0.0	0.0	0.0
Mass (kg)	114.0	0.0	0.0
Mass (%)	100.00	0.00	0.00
Δh_f° (MJ kmol ⁻¹)	259.20	300.90	235.10

Figure 1: Fuel Blend Table

Figure 1 shows the fuel blend table. It allows user to blend 3 different chosen fuels, via a dropdown list which is connected to the fuel table as shown in Appendix 1. The fuel quality determines the ratio between fuel species, if it isn't normalized to 1 the cells will turn red signalling an error, as shown by Figure 2.

Fuel Quality	0.50	0.50	0.50
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Figure 2: non-normalized fuel quality

All fuel parameters are calculated by multiplying their corresponding native value from the fuel table by their specified quality, so that a sum of all 3 will result in the blend specific value that can be used in later calculations.

Equation Balance	
ϕ	0.60
EGR (%)	50.00
α (kmol)	8.0
β (kmol)	18.0
γ (kmol)	0.0

Figure 3: Equation Balance Table

Figure 3 shows the equation balance table. It sums up the α , β and γ values which correspond to the carbon, hydrogen and oxygen respectfully, as the section 2.1 explained. These are retrieved from the fuel blend table. Additionally, this is where the ϕ and EGR (%) is specified. These values are then inserted into one of the chemical balance equations from section 2.1. This results in the product values shown in Figure 4.

Products	
CO ₂ (kmol)	7.20
CO (kmol)	0.00
H ₂ O (kmol)	8.10
O ₂ (kmol)	7.50
N ₂ (kmol)	69.88

Figure 4: Products Table

Lastly, the results table in Figure 5 shows the blend specific properties.

Results	
AFR _s	14.95
LHV (MJ kg ⁻¹)	44.43
HHV (MJ kg ⁻¹)	47.90
Specific CO ₂	3.09

Figure 5: Results Table

2.3 50:50 Methanol Isooctane Blend

2.3.1 Results

Fuel Blend			
Fuel Type	iso-Octane	Methanol	Ethanol
Fuel Quality	0.50	0.50	0.00
Carbon (kmol)	4.0	0.5	0.0
Hydrogen (kmol)	9.0	2.0	0.0
Oxygen (kmol)	0.0	0.5	0.0
Mass (kg)	57.0	16.0	0.0
Mass (%)	78.08	21.92	0.00
Δh°_f (MJ kmol ⁻¹)	259.20	201.50	235.10

Figure 6: Methanol Isooctane Fuel Blend Table

As shown by Figure 6, the mass percentages for iso-Octane and Methanol are 78.08% and 21.92% respectfully. This is due to Methanol being a simpler substance overall. It has 9 less carbon atoms, 18 less hydrogen atoms and 1 more oxygen atom than iso-Octane. As the Figure 7 shows, oxygen is the heaviest atom present in a hydrocarbon fuel. However, a single oxygen atom cannot even out the severe carbon (2nd most massive atom found in hydrocarbon fuel) and Hydrogen deficiency, compared to the iso-Octane. As a result, there are fewer total protons in kmol of Methanol, resulting in much lower mass, compared to iso-Octane.

Molecular Mass:	
Carbon	12
Hydrogen	1
Oxygen	16
Nitrogen	14

Figure 7: Molecular Mass Table

Results	
AFR _s	13.08
LHV (MJ kg ⁻¹)	39.32
HHV (MJ kg ⁻¹)	42.63
Specific CO ₂	2.71

Figure 8: Methanol Isooctane Results Table

Figure 8 shows that the stoichiometric air fuel ratio (calculated by dividing the air mass by the fuel mass) is 13.08. This shows a 12.5% decrease compared to 14.95 AFR_s for pure iso-Octane. This is directly caused by fuel blend density decrease (drop in α , β and γ) as well as the additional oxygen reactant, caused by introduction of Methanol. This means that more fuel is required to achieve the stoichiometric combustion.

Figure 8 also shows a lower heating value (LHV) of 39.32 MJ kg⁻¹. This value decreased by 11.5% from 44.43 MJ kg⁻¹ for the pure iso-Octane. This is caused by 41.2% decrease of CO₂ and H₂O production (which is where energy comes from). However, the 22.3% lower enthalpy of formation for Methanol as well as the overall mass decrease helped to counteract the LHV reduction.

Lastly, Figure 8 also shows the specific CO₂ production (mass ratio between produced CO₂ and combusted fuel) to be 2.71 (dimensionless) for the 50:50 iso-Octane Methanol blend. This decreased by 12.3% from 3.09 for pure iso-Octane. This is due to the CO₂ reduction being higher than the fuel mass reduction.

2.3.2 Enthalpy of Formations

Enthalpy (sum of internal energy and the work-done) of formation is the enthalpy change between the total enthalpy of reactants and the total enthalpy of products when forming 1 mol of products. This value is equal to the released or absorbed energy from the given reaction at constant pressure, with the specified molar quantities of substances.

2.3.3 LHV & HHV

Lower Heating Value (LHV) and Higher Heating Value (HHV) represent in what state the water is in and as a result, what state the substance is considered to be in. LHV is considered to be when water is in gas form, as the enthalpy of formation of gaseous water is lower than that of liquid water, as shown by Figure 9.

Enthalpies of Combustion		
Formula	Substance	Δh (MJ kmol ⁻¹)
CO ₂	Carbon Dioxide	393.5
H ₂ O (g)	Water Gas	241.8
H ₂ O (l)	Water Liquid	285.8

Figure 9: Enthalpies of Combustion

As a result, as one might expect, a liquid fuel is more energy dense than gaseous fuel, as shown by Figure 8.

2.3.4 Ideal Fuel

Author believes ideal fuel to have the following:

- Contains no carbon atoms to prevent CO₂ and CO emission
- It must contain a lot of hydrogen atoms to make it energy dense
- It must have low enthalpy of formation so that the energy yield from the reaction is as high as possible
- It must be light so that the LHV value is high

Author believes that these qualities describe a long chain hydrogen-oxygen molecule the best. Sadly, these kinds of substances aren't readily available.

3 NO_x Emission Model

3.1 Enthalpy Curve Fit

To calculate the initial flame front temperature author had to create a mathematical relation which would retrieve the correct enthalpy of formation (h_f) of CO₂, H₂O, O₂ and N₂ at the specified temperature.

To do so, at first author plotted the required data as the Figure 10 shows. However, as Figure 11 shows, the raw data hasn't been standardised to 293K @ 1 atm. As the raw data didn't include the h at the required point, author has standardised the data so that the h at 300K matches the value from well known 'fuel table' (Springer Science + Business Media, 2011), resulting in the data shown by Figure 10.

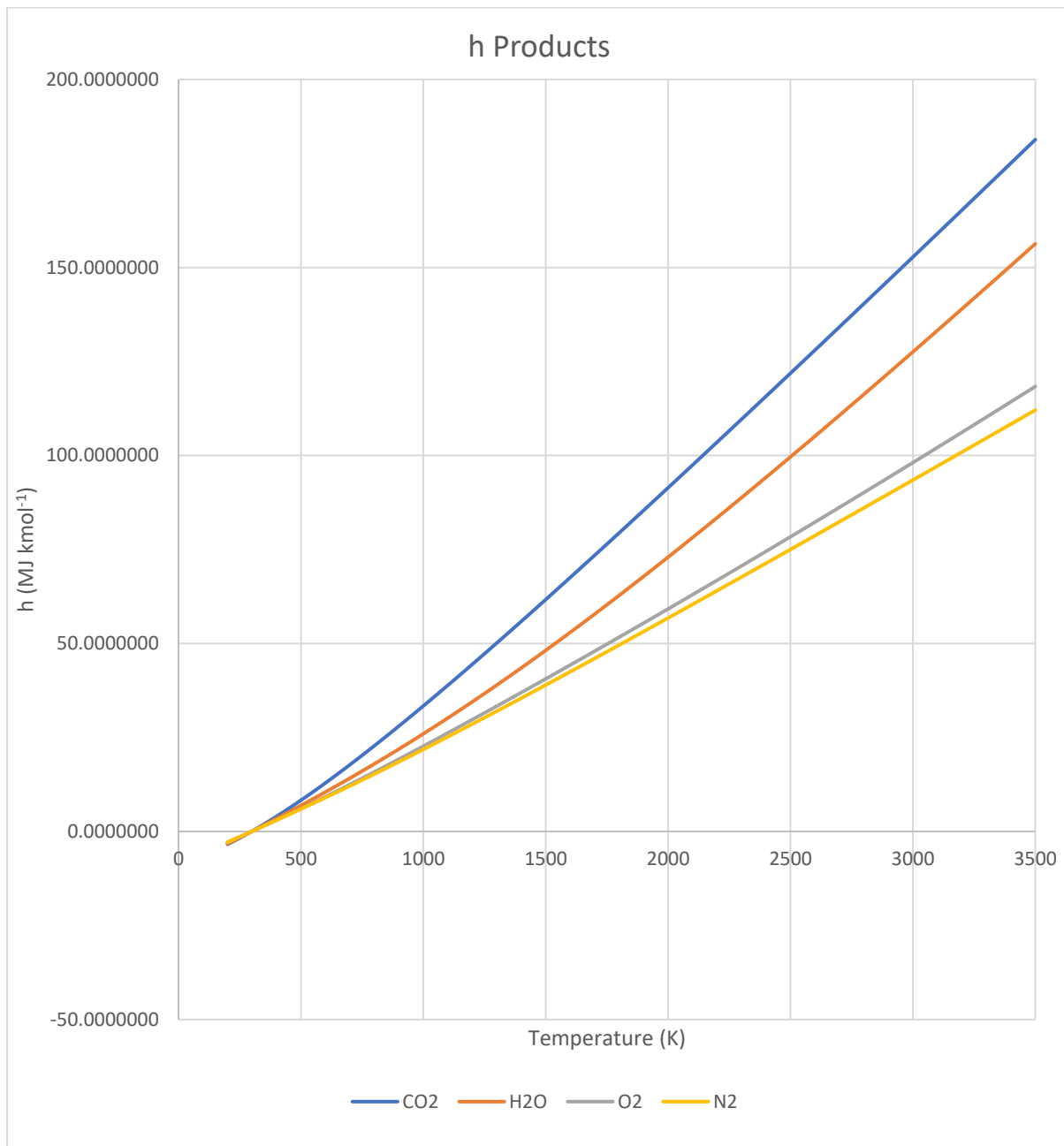


Figure 10: enthalpy of formation of products

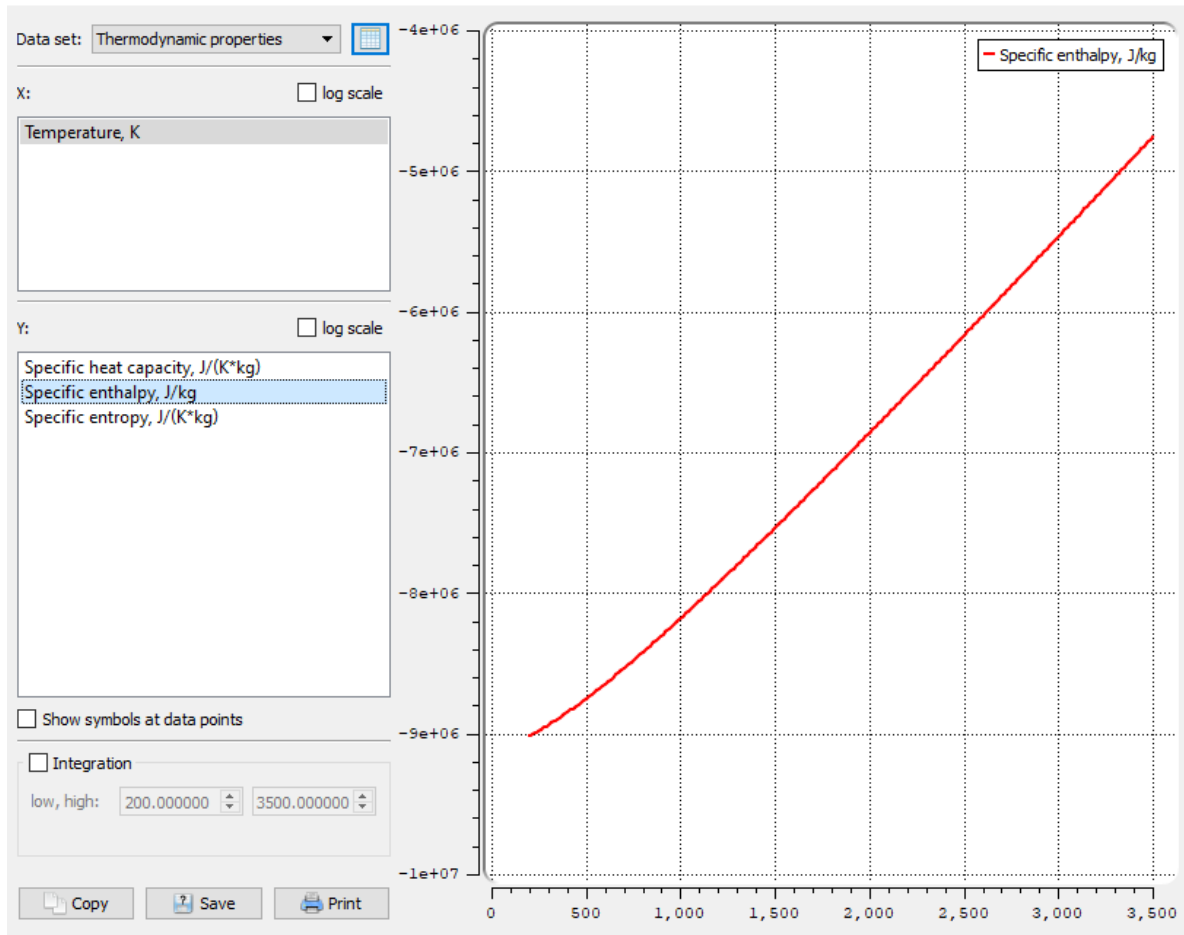


Figure 11: raw data of enthalpy of formation of CO₂ (Convergent Science, 2019)

Author has then decided to use the curve fit tool in MATLAB software to retrieve the required mathematical relation. Author has used 5th order polynomial for all 4 relations as that was the minimal requirement to achieve an R-squared value of 1. Additionally, author has kept 9 decimal points on all polynomial coefficients since the accuracy and the precision is vital for the correct calculation of initial flame front temperature. In addition to that, the data which has been curve fitted had a precision of at least 6 decimal places, therefore high coefficient precision is even more justified. The resultant accuracy is displayed by Figure 12.

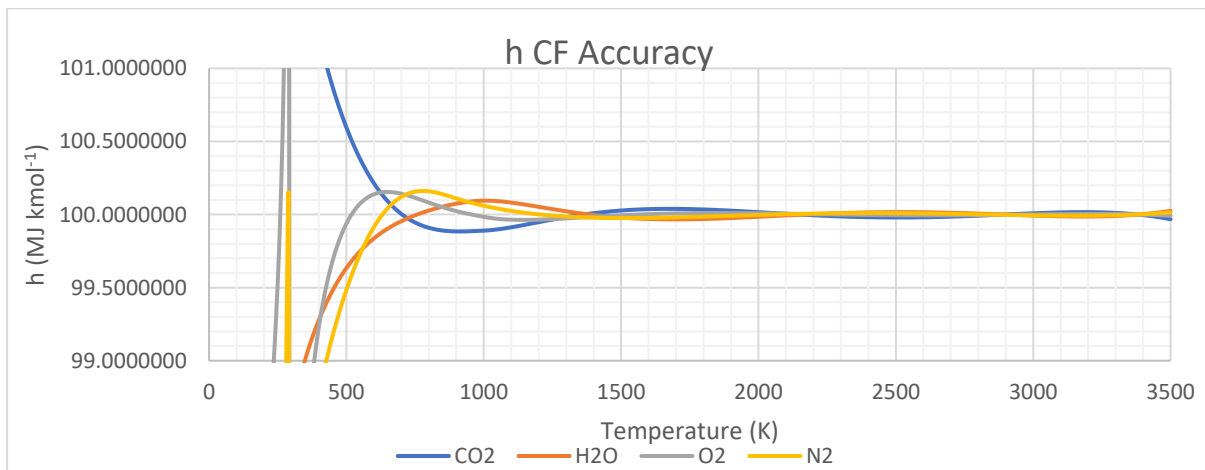


Figure 12: accuracy of the curve fitted enthalpy of formation of products

The accuracy above 500K is satisfactory, especially above 1,500K since then the accuracy increases to under +/- 0.05%. Author believes this result to be good enough since combustion under 500K is not expected.

3.2 NO_x Emission Model Overview

The NO_x calculator settings table shown in Figure 13 computes everything the Zeldovich model requires:

- Δh (change of enthalpy) - based on temperature and the enthalpy of formation of products, as discussed in section 3.1.
- η (molecular air fraction) - based on the calculated air quantity from the fuel composition calculator (discussed in section 2) and the total intake charge quantity which is specified by ideal gas law.
- N₂ and O₂ qualities - based on η , the corresponding quantity from fuel composition calculator and the combustion volume which has been assumed to be constant.
- Σ_{exh} - calculated by multiplying η with the exhaust sum quantity from the fuel composition calculator.

Additionally, it is where the equivalence ratio and EGR % is inputted into the model.

Calculator Settings	
ϕ	1.00
T (K)	1264.198211
Δh	2154.06
η	1.0931E-07
N ₂	0.127311
O ₂	0.000000
Σ_{exh}	6.9507E-06
EGR (%)	0

Figure 13: NO_x calculator settings table

To retrieve the correct initial combustion temperature as well as the corresponding qualities, the temperature from the calculator settings table is manipulated so that the Δh matches Δh_{comb} from the input table. It is calculated with the same method as LHV and HHV from section 2.3.3, however, without the division by fuel mass.

ϕ	Δh_{comb} (MJ)	Flame Temp. (K)	N2	O2	Σ_{exh}
1.00	5065.00	1748.324702	1.909669E-01	0.000000E+00	9.770226E-06
0.99	5014.35	1737.295326	1.909987E-01	5.124772E-04	1.042044E-05
0.98	4963.70	1726.216708	1.910305E-01	1.025125E-03	1.041480E-05
0.97	4913.05	1715.088448	1.910623E-01	1.537944E-03	1.040915E-05
0.96	4862.40	1703.910139	1.910941E-01	2.050933E-03	1.040350E-05
0.95	4811.75	1692.681370	1.911259E-01	2.564093E-03	1.039785E-05
0.90	4558.50	1635.765982	1.912852E-01	5.132461E-03	1.036956E-05
0.85	4305.25	1577.523804	1.914448E-01	7.705114E-03	1.034123E-05
0.80	4052.00	1517.896276	1.916046E-01	1.028206E-02	1.031285E-05
0.75	3798.75	1456.820977	1.917647E-01	1.286332E-02	1.028442E-05
0.70	3545.50	1394.229732	1.919251E-01	1.544889E-02	1.025594E-05
0.65	3292.25	1330.048872	1.920858E-01	1.803879E-02	1.022742E-05
0.60	3039.00	1264.198211	1.922467E-01	2.063303E-02	1.019884E-05

Figure 14: NO_x input table

Once the input table is populated, the corresponding initial combustion temperatures (flame temperatures) are transposed to the Temperature table, where rearranged ideal gas equation is used to calculate the remaining temperatures by using the corresponding cylinder pressure, polytropic index and previous temperature. As shown in Figure 15, it is assumed that the flame temperature at the point of ignition is equal to the mean cylinder temperature.

Temperature	ϕ		1.00	0.99	0.98	0.97	0.96	0.95	0.9	0.85	0.8	0.75	0.7	0.65	0.6
	C.A.	Cyl. P. (bar)	Burn Zone Temperature (K)												
	0	10	1748.32	1737.30	1726.22	1715.09	1703.91	1692.68	1635.77	1577.52	1517.90	1456.82	1394.23	1330.05	1264.20
1	12	1795.26	1783.93	1772.56	1761.13	1749.65	1738.12	1726.68	1619.87	1558.64	1495.93	1431.66	1365.75	1298.14	1228.14
2	14	1835.92	1824.34	1812.71	1801.02	1789.28	1777.49	1765.72	1656.56	1593.95	1529.81	1464.09	1396.69	1327.54	1254.54
3	16	1871.89	1860.08	1848.22	1836.31	1824.34	1812.31	1799.38	1689.02	1625.18	1559.78	1492.77	1424.05	1353.55	1278.55
4	18	1904.20	1892.19	1880.12	1868.00	1855.83	1843.60	1831.31	1718.17	1653.23	1586.71	1518.54	1448.63	1376.91	1301.91
5	20	1933.58	1921.38	1909.13	1896.82	1884.46	1872.04	1859.57	1744.68	1678.73	1611.19	1541.96	1470.98	1398.15	1321.15
6	22	1960.54	1948.17	1935.75	1923.27	1910.73	1898.14	1885.50	1769.01	1702.14	1633.65	1563.46	1491.49	1417.65	1341.65
7	24	1985.48	1972.96	1960.38	1947.74	1935.04	1922.29	1909.50	1791.51	1723.80	1654.44	1583.36	1510.47	1435.69	1358.69
8	26	2008.71	1996.04	1983.31	1970.52	1957.68	1944.78	1931.84	1812.47	1743.96	1673.79	1601.88	1528.14	1452.48	1374.48
9	28	2030.46	2017.65	2004.78	1991.86	1978.88	1965.83	1952.73	1832.09	1762.84	1691.91	1619.22	1544.68	1468.21	1389.21
10	30	2050.91	2037.98	2024.98	2011.93	1998.81	1985.64	1972.42	1850.55	1780.60	1708.96	1635.53	1560.25	1483.00	1403.00
11	32	2070.24	2057.18	2044.06	2030.88	2017.64	2004.35	1991.01	1867.99	1797.38	1725.06	1650.94	1574.95	1496.97	1414.97
12	34	2088.55	2075.38	2062.14	2048.85	2035.50	2022.08	2008.61	1884.51	1813.28	1740.32	1665.55	1588.88	1510.21	1426.21
13	36	2105.97	2092.69	2079.34	2065.94	2052.47	2038.94	2025.36	1900.23	1828.40	1754.84	1679.44	1602.13	1522.81	1437.81
14	38	2122.58	2109.19	2095.74	2082.23	2068.66	2055.03	2041.35	1915.22	1842.83	1768.68	1692.69	1614.77	1534.82	1449.82
15	40	2138.46	2124.97	2111.42	2097.81	2084.13	2070.40	2056.62	1929.54	1856.61	1781.91	1705.35	1626.85	1546.30	1461.30

Figure 15: Temperature table

As Figure 16 shows, the results from the temperature table as well as the transposed N₂ and O₂ qualities are used to drive the Zeldovich model. The gas kinetic collision rate as well as the activation energy used in the model are specified in Equation 6. The forward reaction rate is divided by engine rpm as well as combustion chamber volume to convert the production rate to kmols °⁻¹, as this allows the summation of all reaction rates to be carried out. This is then divided by the corresponding Σ_{exh} and multiplied by a million to retrieve the NO_x production parts per million (PPM) of exhaust gases.

$$\frac{\partial[\text{NO}]}{\partial t} = 4.7 * 10^{13} * [\text{N}_2][\text{O}_2]^{0.5} * \exp\left(\frac{-67,837}{T}\right)$$

Equation 6: Zeldovich Model (Williams, 2019)

NO _x Production	Texh	9.77E-06	1.04E-05	1.04E-05	1.04E-05	1.04E-05	1.04E-05	1.04E-05	1.03E-05	1.03E-05	1.03E-05	1.03E-05	1.02E-05	1.02E-05
	N2	1.91E-01	1.91E-01	1.91E-01	1.91E-01	1.91E-01	1.91E-01	1.91E-01	1.91E-01	1.92E-01	1.92E-01	1.92E-01	1.92E-01	1.92E-01
	O2	0.00E+00	5.12E-04	1.03E-03	1.54E-03	2.05E-03	2.56E-03	5.13E-03	7.71E-03	1.03E-02	1.29E-02	1.54E-02	1.80E-02	2.06E-02
	φ	1.00	0.99	0.98	0.97	0.96	0.95	0.9	0.85	0.8	0.75	0.7	0.65	0.6
	C.A.	Produced NO _x (kmols ⁻¹)												
	Cyl. P. (bar)													
	0	10	0.00E+00	8.29E-15	9.13E-15	8.66E-15	7.72E-15	6.63E-15	2.33E-15	6.17E-16	1.32E-16	2.27E-17	3.07E-18	2.39E-20
	1	12	0.00E+00	2.30E-14	2.55E-14	2.44E-14	2.19E-14	1.89E-14	6.88E-15	1.90E-15	4.24E-16	7.65E-17	1.10E-17	1.20E-18
	2	14	0.00E+00	5.34E-14	5.95E-14	5.72E-14	5.16E-14	4.49E-14	1.68E-14	4.80E-15	1.11E-15	2.09E-16	3.13E-17	3.62E-18
	3	16	0.00E+00	1.09E-13	1.22E-13	1.18E-13	1.07E-13	9.34E-14	3.60E-14	1.06E-14	2.52E-15	4.90E-16	7.63E-17	9.21E-18
	4	18	0.00E+00	2.03E-13	2.28E-13	2.21E-13	2.01E-13	1.76E-13	6.94E-14	2.09E-14	5.11E-15	1.02E-15	1.65E-16	2.07E-17
	5	20	0.00E+00	3.49E-13	3.94E-13	3.83E-13	3.50E-13	3.08E-13	1.24E-13	3.80E-14	9.54E-15	1.96E-15	3.25E-16	4.21E-17
	6	22	0.00E+00	5.68E-13	6.42E-13	6.27E-13	5.74E-13	5.08E-13	2.07E-13	6.49E-14	1.66E-14	3.50E-15	5.95E-16	7.93E-17
	7	24	0.00E+00	8.79E-13	9.97E-13	9.76E-13	8.97E-13	7.95E-13	3.30E-13	1.05E-13	2.74E-14	5.90E-15	1.03E-15	1.40E-16
	8	26	0.00E+00	1.31E-12	1.49E-12	1.46E-12	1.35E-12	1.20E-12	5.03E-13	1.63E-13	4.32E-14	9.48E-15	1.69E-15	2.36E-16
	9	28	0.00E+00	1.88E-12	2.15E-12	2.11E-12	1.95E-12	1.74E-12	7.40E-13	2.43E-13	6.56E-14	1.46E-14	2.65E-15	3.80E-16
	10	30	0.00E+00	2.63E-12	3.01E-12	2.97E-12	2.75E-12	2.45E-12	1.06E-12	3.51E-13	9.63E-14	2.18E-14	4.03E-15	5.89E-16
	11	32	0.00E+00	3.59E-12	4.11E-12	4.06E-12	3.77E-12	3.37E-12	1.47E-12	4.95E-13	1.37E-13	3.16E-14	5.93E-15	8.83E-16
	12	34	0.00E+00	4.80E-12	5.50E-12	5.44E-12	5.06E-12	4.54E-12	2.00E-12	6.81E-13	1.91E-13	4.46E-14	8.51E-15	1.29E-15
	13	36	0.00E+00	6.29E-12	7.22E-12	7.16E-12	6.67E-12	5.99E-12	2.66E-12	9.16E-13	2.61E-13	6.16E-14	1.19E-14	1.83E-15
	14	38	0.00E+00	8.10E-12	9.32E-12	9.26E-12	8.63E-12	7.77E-12	3.49E-12	1.21E-12	3.48E-13	8.34E-14	1.63E-14	2.56E-15
	15	40	0.00E+00	1.03E-11	1.19E-11	1.18E-11	1.10E-11	9.93E-12	4.49E-12	1.58E-12	4.58E-13	1.11E-13	2.20E-14	3.49E-15
	ENO _x (PPM)		0.00	3.94	4.53	4.48	4.17	3.74	1.66	0.57	0.16	0.04	0.01	0.00

Figure 16: NO_x Production table

The entire NO_x emission model is operated by a single sub routine (macro) written in VBA language, as displayed by Figure 17. Upon execution with the “Run Simulation” button, it will:

- Create required variables
- Clear the Results Table
- Calculate in what steps the EGR % should increase in, based on inputted values from the EGR Set Parameters table, as shown in Figure 18
- Start the EGR loop, on every cycle the EGR% value in the Calculator Settings table is altered
 - On first cycle calculate results for 0 EGR %
 - On second cycle calculate results for the first specified EGR %
 - On all other cycles calculate results for the increasing EGR % with the calculated step
- On second EGR cycle and above, write the corresponding EGR % value into the results table
- For all φ values:
 - Use goal seek function to match the enthalpies
 - Populate the input table with the Temperature, O₂, N₂ and exhaust sum values
- Populate the Results table with NO_x PPM values
- Calculate and populate the results table with the NO_x reduction value (0 EGR% being the denominator)
- Calculate and populate the results table with the mean combustion chamber temperature
- On first EGR cycle, calculate the average NO_x PPM for 0 EGR%

This execution causes the Results Table to be populated with the EGR% values, which the calculation has been carried out with, the NO_x PPM emission for all φ values, NO_x reduction % as well as the mean combustion chamber temperature, as shown in Figure 19.

```

' Flame_Temp Macro: Written by Kacper Oskar Kaczmarczyk, for Powertrain Assignment @ UWTSD

Dim n 'initialize variable phi count
Dim i 'initialize variable egr count
Dim EGR_Step 'initialize variable in what steps the EGR % will increase
Dim EGR_n 'initialize current EGR % variable
Dim NOx_0 'initialize the NOx PPM with no EGR % variable|

Range("A4:AS200").ClearContents 'clear the results table

EGR_Step = ((Cells(4, 6).Value - Cells(3, 6).Value) / Cells(5, 6).Value) 'calculate the EGR % step from given parameters

For i = 1 To Cells(5, 6).Value + 2 'go through all specified EGR % values

    If i = 1 Then 'on first EGR cycle
        EGR_n = 0 'set current EGR % to 0
    ElseIf i = 2 Then 'on second EGR cycle
        EGR_n = Cells(3, 6) 'use the specified starting EGR %
    Else 'on all other EGR cycles
        EGR_n = EGR_n + EGR_Step 'add the EGR_Step to the current EGR value
    End If

    Cells(10, 3).Value = EGR_n 'set the EGR% in the Calculator Table to the current EGR value

    If i > 1 Then 'on EGR cycle 2 and above
        Cells(2 + i, 30).Value = EGR_n 'set the EGR % value in the Results table to the current EGR value
    End If

    For n = 1 To 13 'go through all phi values

        Range("C3").Value = Cells(n + 13, 2).Value 'set the phi value in the calculator to the corresponding phi value from the table

        Range("C5").GoalSeek Goal:=Cells(n + 13, 3).Value, ChangingCell:=Range("C4") 'match the enthalpies to find the Temperature

        Cells(n + 13, 4).Value = Range("C4") 'fetch the Temperature value from the calculator into the input table

        Cells(n + 13, 5).Value = Range("C7") 'fetch the N2 value from the calculator into the input table

        Cells(n + 13, 6).Value = Range("C8") 'fetch the O2 value from the calculator into the input table

        Cells(n + 13, 7).Value = Range("C9") 'fetch the exhaust sum value from the calculator into the input table

        Next n 'go to the next phi value

    If i > 1 Then 'on EGR cycle 2 and above

        For n = 1 To 13 'go through all phi values

            Cells(2 + i, 30 + n).Value = Cells(42, 14 + n).Value 'fetch NOx PPM from NOx Production table into Results Table

            Next n 'next phi value

            Cells(2 + i, 44).Value = ((NOx_0 - WorksheetFunction.Average(Range("O42:AA42")))) / NOx_0 * 100 'calculate and populate the results table with the NOx reduction

            Cells(2 + i, 45).Value = WorksheetFunction.Average(Range("O4:AA19")) 'calculate and populate the results table with the mean chamber temperature

        ElseIf i = 1 Then 'on EGR cycle 1
            NOx_0 = WorksheetFunction.Average(Range("O42:AA42")) 'calculate the average NOx PPM for no EGR
        End If

    Next i

```

Figure 17: Flame Temp Macro

Figure 17 shows the code for the “Flame Temp” sub routine, the writing in green are the comments which describe/ explain every line of the code written by the author.

EGR Set Parameters	
From	0
To	20
Steps	10

Figure 18: EGR Set Parameters table

Results															NO _x reduction (%)	Mean Chamber Temp. (K)
EGR (%)	1.00	0.99	0.98	0.97	0.96	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.50		
0.00	0.00	20434.96	24598.37	25569.14	24983.98	23565.07	13562.29	6174.28	2385.22	788.58	220.72	51.15	9.50	0.00	0.00	2424.41
2.00	0.00	14133.44	16976.97	17609.00	17168.38	16157.35	9190.76	4131.05	1573.74	512.35	140.99	32.06	5.83	31.41	2387.38	
4.00	0.00	9799.80	11746.77	12158.14	11828.26	11107.21	6245.34	2771.92	1041.47	333.95	90.37	20.17	3.59	52.83	2351.71	
6.00	0.00	6811.79	8148.19	8415.75	8169.87	7655.13	4255.24	1865.18	691.27	218.35	58.11	12.74	2.22	67.47	2317.33	
8.00	0.00	4746.36	5665.88	5839.72	5657.08	5289.22	2906.93	1258.52	460.16	143.21	37.49	8.07	1.38	77.51	2284.17	
10.00	0.00	3315.10	3949.28	4062.04	3926.73	3663.56	1990.97	851.48	307.19	94.21	24.27	5.13	0.86	84.41	2252.16	
12.00	0.00	2320.86	2759.28	2832.25	2732.21	2543.70	1367.09	577.62	205.65	62.16	15.76	3.27	0.54	89.17	2221.25	
14.00	0.00	1628.55	1932.32	1979.40	1905.55	1770.37	941.04	392.87	138.05	41.13	10.26	2.09	0.34	92.45	2191.37	
16.00	0.00	1145.34	1356.29	1386.55	1332.09	1235.02	649.36	267.89	92.92	27.29	6.70	1.34	0.21	94.73	2162.48	
18.00	0.00	807.30	954.12	973.46	933.34	863.55	449.16	183.14	62.71	18.16	4.39	0.87	0.13	96.31	2134.52	
20.00	0.00	570.27	672.67	684.96	655.41	605.17	311.42	125.51	42.44	12.12	2.89	0.56	0.09	97.41	2107.45	

Figure 19: Results table

Figure 19 shows the exemplary results which are automatically generated when the “Flame Temp” sub routine is executed.

3.3 Results

3.3.1 Iso-Octane NO_x production

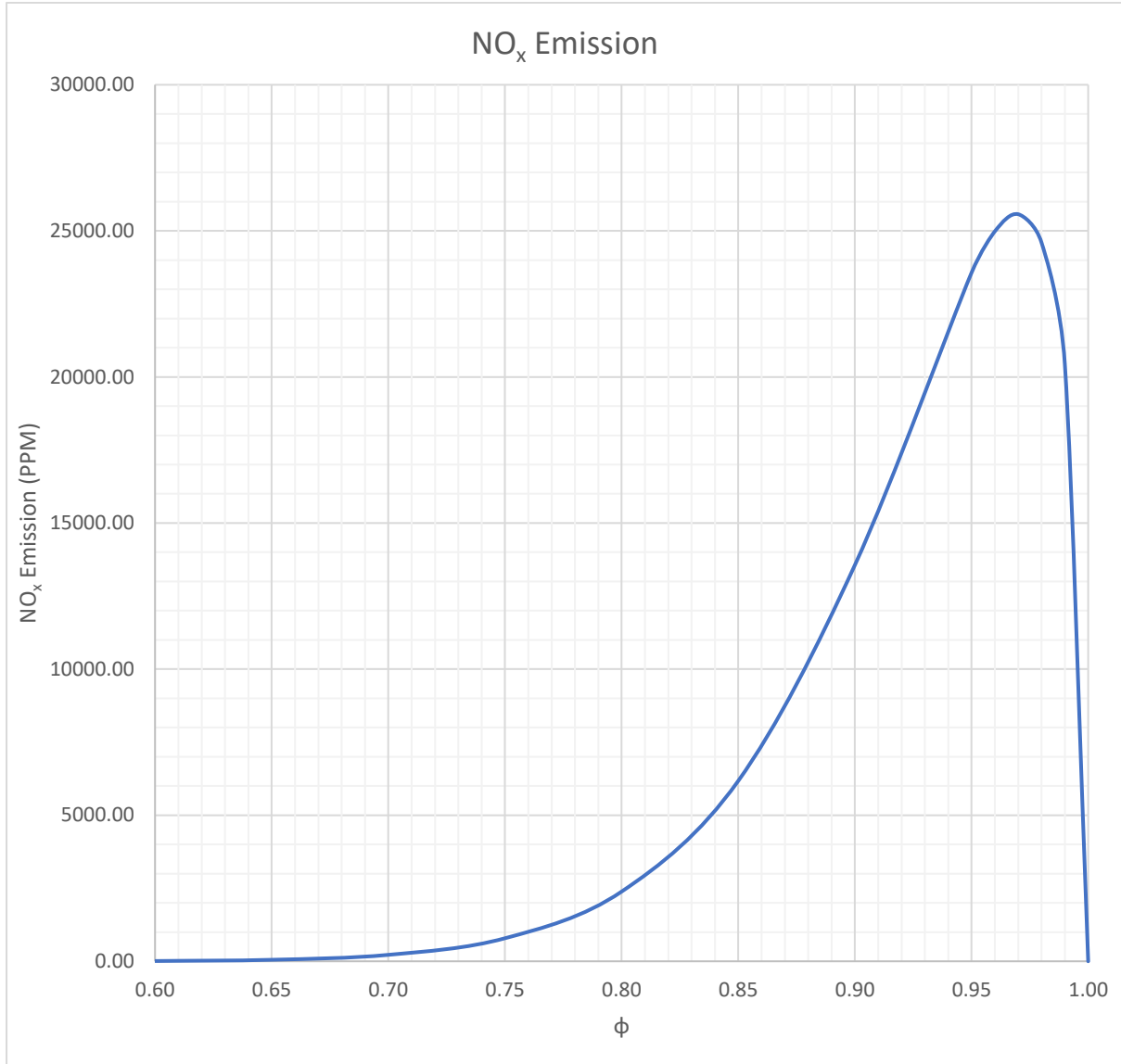


Figure 20: iso-Octane NO_x emission distribution

Figure 20 shows the NO_x PPM production as function of equivalence ratio. It shows that the peak NO_x production occurs at ϕ 0.97. This is because that is the first point at which there is a considerable quantity of O₂ and at the same time the combustion temperatures are still relatively high since the ϕ value is very close to being stoichiometric. As the ϕ decreases the NO_x production decreases due to decrease of mean cylinder temperature. Temperature has drastic effect on the Zeldovich model due to it being inside the 'exp' function, as shown by Equation 6 and Figure 21. The assumption of complete combustion skews the results, as in real scenario the excess of O₂ would still be present even at ϕ values over 1.0, not to mention the many more chemical mechanisms which would be present. As such, author believes that the real peak of NO_x PPM production is higher than what is displayed by Figure 20. Author also believes the N₂ and Σ_{exh} value changes to have very little effect on NO_x production since their corresponding values stay virtually the same.

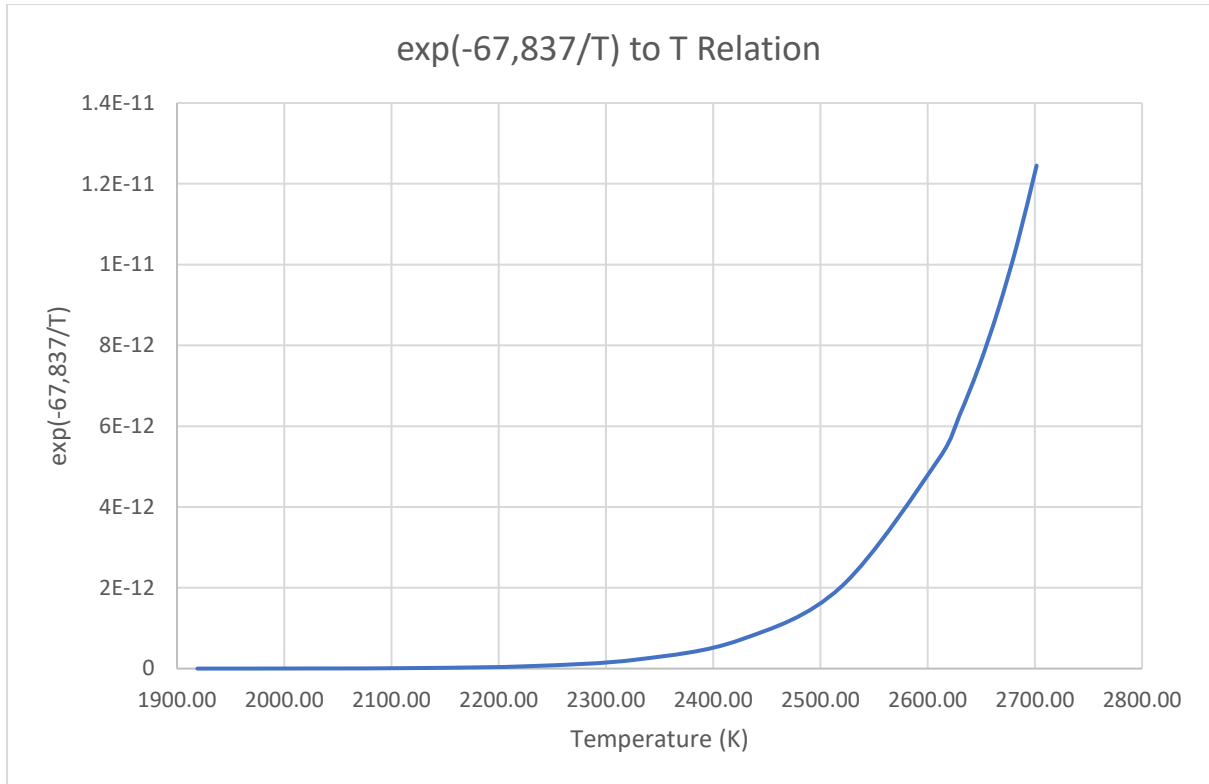


Figure 21: $\exp(-67,837/T)$ to T Relation

3.3.2 Effects of EGR on Iso-Octane NO_x production

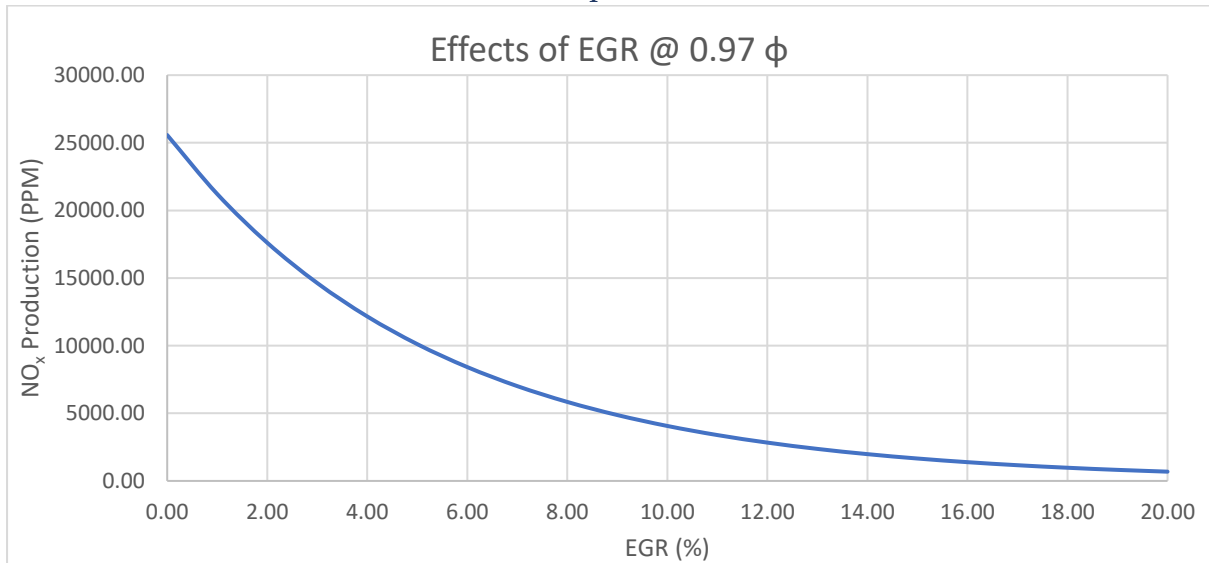


Figure 22: Effects of EGR @ 0.97 ϕ

Figure 22 shows the effects of the introduction of EGR into the combustion chamber. The NO_x production decreases in a logarithmic fashion as the EGR increases. This is due to the introduction of non-combustible substance (EGR), meaning it is unable to release any energy. As a result, this substance can only absorb the energy produced by the reaction of iso-Octane with air, reducing the mean cylinder temperature and as a result, decreasing the likelihood of O_2 and N_2 reaction, which causes the formation of NO. This is better shown by Figure 23.

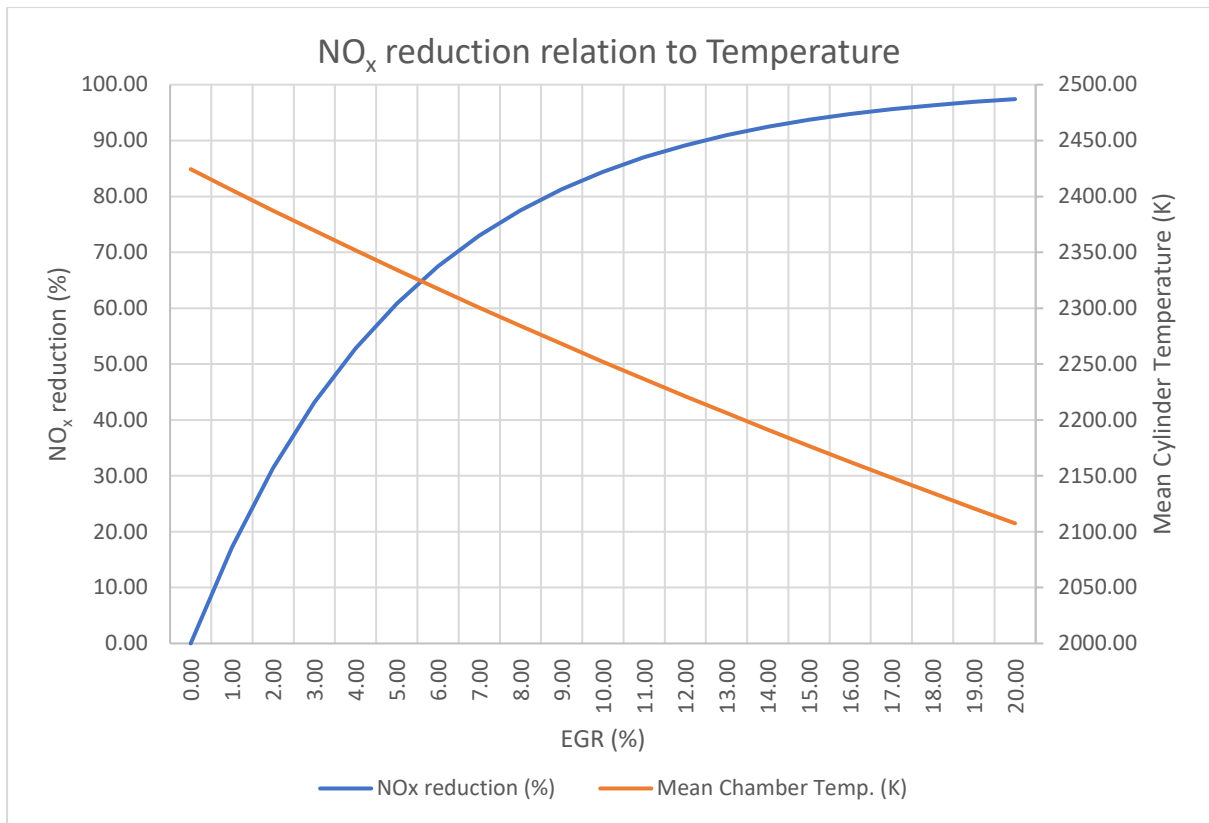


Figure 23: NO_x reduction relation to Temperature

3.3.3 Relations

3.3.3.1 NO_x reduction & EGR

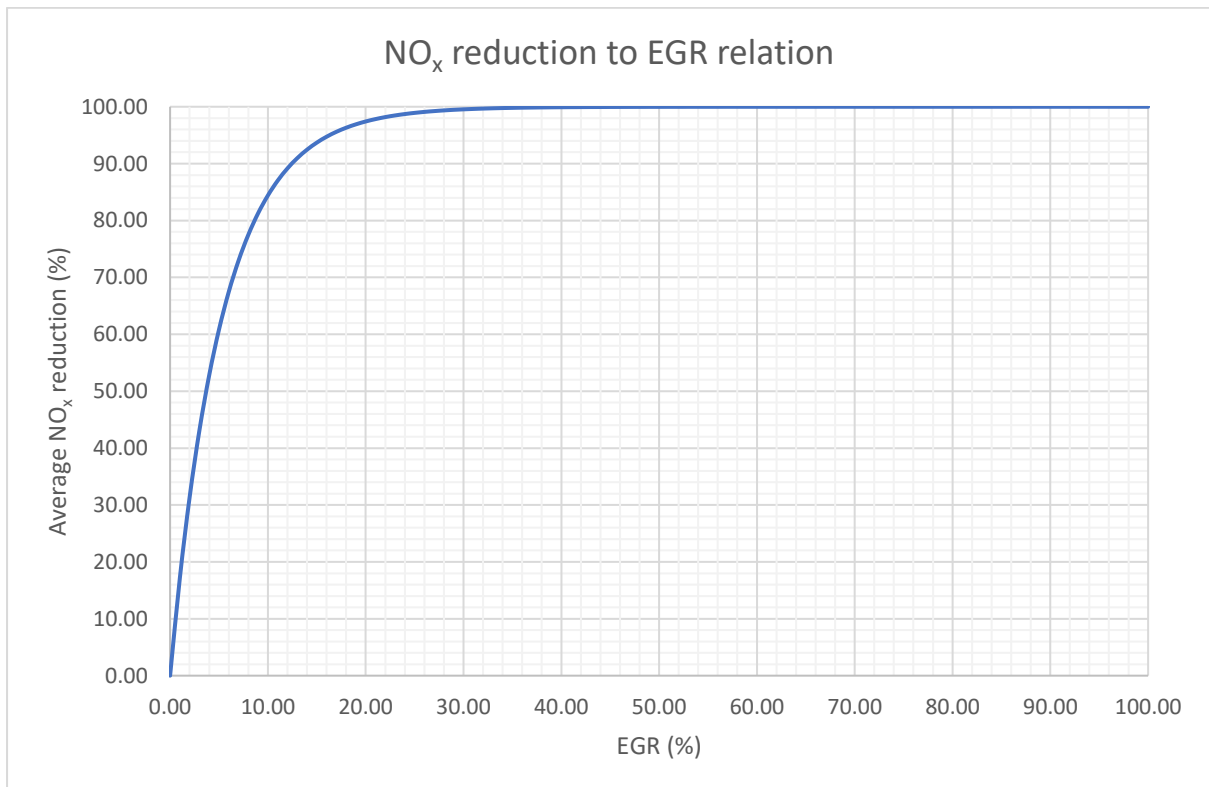


Figure 24: NO_x reduction to EGR relation

Figure 24 shows that as EGR increases the average NO_x reduction increases in logarithmic fashion. It also shows this to occur at a high rate, since at 10% EGR the NO_x is reduced by 84.41% and at 30% EGR the NO_x has been practically eliminated, which means that further increase of EGR doesn't have any advantages.

3.3.3.2 Mean Chamber Temperature & NO_x reduction

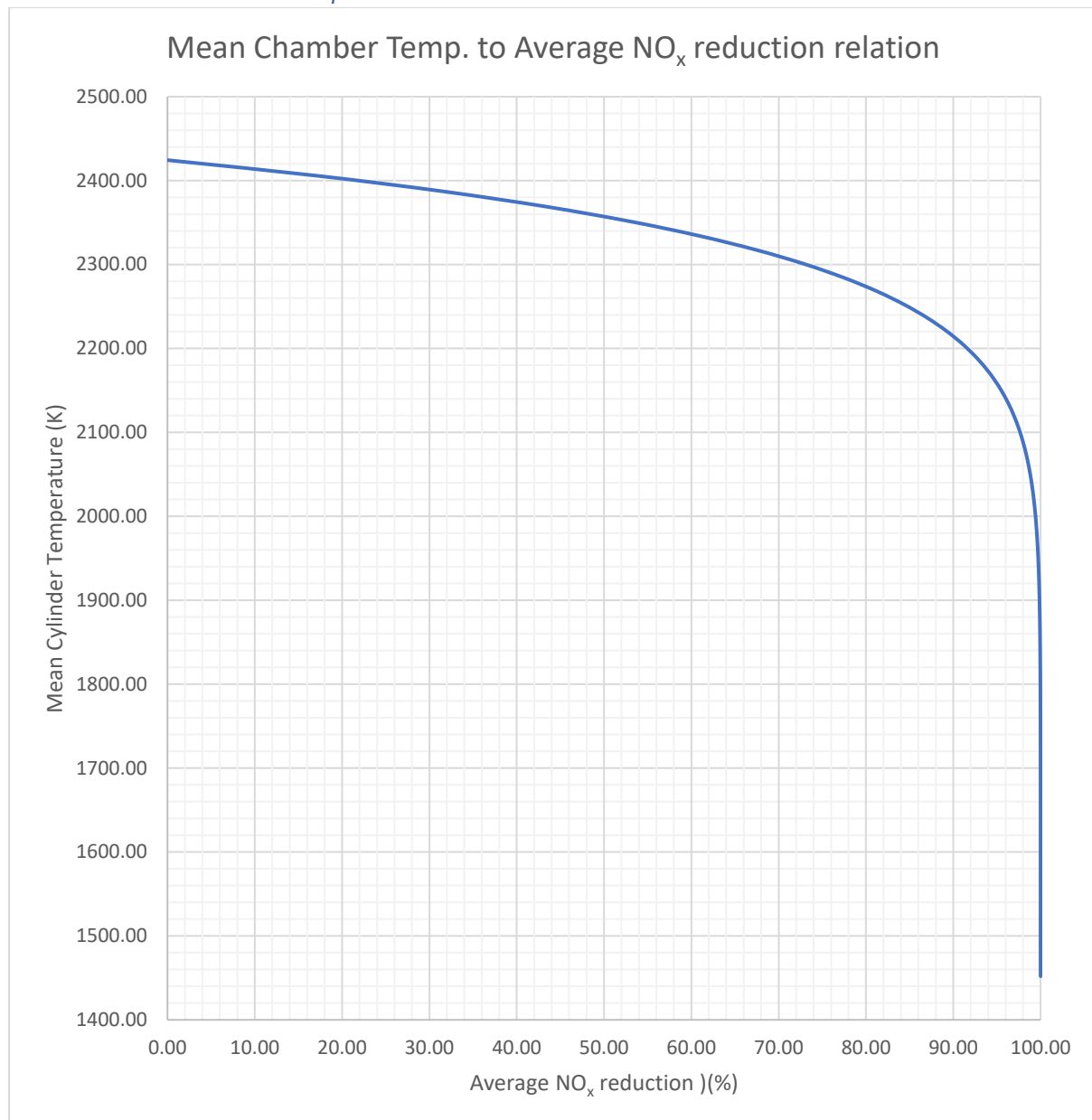


Figure 25: Mean Chamber Temp. to Average NO_x reduction relation

Figure 25 shows that as the mean cylinder temperature decreases the average NO_x reduction increases in logarithmic fashion. This shows that there is a clear relation between temperature reduction and NO_x reduction. This also shows that the first 80% average NO_x reduction can be achieved with a mere 160K reduction. Whereas the next 20% average NO_x reduction requires additional mean cylinder temperature reduction of 550K, making it difficult to justify the complete elimination of NO_x production solely with the introduction of EGR.

3.3.3.3 Mean Chamber Temperature & EGR

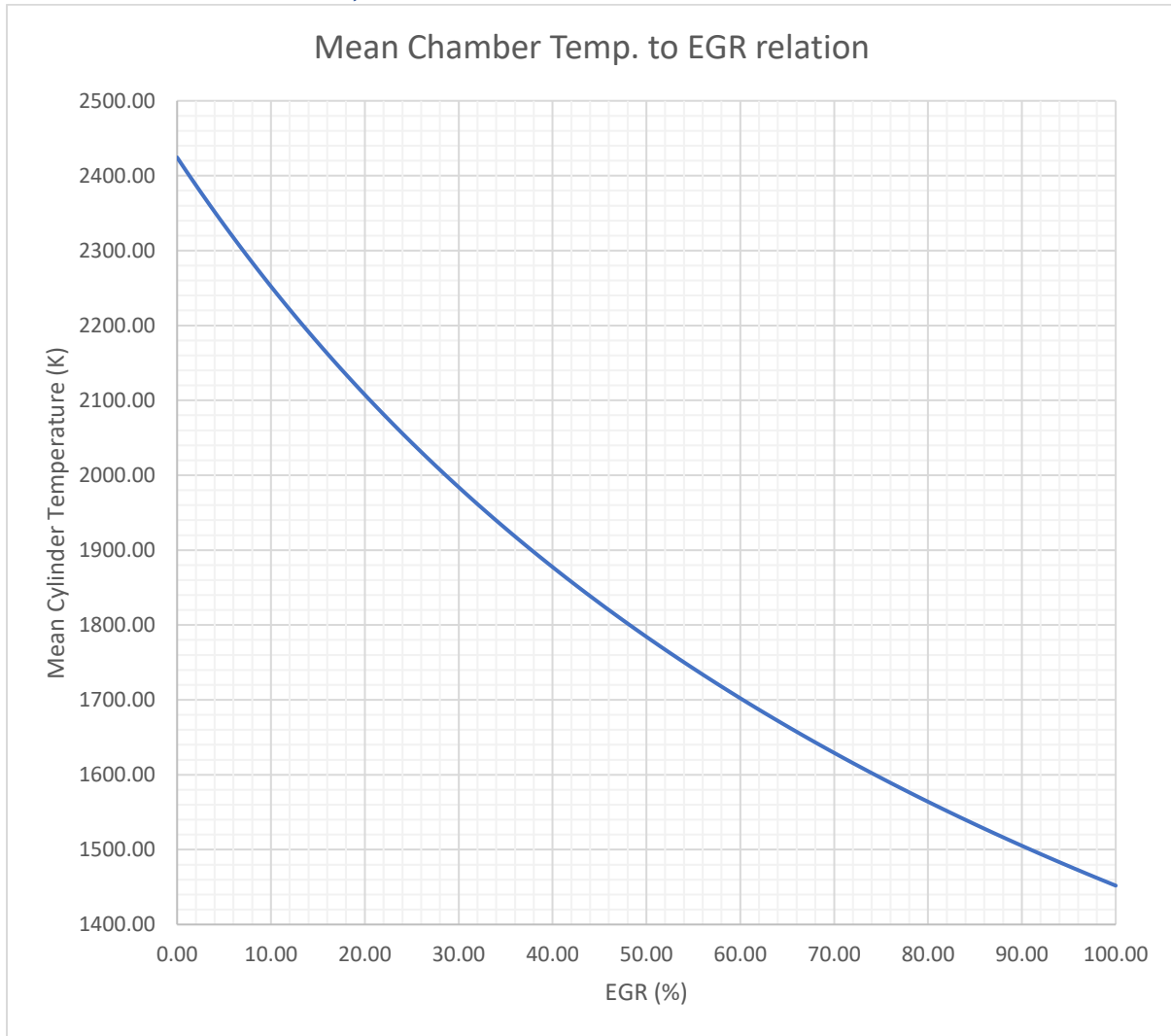


Figure 26: Mean Chamber Temp. to EGR relation

Figure 26 shows that as more EGR is introduced the mean cylinder temperature reduction will increase. Furthermore, the gradient shows that as EGR is increased, the further increase of EGR causes the effect to weaken. However, this relation doesn't have a big effect on the NO_x production due to the relatively low EGR values which are required.

3.3.4 NO_x Production from Bio-Fuel Blends

It has become popular to introduce ethanol (alcohol species from the bio-fuel family) into the gasoline fuel blend, commonly sold from the pumps at the fuel stations. The most common blends are E5 (5% ethanol content) and E10 (10% ethanol content). In other countries like Australia a common fuel alternative to standard 'unleaded' petrol is E85 (commonly 51% to 85% ethanol content), it is most commonly chosen for its performance potential due to higher anti-knock properties, 108 MON vs 90 MON (Minnesota BioFuels Association Dev, 2019) for the standard gasoline counterpart, although these values will largely vary on the very specific blends created batch to batch. It is important to investigate the effects of ethanol content on NO_x emissions. The other effects such as the LHV or specific CO₂ production will have very similar principles to those talked about in section 2.3.

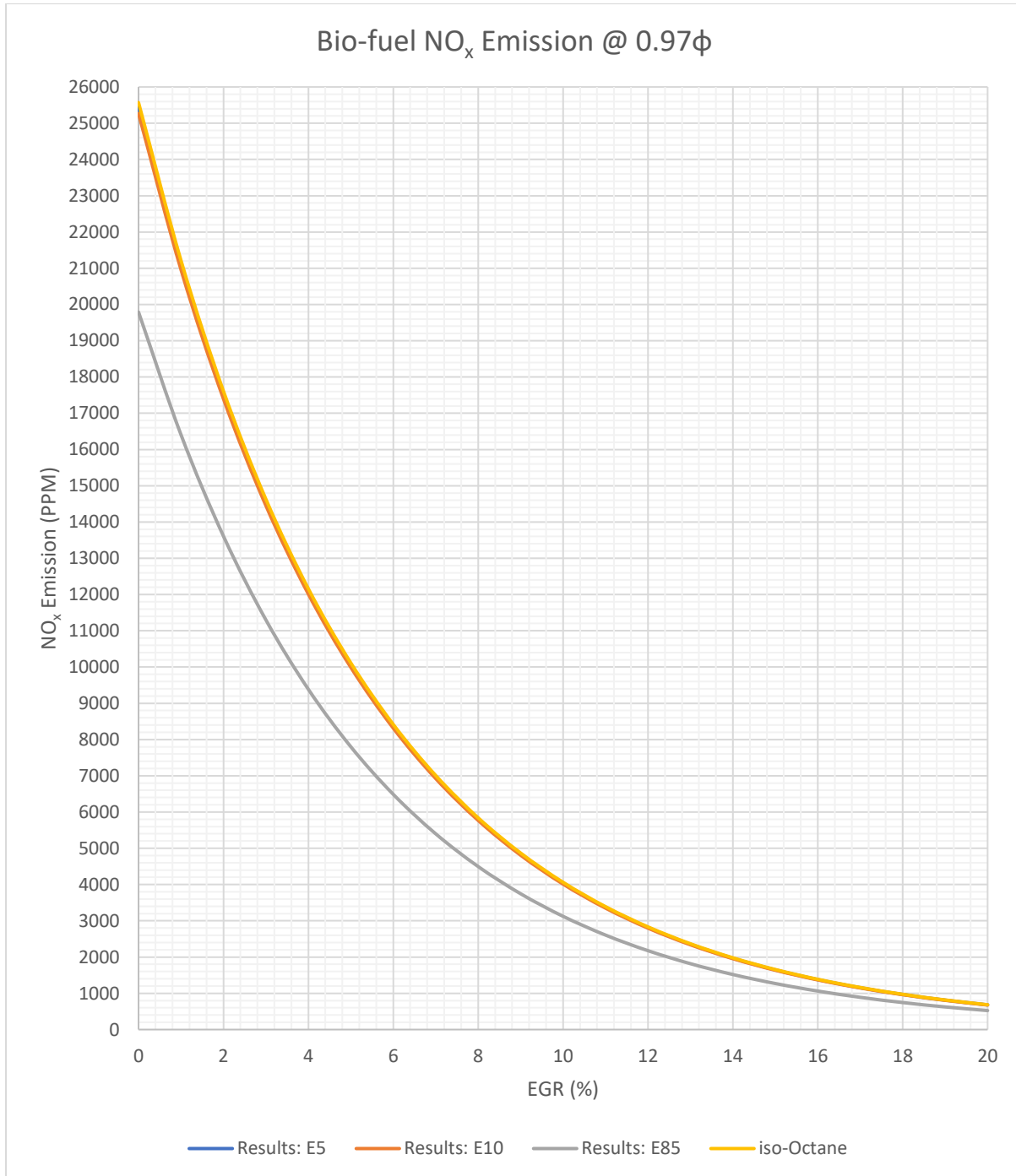


Figure 27: Bio-fuel NOx Emission @ 0.97φ

Figure 27 shows the comparison of NOx emissions @ 0.97 φ between iso-Octane, E5, E10 and E85 fuel blends. It is clear that small ethanol content has minuscule effects on NOx production. However, when ethanol quality is high, such as in the case of E85, the NOx is reduced by 22.6% with no EGR. This is due to the reduction of O₂ and N₂ reactants by 65.8% and 64.6% respectively, which is caused by richer stoichiometric AFR. The flame temperature, however, stays practically the same due to almost the same ratio between carbon, hydrogen and oxygen reactants. Sadly, this doesn't scale well with the introduction of EGR. This is because all fuel blends will have the same asymptotic nature towards the point of no emitted NOx. The reduction of NOx can be further explained by Figure 28.

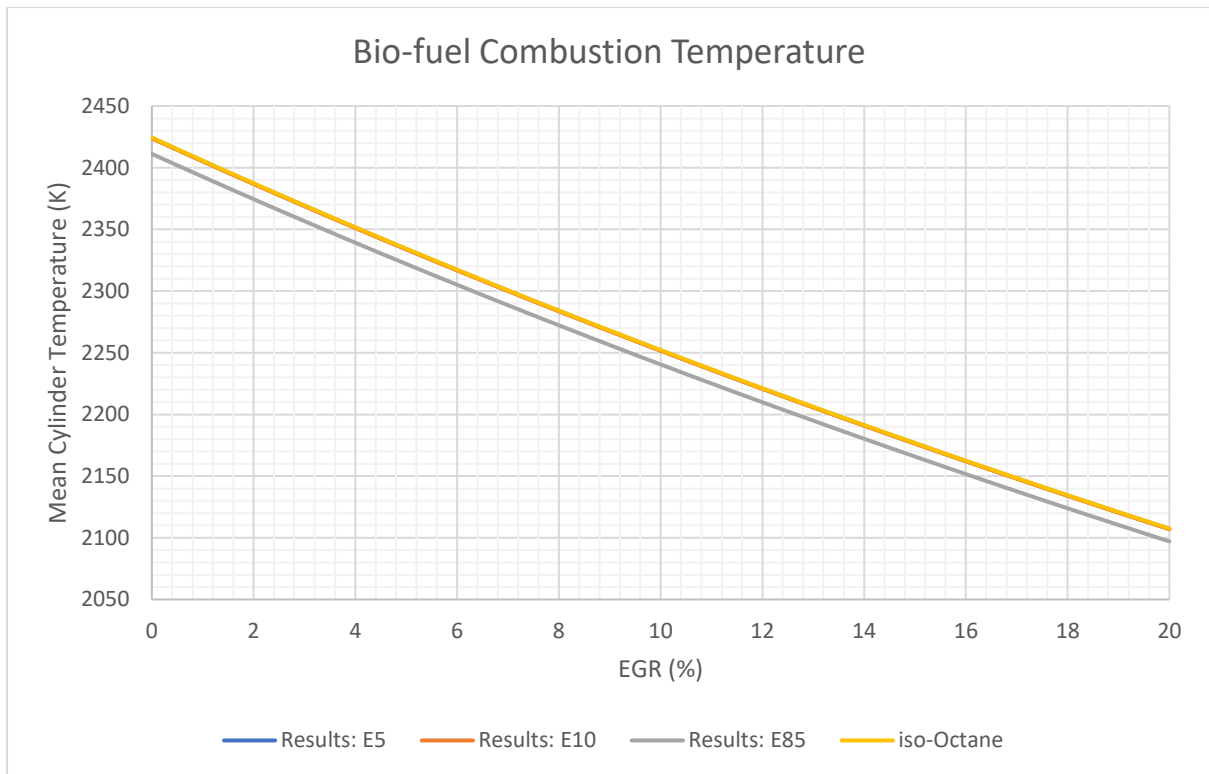


Figure 28: Bio-fuel Combustion Temperature

Figure 28 shows that the same mean cylinder temperature occurs at 0.8% EGR earlier for E85 than for iso-Octane, this explains why the NO_x production from Figure 27 for E85 occurs at lower EGR compared to iso-Octane.

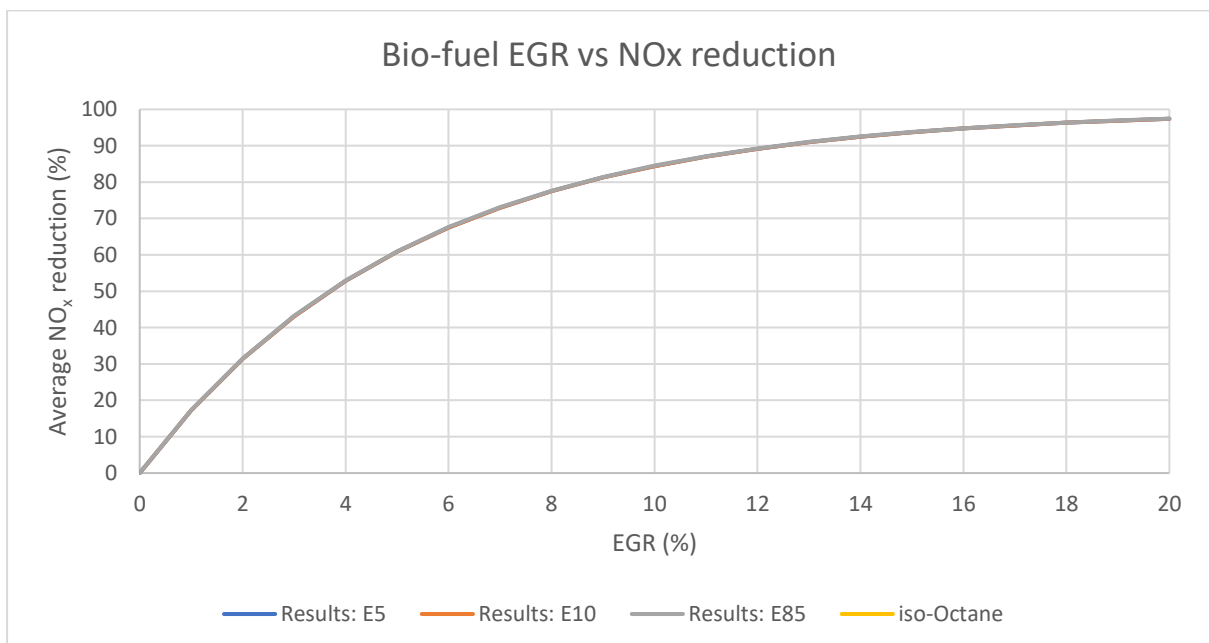


Figure 29: Bio-fuel EGR vs NO_x reduction

Lastly, Figure 29 shows that all investigated fuels have the same parabolic in nature relation between average NO_x reduction (as a %) and the introduction of EGR, this is due to dimensionless axis.

4 Conclusion

The work displayed in section 2 shows that it is possible to calculate all important fuel blend characteristics with great confidence, as long as appropriate chemical balance equations are used. However, the fuel blend model created by author is incomplete as it doesn't consider other substances such as anti-gelling or octane additives, which alter the reaction. Author's model also doesn't consider the engine specific effects on the reaction, such as: spark formation, flame formation, chamber geometry, in-cylinder turbulence, wall temperatures (which will alter depending on the heat release), fuel deposition, after combustion reactions (mainly in the exhaust) etc. Due to the complexity of such model, author has decided it to be beyond the scope of this investigation.

Furthermore, author believes the model from section 3 to be good enough for the comparative use, e.g. the % of difference due to an effect which is included in the model, such as the introduction of EGR, different fuel species or leaner AFR. Author is aware that due to the reasons already mentioned, as well as the severe simplification of the combustion process, specially the NO_x formation, of which author only attempted to model a single reaction, the NO_x model from section 3 is believed to retrieve over estimated absolute values. This is mainly due the lack of reverse formation rate, which would cause a decrease in the simulated NO_x production PPM values.

Author is aware of more advanced NO_x modelling methods, such as the Advanced Zeldovich model which attempts to improve the modelling accuracy by accounting for more physical phenomena, such as a reaction reverse rate. However, author believes the usage of such models in constant volume, 0D, models such as the one showcased in section 3 to be severely undesirable since much more accurate modelling techniques employed by software packages such as ANSYS Chemkin or even more advanced Converge (due to the implementation of the previously discussed points as well as extra dimensions compared to Chemkin) are available. This makes modelling methods the likes of Advanced Zeldovich model extremely unoptimized for professional applications.

5 References

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Wolk, B. M., 2014. Fundamental Interactions in Gasoline Compression Ignition Engines with Fuel.

6 Appendix

Fuel Table																
Formula	Fuel	Carbon	Hydrogen	Oxygen	M (kg/kmol)	Tb (°C)	cp _{ga} (kJ/kg·K)	T _{ig} (°C)	HHV (MJ/kg)	LHV (MJ/kg)	h _f gb (kJ/kg)	AFRs	T _f (K)	h (kJ/mol)	RONd	MONE
CH4	Methane	1	4	0	16.04	161	2.21	537	55.536	50.048	510	17.2	2,226	74.4	120	120
C2H2	Acetylene	2	2	0	26.04	84	1.6	305	49.923	48.225	—	13.2	2,540	8.7	50	50
C2H4	Ethylene	2	4	0	28.05	104	1.54	490	50.312	47.132	—	14.7	2,380	52.4	—	—
C2H6	Ethane	2	6	0	30.07	89	1.75	472	51.902	47.611	489	16.1	2,370	83.8	115	99
C3H8	Propane	3	8	0	44.1	42	1.62	470	50.322	46.33	432	15.7	2,334	104.7	112	97
C4H10	n-Butane	4	10	0	58.12	0.5	1.64	365	49.511	45.725	386	15.5	2,270	146.6	94	90
C4H10	iso-Butane	4	10	0	58.12	12	1.62	460	49.363	45.577	366	15.5	2,310	153.5	102	98
C5H12	n-Pentane	5	12	0	72.15	36	1.62	284	49.003	45.343	357	15.3	2,270	173.5	62	63
C5H12	iso-Pentane	5	12	0	72.15	28	1.6	420	48.909	45.249	342	15.3	2,310	178.5	93	90
C6H14	n-Hexane	6	14	0	86.18	69	1.62	233	48.674	45.099	335	15.2	2,271	198.7	25	26
C6H14	iso-Hexane	6	14	0	86.18	50	1.58	421	48.454	44.879	305	15.2	2,300	207.4	104	94
C7H16	n-Heptane	7	16	0	100.2	99	1.61	215	48.438	44.925	317	15.2	2,273	224.2	0	0
C8H18	n-Octane	8	18	0	114.23	126	1.61	206	48.254	44.786	301	15.1	2,275	250.1	20	17
C8H18	iso-Octane	8	18	0	114.23	114	1.59	418	48.119	44.651	283	15.1	2,300	259.2	100	100
C9H20	n-Nonane	9	20	0	128.6	151	1.61	—	48.119	44.688	295	15.1	2,274	274.7	—	—
C10H22	n-Decane	10	22	0	142.28	174	1.61	210	48.002	44.599	277	15.1	2,278	300.9	41	38
C10H22	iso-Decane	10	22	0	142.28	171	1.61	—	48.565	44.413	—	15.1	2,340	—	113	92
C12H26	n-Dodecane	12	26	0	170.33	216	1.61	204	47.838	44.574	256	15	2,276	350.9	88	90
CH4O	Methanol	1	4	1	32.04	65	1.37	385	22.663	19.915	1,099	6.5	2,183	201.5	106	92
C2H6O	Ethanol	2	6	1	46.07	78	1.42	365	29.668	26.803	836	9	2,144	235.1	107	89
H2	Hydrogen	0	2	0	2.02	253	14.47	400	141.72	119.96	451	34.3	2,345	0	—	—

Appendix 1: Fuel Table from the Database sheet