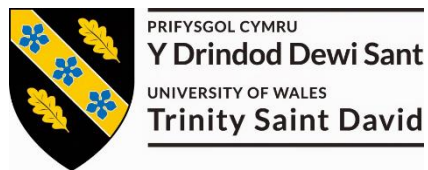


Formation and Destruction of Nitrogen Oxides

M6X00417

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School of Automotive Engineering



'This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has lead to the award of a degree.'

Signed: Tristan Reed

Date: 24/04/2018

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1. Abstract

The report focuses on the theoretical production of nitrogen oxide gases which are harmful to the environment and must be limited to pass emissions tests. The theory that has been researched and used to create this model has been explained in detail from the start of combustion temperature modelling through to the theoretical production of nitrogen oxides using two different equations. The theoretical data produced has then been compared to the actual engine data that has been acquired for the Ford Fox Engine which is a 1 litre 3-cylinder gasoline turbo direct injection engine. The comparisons are then used to check the accuracy of the model produced and a conclusion taken from this has been written. From this conclusion suggestions for improvements on the model have been completed.

2. Objectives

The aim of this dissertation is to create a theoretical model for the production of nitrogen oxides during combustion. The theoretical model must then be compared to real data to acquire a comparison to base how accurate the theoretical model is. Using data taken from the Ford Fox engine this comparison can be achieved. As well as the accuracy of another aim for this model is to be able to see from the results how the production and destruction of nitrogen oxides occurs, and which mechanisms govern this behavior. Through analysis of the results it should be possible to see which parts of the model work more accurately than others and come to logical conclusions as to why this might happen. From these conclusions suggestions can be made for further improvement to make the model more accurate.

3. Theory and Application

This section will cover the theory and methodology used in the combustion model. All the following methods and equations have been used over the full 2 revolution, 4 stroke cycle for 15 different RPM's using the data from the Ford Fox engine.

3.1. POLYTROPIC PROCESS

The calculated theoretical pressure values for the compression and expansion regions of the two-revolution combustion cycle can be predicted using the laws of the polytropic process. The polytropic process is essentially a combination of the isothermal and isentropic processes, for a system to abide by the laws of isothermal compression/expansion the temperature conditions must be constant. Therefore, an ideal isothermal process must occur very slowly. Whereas this is the opposite for an ideal isentropic process which must occur very fast to avoid losses through heat energy. By combining these two processes more realistic theoretical pressure data can be calculated as the speed of the compression/expansion process falls somewhere between that of the isothermal and isentropic processes. At this point it should be noted

that this calculation method's results may be inaccurate during the intake and exhaust phases of the 4-stroke cycle, the reason for this being the fact that at these points the system is not closed as there will be an open valve allowing for air flow and therefore a dissipation of pressure from within the cylinder. The polytropic process is governed by the following equation:

$$pV^n = \text{Constant} \quad (1)$$

Where p is the pressure, V is the cylinder displacement and n is the polytropic index, which has different values for compression and expansion. For most engines this value falls between 1 and 1.4. As pV^n is equal to a constant value the following equation is true and can be rearranged to calculate the rise and fall in pressure.

$$p_1 V_1^n = p_2 V_2^n \quad (2)$$

$$p_2 = p_1 \left(\frac{V_2}{V_1} \right)^n \quad (3)$$

Where P_1 and P_2 are the initial and final pressures respectively and V_1 and V_2 are the initial and final displacement volume respectively. To use this equation the value for n , the polytropic index must first be calculated. This can be done with a bit of simple data manipulation.

$$\text{Log}(P) + \text{Log}(V^n) = \text{Constant} \quad (4.1)$$

$$\text{Log}(P) + n\text{Log}(V) = \text{Constant} \quad (4.2)$$

$$\therefore \text{Log}(P_1) + n\text{Log}(V_1) = \text{Log}(P_2) + n\text{Log}(V_2) \quad (4.3)$$

$$n(\text{Log}(V_1) - \text{Log}(V_2)) = \text{Log}(P_2) - \text{Log}(P_1) \quad (4.4)$$

$$n = \frac{\text{Log}(P_2) - \text{Log}(P_1)}{\text{Log}(V_1) - \text{Log}(V_2)} \quad (4.5)$$

By plotting the logarithm of the volume data vs the logarithm of the pressure data a graph similar to the following is produced.

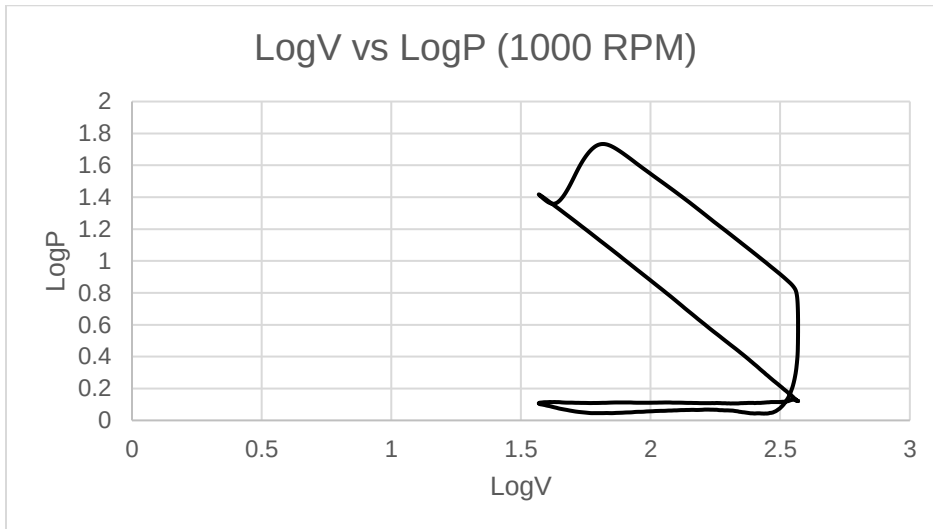


Figure 1a

The gradient of the straight lines produced in this graph are the polytropic indexes for compression (lower line) and expansion (higher line). An average is taken from the last 20 degrees before compression ends i.e. 20 degrees before the start of combustion. For expansion the same is done from 20 degrees after combustion occurs. These polytropic indexes can then be used in equation 3 to predict engine pressures as if combustion did not occur.

3.2. LOCATING COMBUSTION

The crank angle range in which combustion starts and ends can be located by using the calculated theoretical engine pressures without combustion. By comparing this with the engine data provided it is possible to locate combustion and its duration in the following way. The results from the polytropic process pressure calculations will not have a spike of pressure where combustion occurs whereas the real data does. By comparing the difference between the pressures, the start of combustion can be seen when the difference between the two becomes positive.

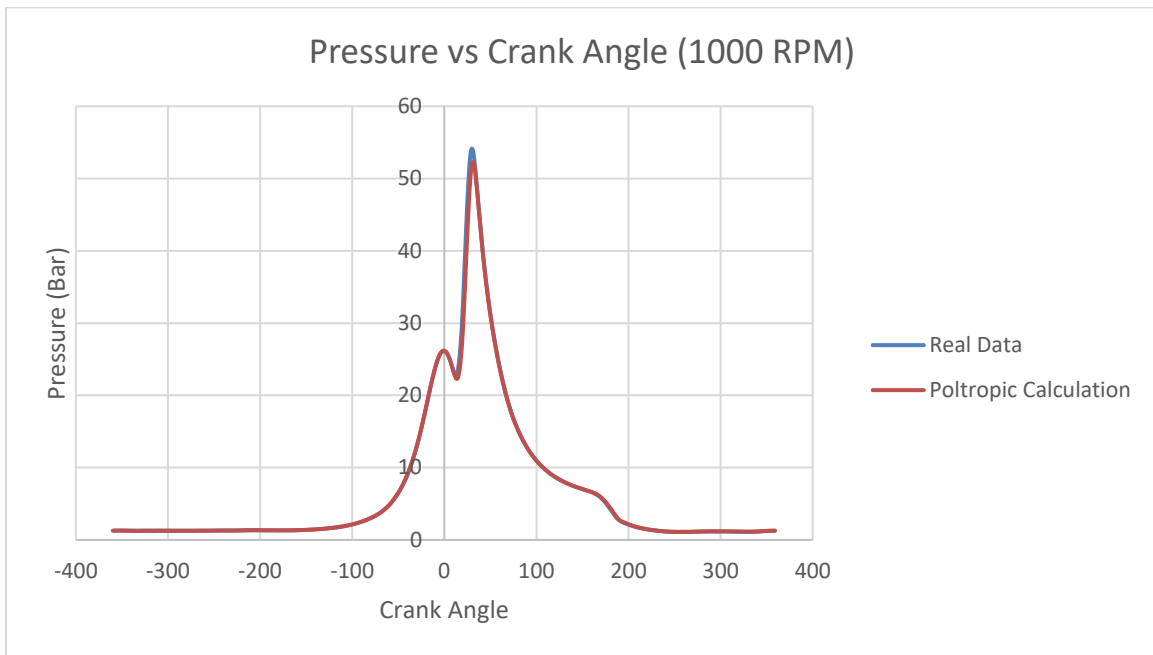


Figure 2a

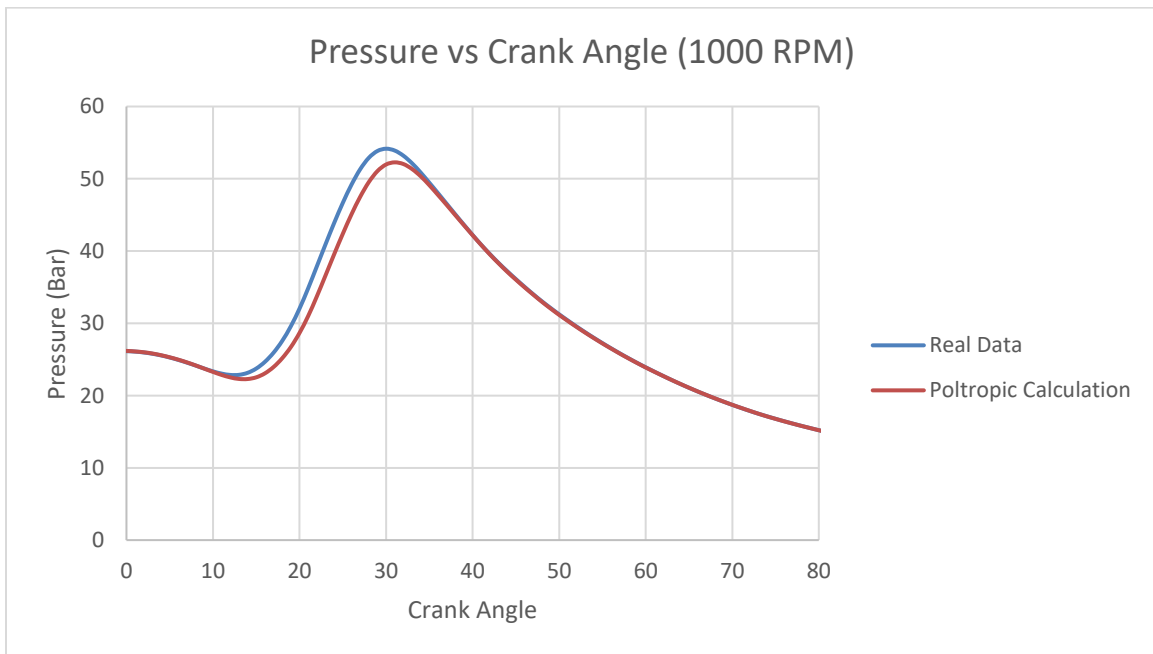


Figure 3a

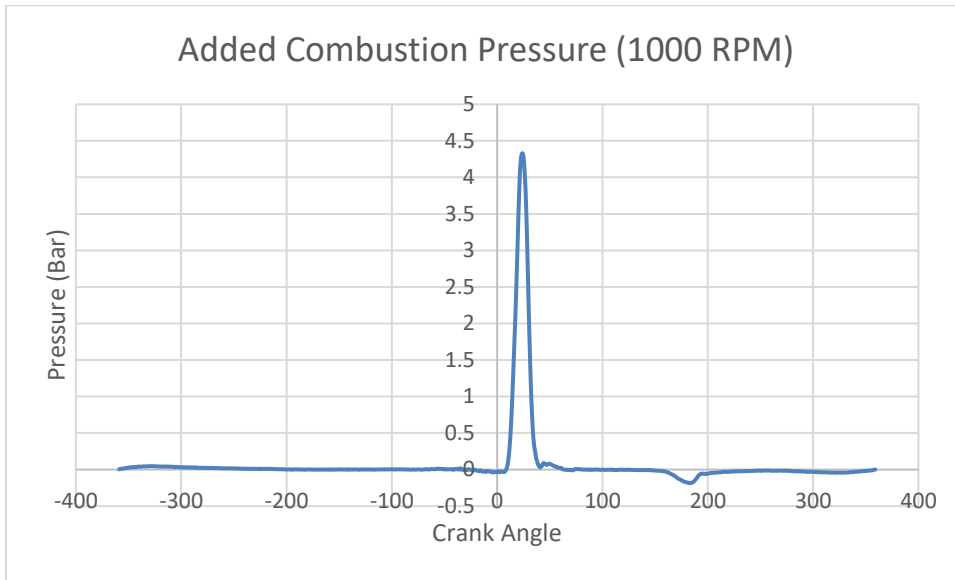


Figure 4a

Figures 2a and 3a show what this looks like when the real data is plotted alongside the calculated pressures and figure 4a shows the difference between the two i.e. the added pressure during combustion.

3.3. MASS FRACTION BURNED

The added pressures can be used show the way in which the fuel burns. This is referred to as the mass fraction burned (MFB). The MFB can be calculated by dividing the combustion pressure at each degree by the sum of the extra pressures during combustion. When plotted against crank angle a graph like figure 5a is produced.

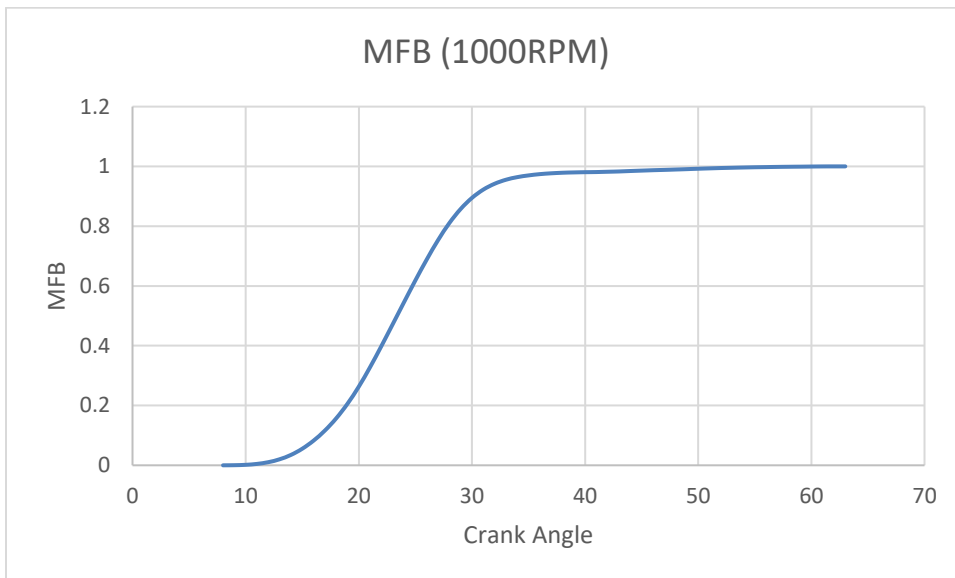


Figure 5a

The basic equation for this MFB curve is called the Wiebe Function and is as follows:

$$x_b = 1 - \exp \left[-a \left(\frac{\theta - \theta_0}{\Delta\theta} \right)^{m+1} \right] \quad (5)$$

Where θ is the crank angle, θ_0 is the angle at the start of combustion, $\Delta\theta$ is the burn duration and a and m are adjustable parameters.

3.4. TWO-ZONE COMBUSTION TEMPERATURE MODELLING

Combustion inside the cylinder can be modelled in several different ways. However, without the use of FEA (finite element analysis) or CFD (computational fluid dynamics) programs this becomes limited. A 2-zone model therefore seems plausible without the use of such programs. As the name suggest there are two zones in this model, the unburned zone and the burned zone. Each zone has a different pressure and temperature. The burned zone is the zone in which combustion is occurring/ has already occurred. Starting with a very small volume when the spark ignites and eventually “consuming” the entirety of the cylindrical volume. The unburned zone is everything else. The burned zone is essentially following the flame front over the duration of combustion.

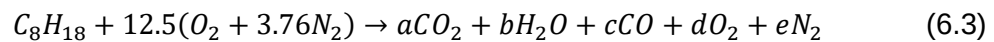
3.4.1. Specific Gas Constants

For both zones in the combustion models a rearrangement of the ideal gas law equation is used. This is only used up until the start of combustion for the unburned zone.

$$pV = mRT \quad (6.1)$$

$$T = \frac{pV}{mR} \quad (6.2)$$

Because there's a mixture of fuel, air and recirculated exhaust gases (EGR) a specific gas constant (R) must be calculated throughout the combustion duration. There is a different specific gas constant in each zone as the burned zone contains the products from the reaction and the unburned zone contains the reactants. Using the general equation for combustion for isooctane shown in equation 6.3 the specific gas constant can be calculated as show in equations 6.4-6.17.



$$R = \frac{\tilde{R}}{M} \quad (6.4)$$

The specific gas constant is R and is equal to the universal gas constant $\tilde{R}$ divided by the molar mass of the species in question M . a, b, c, d and e can be calculated in the by balancing either side of the equation.

When the mixture is rich there will initially be no production of carbon monoxide and when the mixture is lean there is initially no production of oxygen. For rich mixtures the values a, b, d and e are calculated in the following way:

$$a = 8\phi \quad (6.5)$$

$$b = 9\phi \quad (6.6)$$

$$d = \frac{25 - 2a - b}{2} \quad (6.7)$$

$$e = 47 \quad (6.8)$$

For lean mixtures the values for a, b, c and e are calculated as follows.

$$a = 25 - b - 8\phi \quad (6.9)$$

$$b = 9\phi \quad (6.10)$$

$$c = 8\phi - a \quad (6.11)$$

$$e = 47 \quad (6.12)$$

Where ϕ is the fuel-air equivalence ratio. The fuel-air equivalence ratio is calculated from the λ values taken from the Ford engine data:

$$\phi = \frac{1}{\lambda} \quad (6.13)$$

The specific gas constants for reactants and products are calculated respectively as follows, the second equation includes the molar masses for each molecule.

$$R_{reactants} = \frac{\phi C_8H_{18} + 12.5 \times (O_2 + (3.76 \times N_2)) + EGR\% \times (aCO_2 + bH_2O + cCO + dO_2 + eN_2)}{\phi + 12.5 \times (1 + 3.76) + EGR\%(a + b + c + d + e)} \quad (6.14)$$

$$R_{reactants} = \frac{\phi 114 + 12.5 \times (32 + (3.76 \times 28)) + EGR\% \times (a44 + b18 + c28 + d32 + e28)}{\phi + 12.5 \times (1 + 3.76) + EGR\%(a + b + c + d + e)} \quad (6.15)$$

$$R_{products} = \frac{(1 + EGR\%) \times (aCO_2 + bH_2O + cCO + dO_2 + eN_2)}{(1 + EGR) \times (a + b + c + d + e)} \quad (6.16)$$

$$R_{products} = \frac{(1 + EGR\%) \times (a44 + b18 + c28 + d32 + e28)}{(1 + EGR) \times (a + b + c + d + e)} \quad (6.17)$$

Where EGR% represents the percentage of exhaust gas recirculation, the data for this is available from the Ford data.

3.4.2. Unburned Zone Temperature Modelling

Prior to combustion the entire volume of the cylinder is represented by the unburned zone. The temperatures can be calculated using equation 6.2, where R is the specific gas constant for the reactants as combustion is yet to occur. The mass (m) represents the mass of the fuel, air and EGR inside the cylinder and can be calculated using the fuel flow data taken from the Ford data. The data for fuel flow is given in kilogram per hour. This can be converted to kilogram per revolution and then to kilogram per 2 revolution cycle per cylinder. Now with a known fuel mass the Ford data can be referenced for the air-fuel ratio and EGR% and a total mass inside the cylinder can be calculated.

3.4.2.1. Isentropic Expansion

During combustion the temperatures of the unburned zone can be modelled according to the laws of isentropic expansion. The reason we can do this is that the cylinder is now a closed system due to both intake and exhaust valves being closed at this point. Because of this we can assume that over the duration of combustion there is no change in entropy within the system. With this assumption the formula for isentropic expansion can be derived in the following way. The entropy of a gas in its specific form is:

$$s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right) \quad (7.1)$$

Where s_1 and s_2 are the initial and final values for entropy, c_p is the specific heat at constant pressure, T_1 and T_2 are the initial and final temperatures, R is the universal gas constant and p_1 and p_2 are the initial and final pressures. We know there is no change in entropy so $s_2 - s_1 = 0$ therefore,

$$c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right) = 0 \quad (7.2)$$

$$c_p \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{p_2}{p_1}\right) \quad (7.3)$$

This can be divided by c_p and take the exponential function from each side to get rid of the natural logarithm.

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{p_2}{p_1}\right)^{\frac{R}{c_p}} \quad (7.4)$$

Next, we need to use the ratio of specific heats denoted by the symbol gamma which has the following law:

$$\gamma = \frac{c_p}{c_v} \quad (7.5)$$

Where c_v is the specific heat at constant volume. Using the equation 7.5 and 7.6 the equation 7.9 can be formed.

$$R = c_p - c_v \quad (7.6)$$

$$\frac{R}{c_p} = 1 - \frac{c_v}{c_p} \quad (7.7)$$

$$\frac{R}{c_p} = 1 - \frac{1}{\gamma} \quad (7.8)$$

$$\frac{R}{c_p} = \frac{\gamma - 1}{\gamma} \quad (7.9)$$

By substituting equation 7.9 into equation 7.4 we get the equation for isentropic expansion/compression. Which can be rearranged to calculate the new temperature at each degree, shown in equation 7.11.

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} \quad (7.10)$$

$$T_2 = T_1 \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} \quad (7.11)$$

3.4.2.2. Calculating the Ratio of Specific Heats

To be able to use the equation for isentropic expansion the ratio of specific heats must be calculated. This can be done by calculating the specific heat at constant pressure of the species involved. For the mixture of molecules in the air the following equation can be used:

$$c_p = R(a_{i1} + a_{i2}T + a_{i3}T^2 + a_{i4}T^3 + a_{i5}T^4) \quad (8.1)$$

Where R is the universal gas constant, T is the temperature and all a_i values are constants taken from the NASA equilibrium code. This must be repeated for each species of molecule, c_v can then be calculated from knowing $c_v = c_p - R$ and therefore the ratio of specific heats can be calculated using $\gamma = \frac{c_p}{c_v}$. Similarly, this can be done for the fuel using the following equation:

$$c_p = A_{f1} + A_{f2}t + A_{f3}t^2 + A_{f4}t^3 + \frac{A_{f5}}{t^2} \quad (8.2)$$

Where $t = T/1000$ and A_f values are constants. Once the ratio of specific heats for the air and fuel have been calculated an appropriate value for the ratio of specific heats can be calculated for the mixture of fuel and air, depending on the fuel equivalence ratio. A polynomial of this ratio of specific heats against temperature can then be plotted for each

fuel equivalence ratio, this can then be used to calculate temperatures in the unburned zone during combustion.

3.4.3. Average Combustion Temperature Modelling

The average combustion temperature throughout the cylinder can be modelled using the ideal gas equation. A specific gas constant is required and can be calculated using the MFB.

$$R_{average} = (MFB \times R_{products}) + ((1 - MFB) \times R_{reactants}) \quad (8.3)$$

$$T = \frac{pV}{mR} \quad (8.4)$$

The average combustion temperature gives us an idea of how long it takes for the cylinder to reach the burned zone temperatures.

3.4.4. Burned Zone Temperature Modelling

The burned zone temperatures can be calculated by first calculating the volume of the burned zone.

$$V_{unburned} = \frac{((1 - MFB) \times m)R_{unburned}T_{unburned}}{p} \quad (9.1)$$

$$V_{burned} = V_{cylinder} - V_{unburned} \quad (9.2)$$

The temperature of the burned zone can then be calculated once again using the ideal gas equation.

$$T_{burned} = \frac{pV_{burned}}{(MFB \times m)R_{burned}} \quad (9.3)$$

3.5. DISSOCIATION OF MOLECULES

At high temperatures such as those that occur during combustion there is a lot of available energy. When this energy is sufficient it will overcome the forces in the bonds that hold molecules together and they will split apart to form their constituent atoms/ molecules. This is called molecular dissociation. Molecular dissociation occurs through several different ways during combustion and these dissociated molecules are key to the production and destruction of nitrogen oxides. The following is a list of the molecules that dissociate and what they dissociate to form.



3.5.1. Gibbs Free Energy

By assuming that reactions inside the combustion chamber reach equilibrium the Gibbs free energy change equation can be manipulated in the following way to calculate the rates in which dissociation occurs.

$$\Delta G = \Delta G^0 + RT \ln Q \quad (11.1)$$

Where ΔG is the Gibbs free energy change, ΔG^0 is the Standard Gibbs free energy change, R is the universal gas constant, T is the temperature and Q is the reaction quotient. When equilibrium is reached there is no change in free energy therefore $\Delta G = 0$. The equation for the reaction quotient for the reaction $aA + bB = cC + dD$ is as follows:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (11.2)$$

The reaction quotient is what designates whether the forward or reverse reactions are dominating at any time during the reaction process. This can be done by comparing Q with K , the equilibrium constant. If K is less than Q the reaction favors the reactants, where as if K is greater the reaction favors the products. At equilibrium K is equal to Q . By keeping this in mind along with ΔG being equal to 0 the following equation can be used.

$$\Delta G^0 = -RT \ln K \quad (11.3)$$

To find that equilibrium constant this can be rearranged:

$$\frac{-\Delta G^0}{RT} = \ln K \quad (11.4)$$

$$e\left(\frac{-\Delta G^0}{RT}\right) = e(\ln K) \quad (11.5)$$

$$K = e^{-\frac{\Delta G^0}{RT}} \quad (11.6)$$

Values for ΔG^0 for each molecule or atom have been acquired online from JANAF tables for the temperature range required. For any reaction:

$$\Delta G^0 = \sum \Delta G_{products}^0 - \sum \Delta G_{reactants}^0 \quad (11.7)$$

From the JANAF tables the values for ΔG^0 for all the molecular dissociation reactions can be calculated with regards to temperature. A polynomial can then be created in Matlab to enable the calculations for ΔG^0 to be possible at any of the combustion temperatures.

3.5.2. Daltons Law of Partial Pressures

Daltons law of partial pressures states that the total pressure exerted by a gas that is a mixture of molecules is the sum of the pressures of each species of gaseous molecule.

$$P = p_1 n_1 + p_2 n_2 + p_3 n_3 \dots \quad (12.1)$$

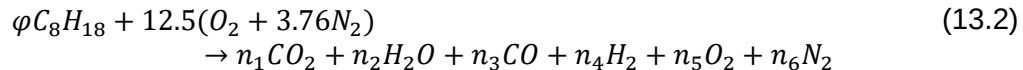
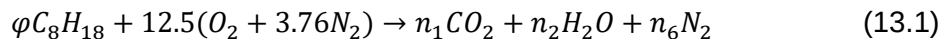
Where P is the total pressure, p_n is the partial pressure and n_n is the number of moles of a species. Therefore, the partial pressure for an individual species can be represented by equation 12.2.

$$p_x = \frac{n_x}{n_T} P \quad (12.2)$$

Where p_x is the partial pressure of a molecule, n_x is the number of moles of this molecule and n_T is the total number of moles.

3.5.3. Dissociation of Oxygen from Water and Carbon Dioxide

When oxygen dissociates from water and carbon dioxide, hydrogen gas and carbon monoxide is formed simultaneously. This means that general equation for the combustion of isooctane (13.1) must be updated (13.2)



From this equation, a set of other equations can be formed showing what we know by balancing the equation.

$$\text{Carbon} \quad 8\phi = n_1 + n_3 = n_3 \left(\frac{n_1}{n_3} + 1 \right) \quad (13.3)$$

$$\text{Hydrogen} \quad 18\phi = 2n_2 + 2n_4 \therefore 9\phi = n_2 + n_4 = n_4 \left(\frac{n_2}{n_4} + 1 \right) \quad (13.4)$$

$$\text{Oxygen} \quad 25 = 2n_1 + n_2 + n_3 + 2n_5 \quad (13.5)$$

$$\text{Nitrogen} \quad 47 = n_6 \quad (13.6)$$

By reviewing the equilibrium constant and Dalton's law of partial pressures two more equations can be acquired.

For the dissociation of CO_2 ,



At equilibrium,

$$KCO_2 = \frac{[CO_2]}{[CO][O_2]^{\frac{1}{2}}} \quad (13.8)$$

We know from the ideal gas equation that,

$$\frac{n}{v} = \frac{p}{RT} \quad (13.9)$$

Where in this case, p is the partial pressure related to a specific molecule.

By representing the concentration as $\frac{n}{v}$ we can substitute 13.9 into 13.8,

$$KCO_2 = \frac{\left(\frac{p_{CO_2}}{RT} \right)}{\left(\frac{p_{CO}}{RT} \right) \left(\frac{p_{O_2}}{RT} \right)^{\frac{1}{2}}} = \frac{p_{CO_2}}{p_{CO} \times p_{O_2}^{\frac{1}{2}}} \quad (13.10)$$

From Daltons law of partial pressures,

$$p_{CO_2} = \frac{n_1}{n_t} P \quad (13.11)$$

$$p_{CO} = \frac{n_3}{n_t} P \quad (13.12)$$

$$p_{O_2} = \frac{n_5}{n_t} P \quad (13.13)$$

By substituting this equations into the equation for the equilibrium constant for carbon dioxide we get,

$$KCO_2 = \frac{\frac{n_1}{n_t} P}{\frac{n_3}{n_t} P \times \left(\frac{n_5}{n_t} P\right)^{\frac{1}{2}}} \quad (13.14)$$

This simplifies to,

$$KCO_2 = \frac{n_1}{n_3 \times \left(\frac{n_5}{n_t} P\right)^{\frac{1}{2}}} \quad (13.15)$$

The same method can be used for the equilibrium constant for water, resulting in the equation,

$$KH_2O = \frac{n_2}{n_4 \left(\frac{n_5}{n_t} P\right)^{\frac{1}{2}}} \quad (13.16)$$

These six equations (13.3-13.6, 13.15,13.16) allow the amount of oxygen that dissociates to be calculated using the following method found in Transport Fuels and Technology by Eric M. Gooder. The method revolves around using a guessed value for the mols of oxygen divided by the total number of mols i.e. $\frac{n_5}{n_T}$. This guess is then used to calculate a value for the mols of oxygen which is divided by the total number of mols. The difference between these two values is the error, by changing the guess, the correct number of mols can be found when the error is negligible.

The following equations and diagrams will show how this is implemented into excel to give a clear methodology. The numbers down the side represent the cells depicted in the table below.

1	<i>Guess value for $\left(\frac{n_5}{n_T}\right)$</i>	(13.17)
---	--	---------

2	$\frac{n_1}{n_3} = KCO_2 \left(\frac{n_5}{n_T} P\right)^{\frac{1}{2}}$	(13.18)
---	--	---------

3	$n_3 = \frac{8\phi}{1 + \frac{n_1}{n_3}}$	(13.19)
---	---	---------

4	$n_1 = 8\phi - n_3$	(13.20)
---	---------------------	---------

$$5 \quad \frac{n_2}{n_4} = KH_2O \left(\frac{n_5}{n_T} P \right)^{\frac{1}{2}} \quad (13.21)$$

$$6 \quad n_4 = \frac{9\phi}{1 + \frac{n_2}{n_4}} \quad (13.22)$$

$$7 \quad n_2 = 9\phi - n_4 \quad (13.23)$$

$$8 \quad n_5 = \frac{25 - 2n_1 - n_2 - n_3}{2} \quad (13.24)$$

$$9 \quad \text{calculated} \frac{n_5}{n_T} \quad (13.25)$$

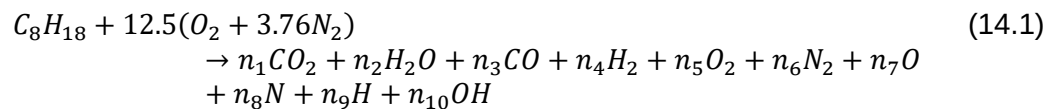
$$10 \quad \text{Error} = \text{calculated} \frac{n_5}{n_T} - \text{Guess value for } \left(\frac{n_5}{n_T} \right) \quad (13.26)$$

1	2	3	4	5	6	7	8	9	10

The solver function can be used in excel to change the guess value in cell 1 until the error is zero or as close to zero as possible.

3.5.4. Other Dissociation Mechanisms

To be able to use the extended Zel'Dovich mechanism, the following dissociation mechanisms must be calculated. Once these have been calculated the combustion equation must be further updated as follows:



The remaining mechanisms are as follows:





With polynomial equations for the equilibrium constant values calculated using the standard Gibbs free energy data found on the JANAF website these dissociations can be calculated from the following equations:

$$K_{O_2} = \frac{[O_2]}{[O][O]} \quad (14.6)$$

$$K_{O_2} = \frac{\left(\frac{n_5}{n_T} P\right)}{\left(\frac{n_7}{n_T} P\right)\left(\frac{n_7}{n_T} P\right)} \quad (14.7)$$

$$K_{O_2} = \frac{n_5}{\left(\frac{n_7}{n_T} P\right)^2} \quad (14.8)$$

$$\frac{(n_7)^2}{n_T} = \frac{n_5}{K_{O_2} \times P} \quad (14.9)$$

$$n_7 = \sqrt{\frac{(n_5 \times n_T)}{K_{O_2} \times P}} \quad (14.10)$$

The same method can be used to calculate the dissociation of the nitrogen and hydrogen gas giving similar equations:

$$n_8 = \sqrt{\frac{(n_6 \times n_T)}{K_{N_2} \times P}} \quad (14.11)$$

$$n_9 = \sqrt{\frac{(n_4 \times n_T)}{K_{H_2} \times P}} \quad (14.12)$$

For the dissociation of water into hydrogen and hydroxyl (OH) the equation is rearranged as follows:

$$K_{H_2O_{OH}} = \frac{[H_2O]}{[OH][H]^{\frac{1}{2}}} \quad (14.13)$$

$$KH_2O_{OH} = \frac{\left(\frac{n_2}{n_T} P\right)}{\left(\frac{n_{10}}{n_T} P\right) \left(\frac{n_4}{n_T} P\right)^{\frac{1}{2}}} \quad (14.14)$$

$$KH_2O_{OH} = \frac{n_2}{n_{10} \left(\frac{n_4}{n_T} P\right)^{\frac{1}{2}}} \quad (14.15)$$

$$n_{10} = \frac{n_2}{KH_2O_{OH} \left(\frac{n_4}{n_T} P\right)^{\frac{1}{2}}} \quad (14.16)$$

3.6. ZEL'DOVICH MECHANISM

The formation and destruction of nitrogen oxides is governed by the following equations, these are referred to as the extended Zel'Dovich Mechanism.



The rate in which NOx is formed via this mechanism is as follows:

$$\frac{d[NO]}{dt} = k_1^+[O][N_2] + k_2^+[N][O_2] + k_3^+[N][OH] - k_1^-[NO][N] - k_2^-[NO][O] - k_3^-[NO][H] \quad (15.4)$$

Where the k values are rate constants shown in the table below in $\frac{cm^3}{mol.s}$:

K	Reaction	Rate Constant
1+	$O + N_2 \rightarrow NO + N$	$7.6 \times 10^{13} \exp \left[-\frac{38000}{T} \right]$
1-	$N + NO \rightarrow N_2 + O$	1.6×10^{13}
2+	$N + O_2 \rightarrow NO + O$	$6.4 \times 10^9 T. \exp \left[-\frac{3150}{T} \right]$
2-	$NO + O \rightarrow O_2 + N$	$1.5 \times 10^9 T. \exp \left[-\frac{19500}{T} \right]$
3+	$N + OH \rightarrow NO + H$	4.1×10^{13}
3-	$NO + H \rightarrow OH + N$	$2.0 \times 10^{14} \exp \left[-\frac{23650}{T} \right]$

Figure 6

The values required to use the mechanism are concentrations meaning that the calculated mols of each species from dissociation must be converted to concentrations. We know that,

$$\begin{aligned} \alpha(\phi C_8H_{18} + 12.5(O_2 + 3.76N_2)) \\ \rightarrow \alpha(n_1CO_2 + n_2H_2O + n_3CO + n_4H_2 + n_5O_2 + n_6N_2 + n_7O \\ + n_8N + n_9H + n_{10}OH) \end{aligned} \quad (15.5)$$

Where α is a constant that incorporates EGR masses in order to calculate the concentration. We know the fuel mass and therefore can calculate α :

$$\alpha = \frac{fuel\ mass}{\phi \times 114} \quad (15.6)$$

Where 114 represents the molar mass of isooctane.

The concentration of any of the species can then be calculated:

$$[n_n] = \frac{\alpha \times n_n}{v_{burned}} \quad (15.7)$$

Where n_n represents a species of molecule or atom.

The concentration of NOx produced per second can now be calculated and can be manipulated to calculate the NOx produced per degree, then to the kmols produced per degree which allows us to calculate the parts per million (ppm) of NOx produced per degree. The summation of this is the ppm of NOx produced over the combustion cycle. The manipulation method is shown below:

$$\frac{[NO]}{degree} = \frac{d[NO]}{dt} \times \left(\frac{1}{RPM \times 6} \right) \quad (15.8)$$

$$\frac{kmolNO}{degree} = \frac{[NO]}{degree} \times v_{burned} \quad (15.9)$$

$$\frac{ppmNO}{degree} = \frac{\frac{kmolNO}{degree} \times 10^6}{n_T \times \alpha} \quad (15.10)$$

The results for the ppm of NO_x produced over the combustion cycle can then be compared to Ford engine data to give an idea of how accurate the theoretical calculations are.

It should be noted that prior to using the extended Zel'Dovich mechanism a much more simplified equation was used. This equation is based on the Zel'Dovich mechanism but has several assumptions and therefore is potentially less accurate, the following equation is found in "Simulating Combustion" by Günter P. Merker, Christian Schwarz, Gunnar Stiesch, and Frank Otto.

$$\frac{d[NO]}{dt} = 4.7 \times 10^{13} [N_2][O_2]^{\frac{1}{2}} \exp \left\{ -\frac{67837}{T} \right\} \quad (15.11)$$

4. Results and Analysis

4.1. ANALYSIS OF ENGINE DATA

Using the engine data provided a graph can be produced showing how the pressure acts against the crank angle.

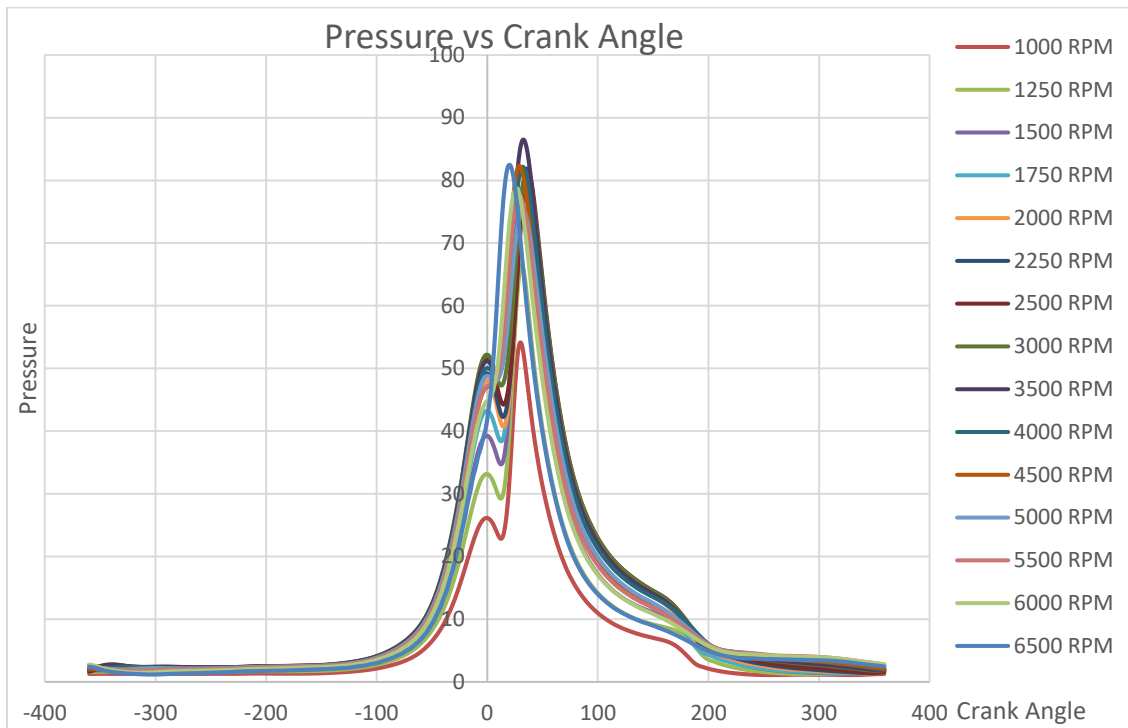


Figure 7

From figure 7 and 8 we can see that the highest peak pressure is at 3500 RPM reaching a maximum of 86.48 bar. We can see that in figure 9 the lower RPM's have higher figures for added pressure from combustion with 2000 RPM being the maximum at 5.34 bar of additional pressure. This is due to that fact that at lower RPM's the pressure build up purely from the motion of compression and expansion is lower than that at high RPM's. The reason the highest combustion pressure is at 3500 RPM is due to that fact that the sum of extra pressures during combustion is highest at this point, this is shown in figure 10. It is likely that the maximum pressure occurs at this point due to several reasons. From figure 11 we can see that the turbo is not at its maximum pressure, however it is producing a high amount of boost pressure of 171.3kPa, this results in a more homogenous mixture of fuel and air as the air speed from this boost pressure will be fast enough. The reason that the highest peak pressure doesn't occur when the turbo pressure is the highest at 5500 RPM is likely due to one of two things, there isn't enough time for combustion to happen completely or the engine is choking because the airspeed has reached its maximum at the speed of sound.

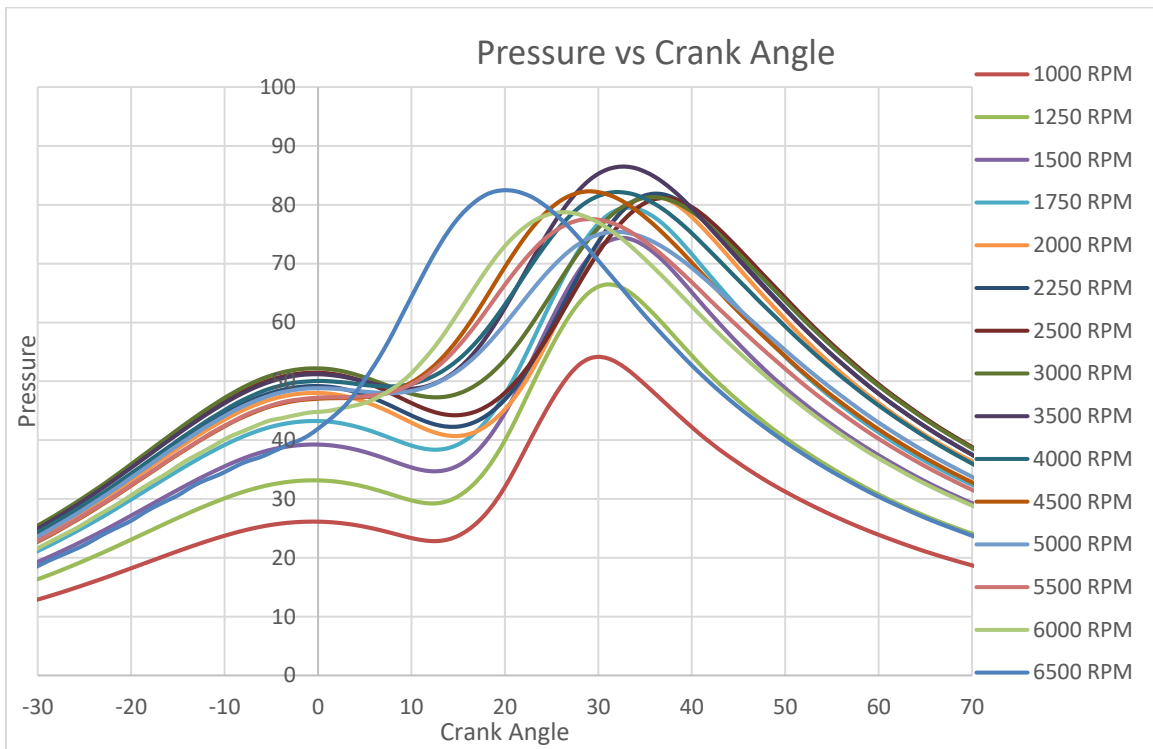


Figure 8

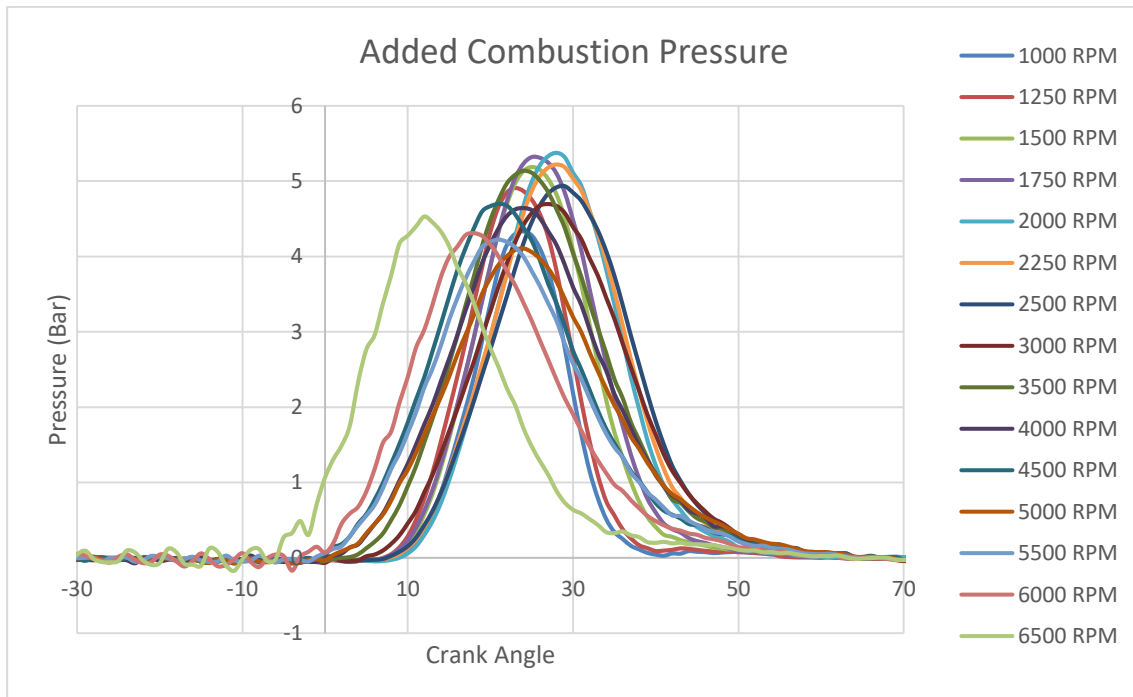


Figure 9

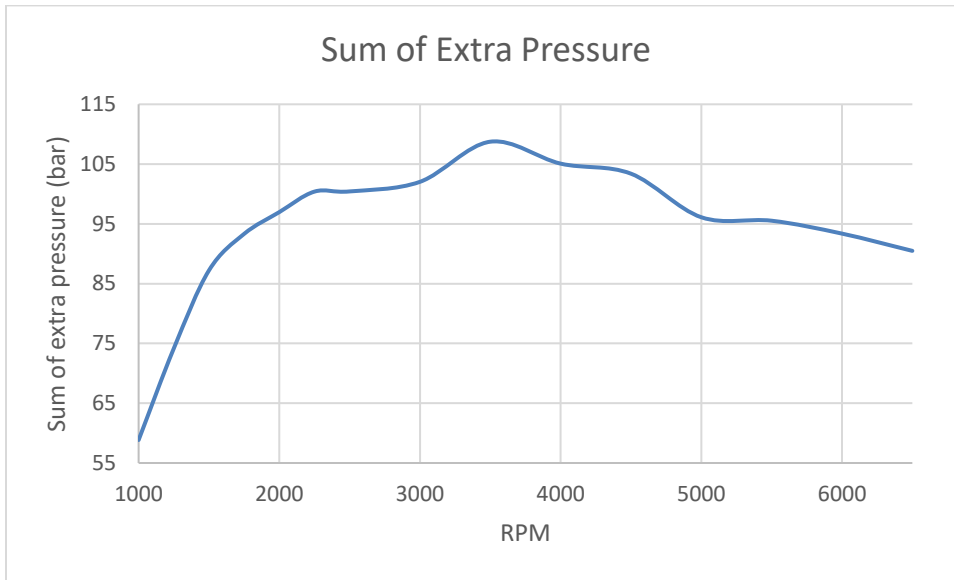


Figure 10

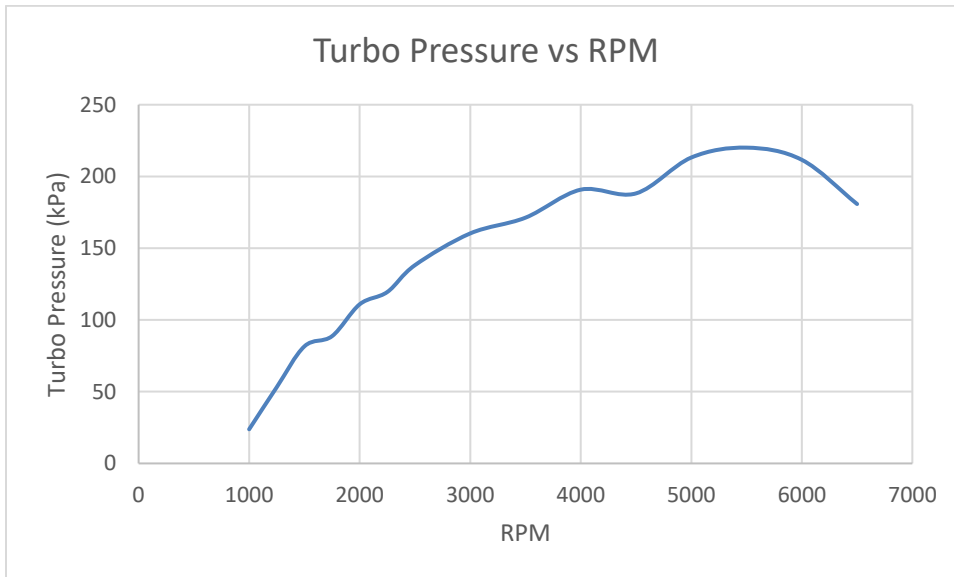


Figure 11

4.2. BURNED-ZONE TEMPERATURE ANALYSIS

Whilst temperatures have been calculated for burned-zone and unburned-zone as well as the average cylinder temperature, the only important temperatures for the production of NO_x are the burned-zone temperatures. (Figures for all zone temperatures for each RPM will be in the appendix) Figure 12 shows the burned-zone temperatures for each RPM plotted against the crank angle. From this graph we can see that the higher combustion temperatures tend to occur at the higher RPM's. At 6500 RPM the highest combustion temperatures are reached. The reason this occurs is quite simple, from the

rearrangement of the ideal gas equation $T = \frac{Pv}{mR}$ we can see that for a higher temperature to occur the pressure and volume must be larger or the mass or specific gas constant must be smaller. From the figure 13 we can see that the specific gas constant is larger at 6500 RPM. However, the mass in the cylinder is less as shown in figure 14, this is what causes a higher temperature at this RPM.

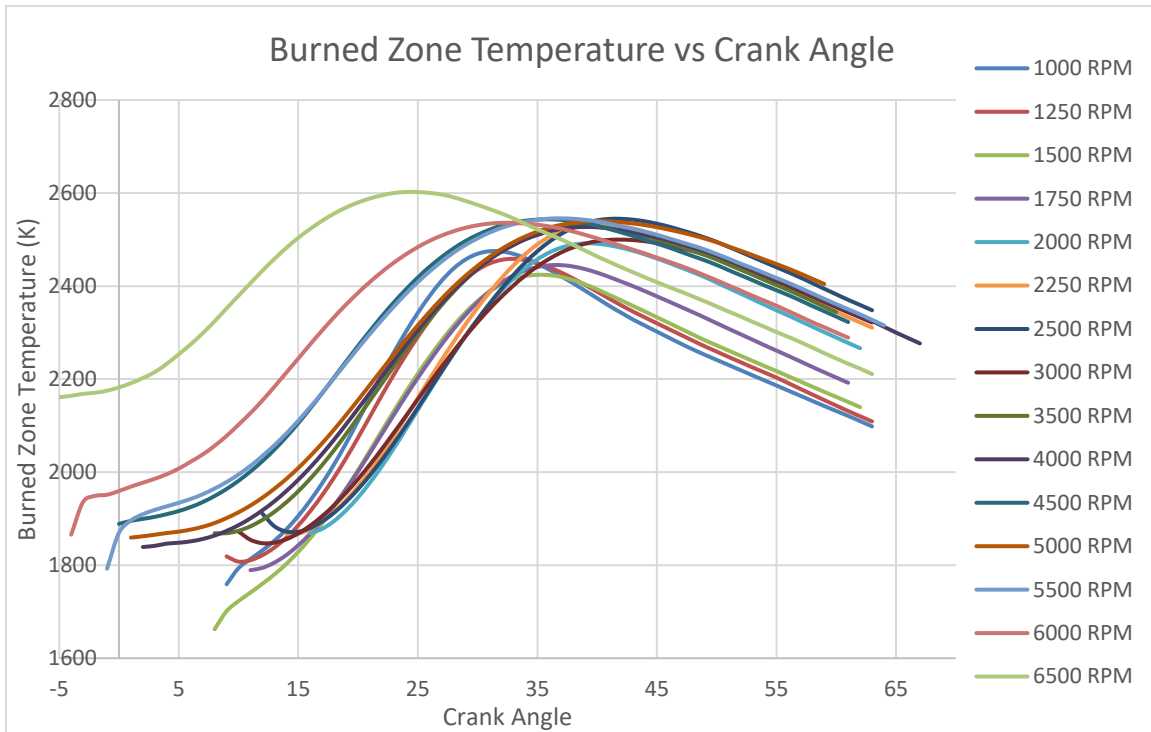


Figure 12

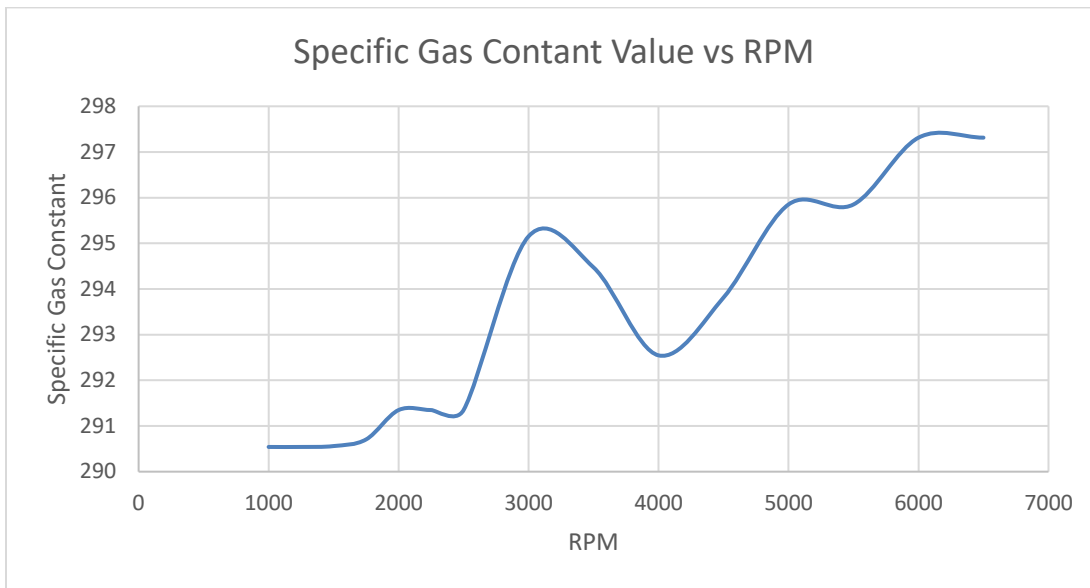


Figure 13

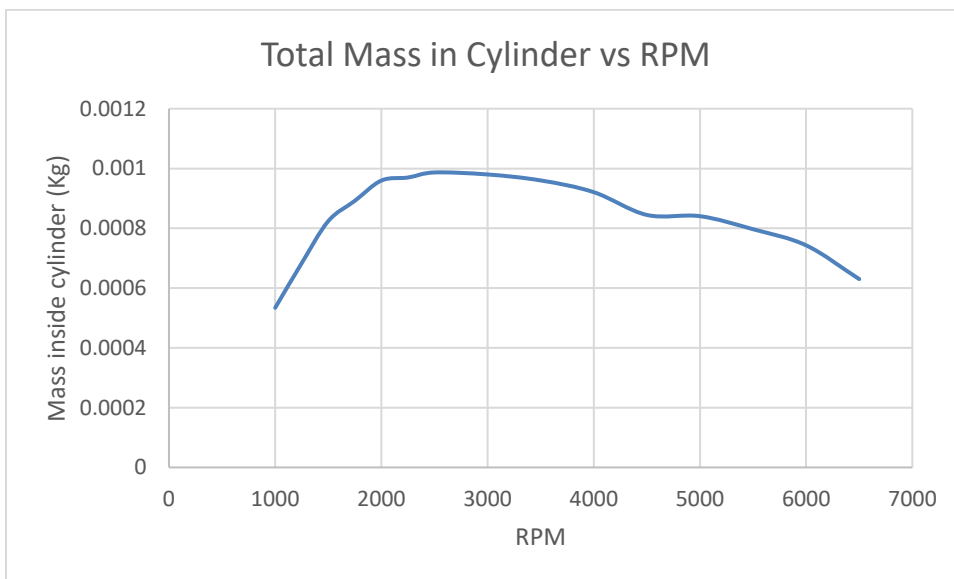


Figure 14

4.3. ANALYSIS OF EQUILIBRIUM CONSTANTS

Unfortunately, since the equilibrium constants tend towards infinity very quickly at low temperatures it is impossible to plot these directly onto a graph for comparison, this is shown in figure 15.

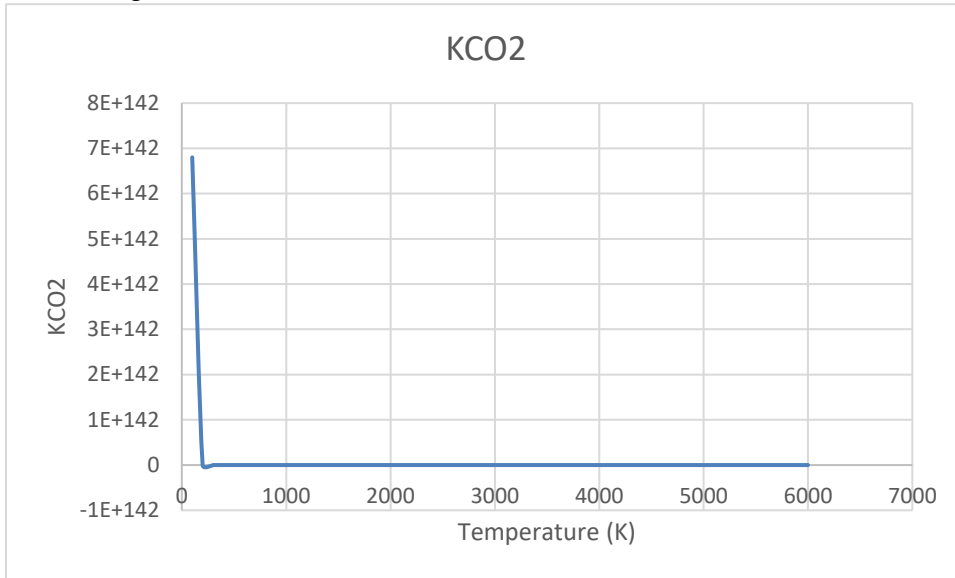


Figure 15

However, by comparing the standard free energy change vs temperature we can get an idea of how readily each species dissociates.

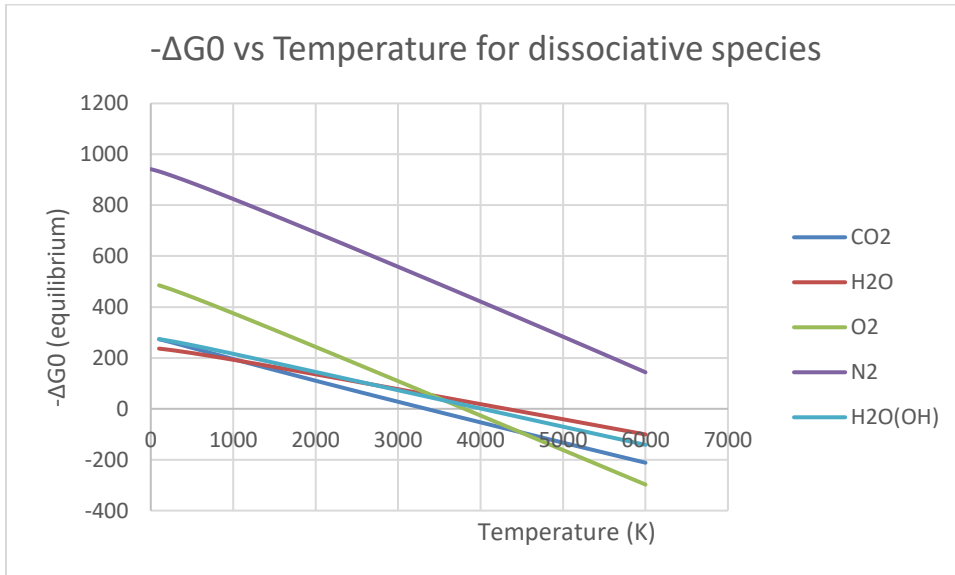


Figure 16

Figure 16 shows the negative of the standard free energy change vs temperature. By comparing these figures to the equation used to calculate the equilibrium constant we

can see that the higher the value of $-\Delta G^0$ the higher the value for the equilibrium constant will be.

$$K = e^{\frac{\Delta G^0}{RT}} \quad (16.1)$$

Because the equilibrium constant is on the bottom of the dissociation equations for every species, a higher value of K will result in lower amount of dissociation. The graph shows that N_2 is much less likely to dissociate than the other species. This occurs because the two nitrogen atoms that make up the nitrogen molecule are bound by a triple bond. This bond requires a lot more energy to break and therefore requires much higher temperatures for dissociation to occur. When $-\Delta G^0$ becomes negative dissociation happens very readily as the equilibrium constant tends towards 0, when this occurs almost all the species will dissociate. We can see that for most of the species this occurs somewhere in the region between 3000K and 5000K. However, for N_2 this doesn't even occur at 6000K. By comparing this graph with the maximum combustion temperature of 2602K at 6500 RPM we can see that combustion temperatures inside the cylinder of this engine are not high enough for any species to fully dissociate.

4.4. DISSOCIATION OF DIFFERENT SPECIES

4.4.1. Oxygen (Molecule)

Figure 17 shows the mols of oxygen produced over the various RPM ranges. Figures 18 and 19 show the two different groupings from figure 17. The results from figures 17, 18 and 19 show the results that we would expect to see. At 1000-1750 RPM the engine is running lean and therefore should produce more oxygen as there is an abundance in the cylinder of the engine that is not involved in the formation of water or carbon dioxide during combustion. Figure 18 shows that at 1000 RPM the most oxygen is produced we can see by comparison with figure 20 that this is caused by higher burned zone temperatures at this RPM. Figure 17 shows us that between 2000-5500 RPM the amount of oxygen being produced is roughly 5 times less than that of 1000-1750 RPM. This occurs because from 2000 RPM onwards the engine is not running lean anymore and is instead tending towards running rich, shown in figure 21. 2000 RPM is close to stoichiometric fuel equivalence ratio and goes to around up to around 9% rich at 5500 RPM. After this point the engine is running greater than 10% rich and we can see from figure 19 that this causes a dramatic drop in the amount of oxygen that dissociates.

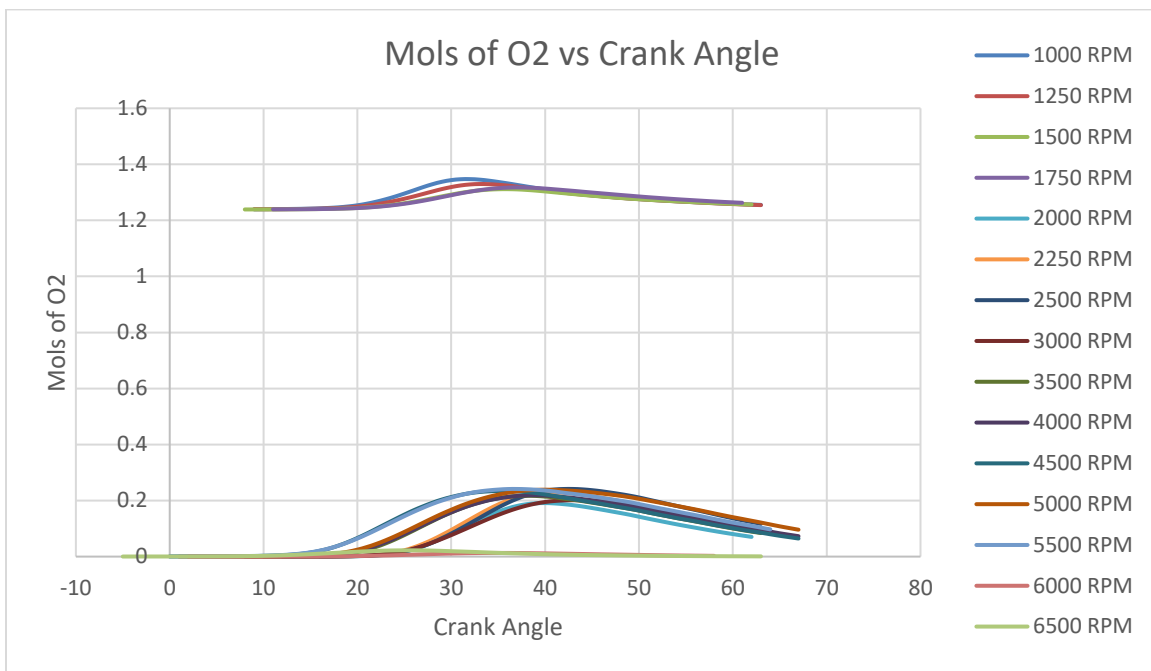


Figure 17

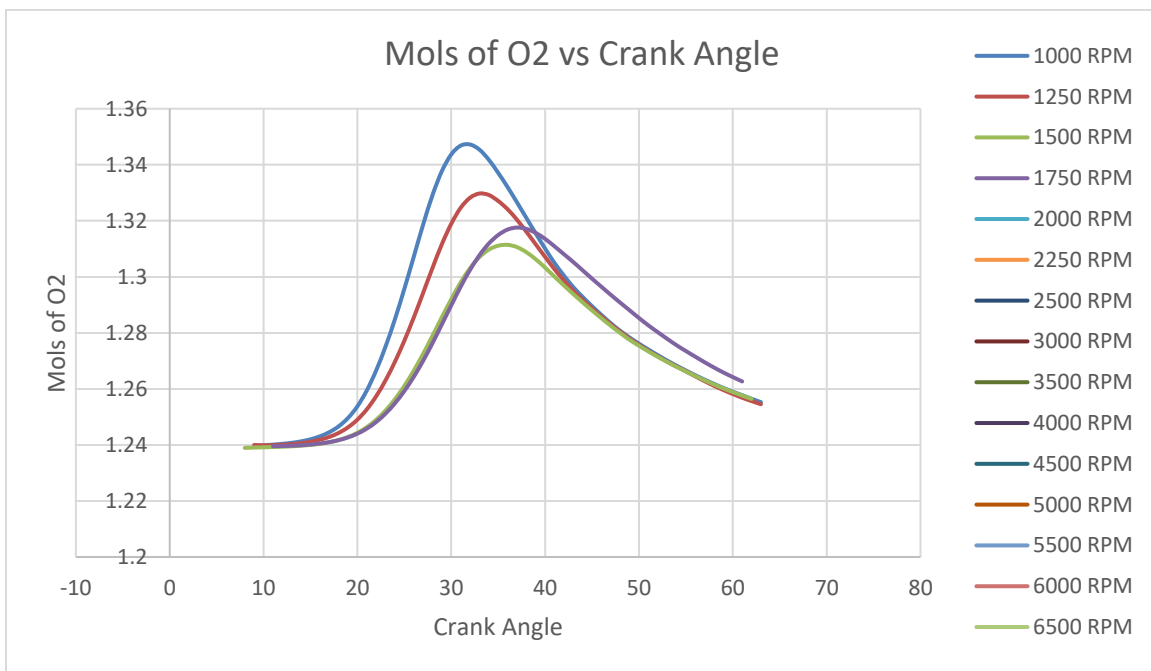


Figure 18

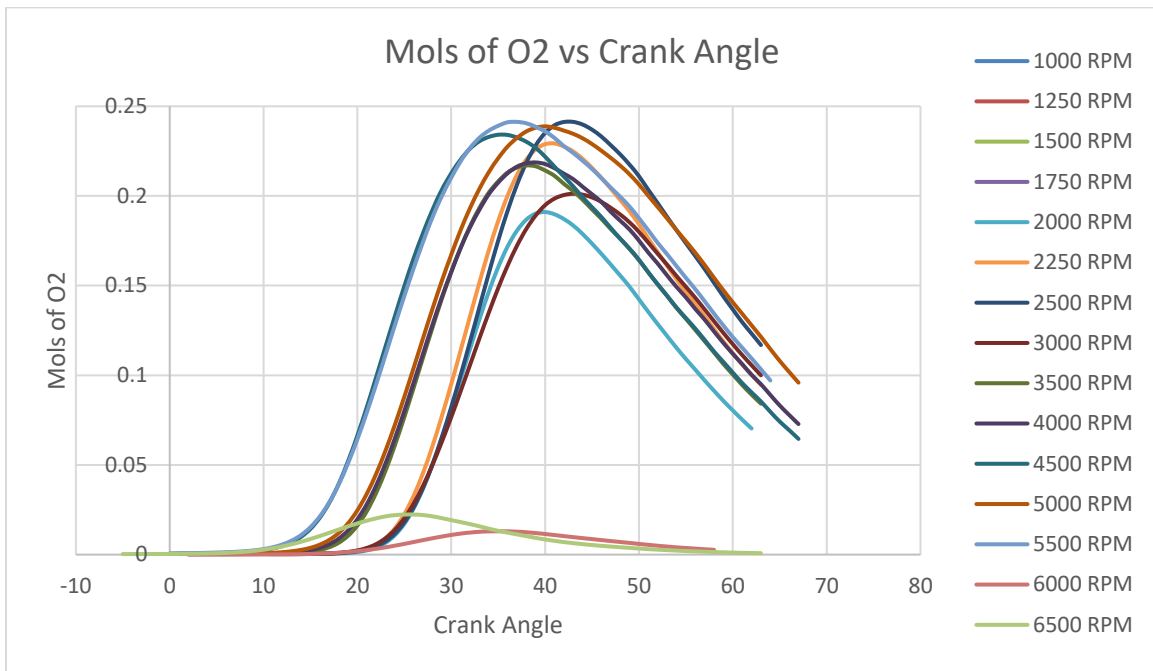


Figure 19

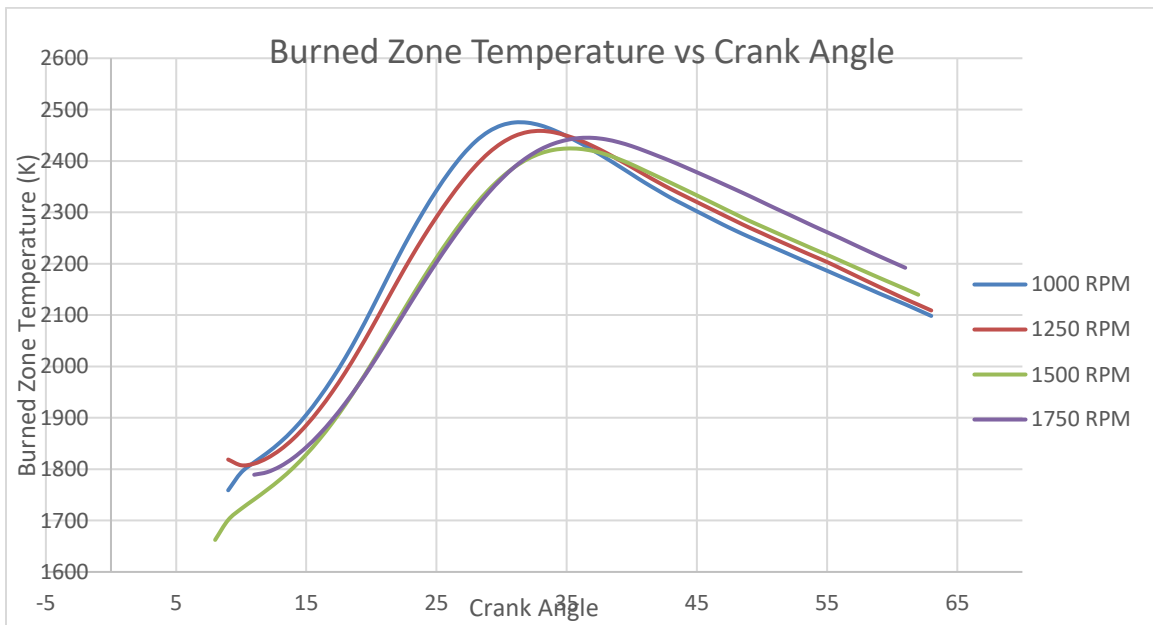


Figure 20

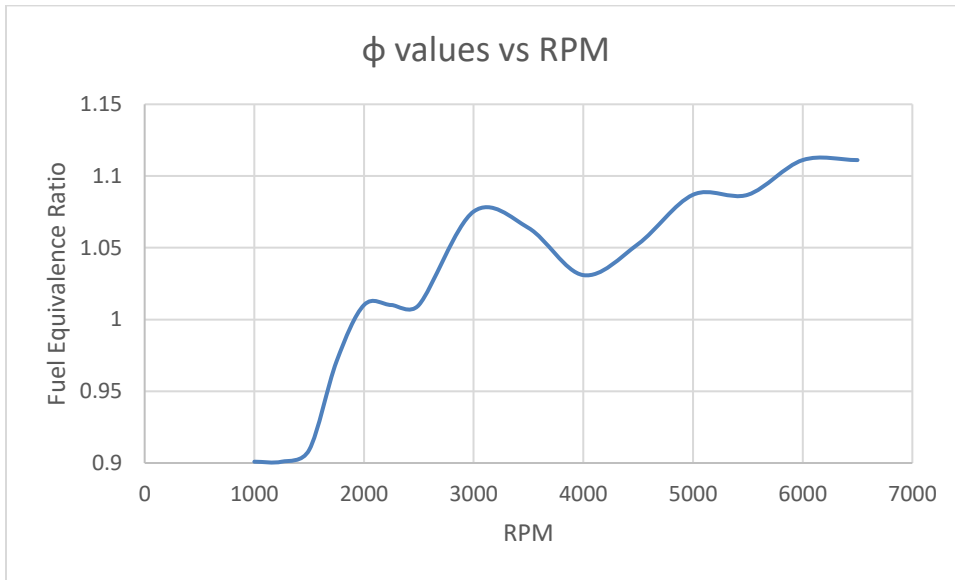


Figure 21

4.4.2. Oxygen (Atom)

Figure 22 shows the mols of oxygen atoms that are formed from the dissociation of the oxygen molecules, whilst the general trend is similar to that of the mols of oxygen molecules, with the lower RPM's producing more. We can clearly see that the amount that the two highest RPM's are producing is of a greater magnitude than before. This is occurring despite there being a much lower initial amount of oxygen available for dissociation. This happens because on average the burned-zone temperatures at the higher RPM's are greater. A higher temperature results in a lower value for K_{O_2} and therefore the oxygen dissociates more readily.

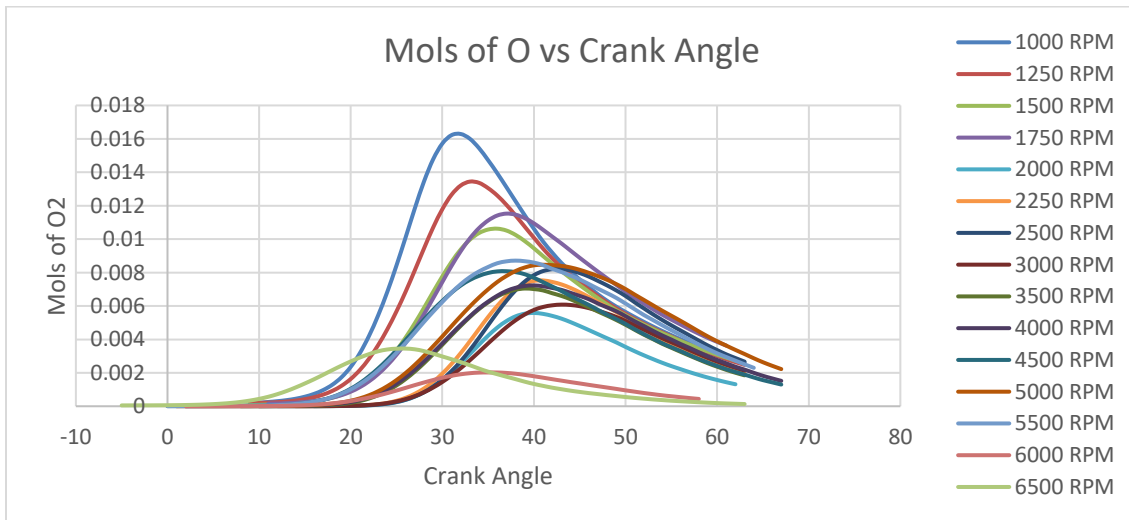


Figure 22

4.4.3. Nitrogen

The graph below shows the amount of nitrogen atoms that are formed from the dissociation of nitrogen molecules.

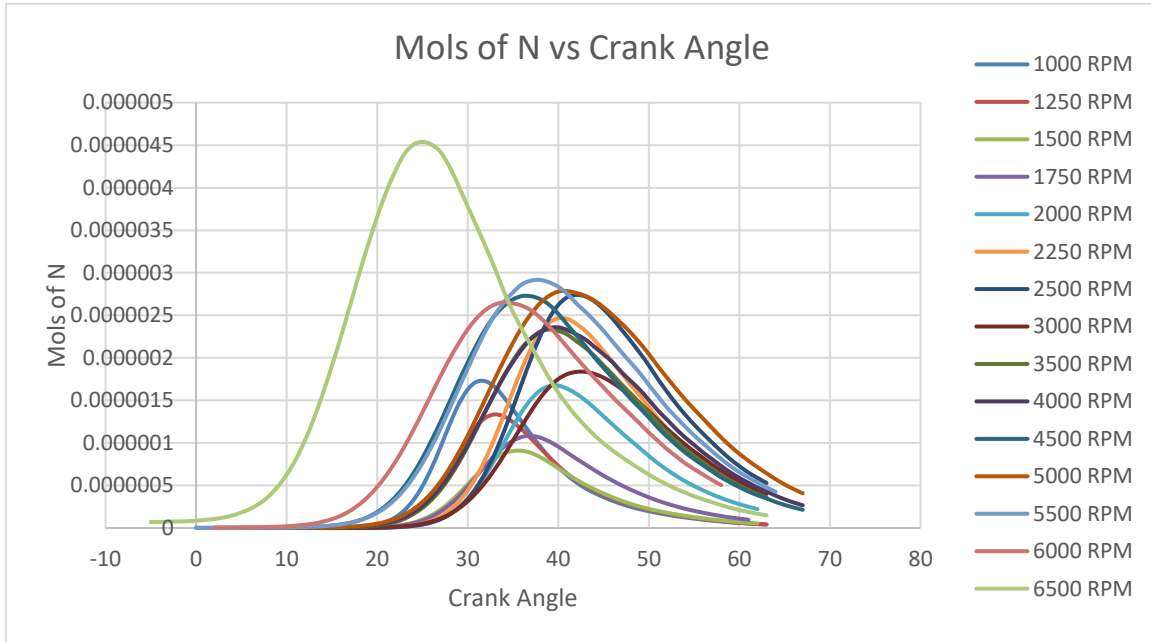


Figure 23

Just by looking at the axis we can see that the amount of nitrogen that dissociates is several factors of ten lower than that of the oxygen, even with 47 mols of nitrogen in the combustion chamber, this goes to show just how reluctant nitrogen is to dissociate. We can see from figure that more nitrogen dissociates at higher RPM's, this is once again down to that fact that the temperatures of the burned-zone are higher.

4.4.4. Hydrogen

Figure 24 shows that there is significantly more hydrogen at 6000 and 6500 RPM, as expected this results in a higher amount of dissociated hydrogen produced in figure 25.

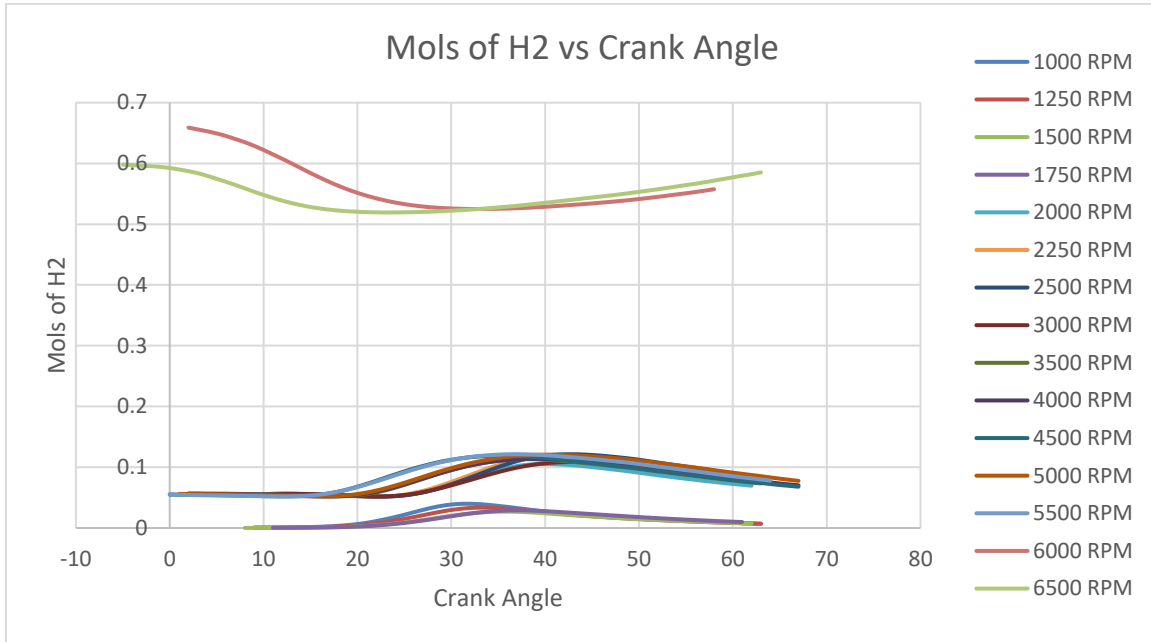


Figure 24

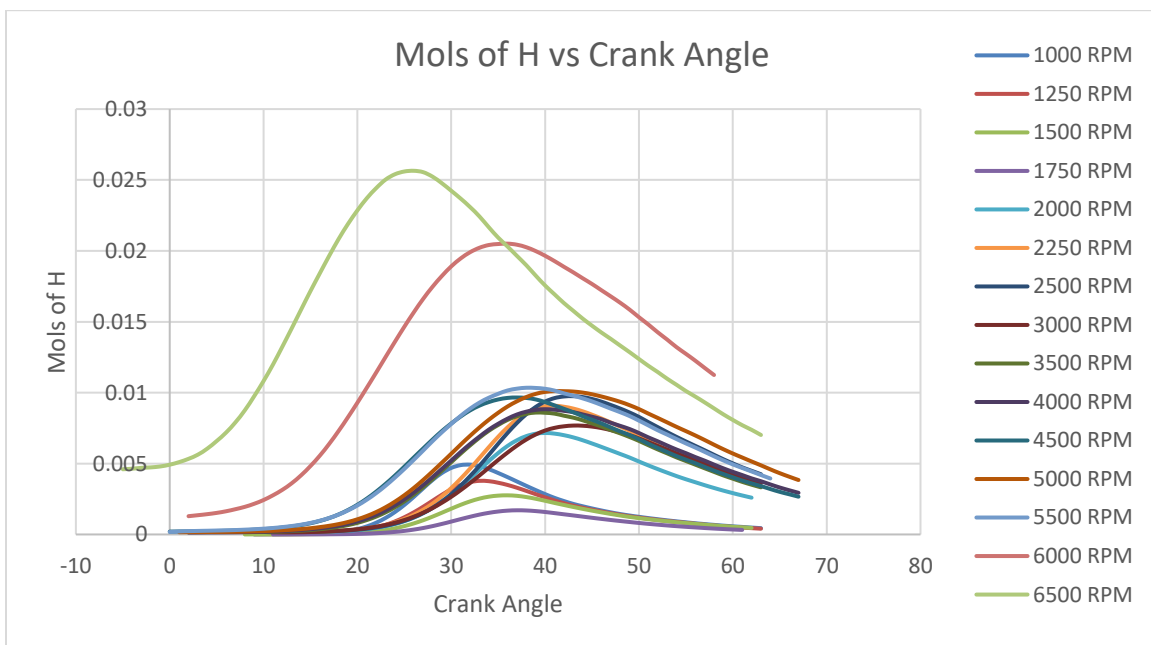


Figure 25

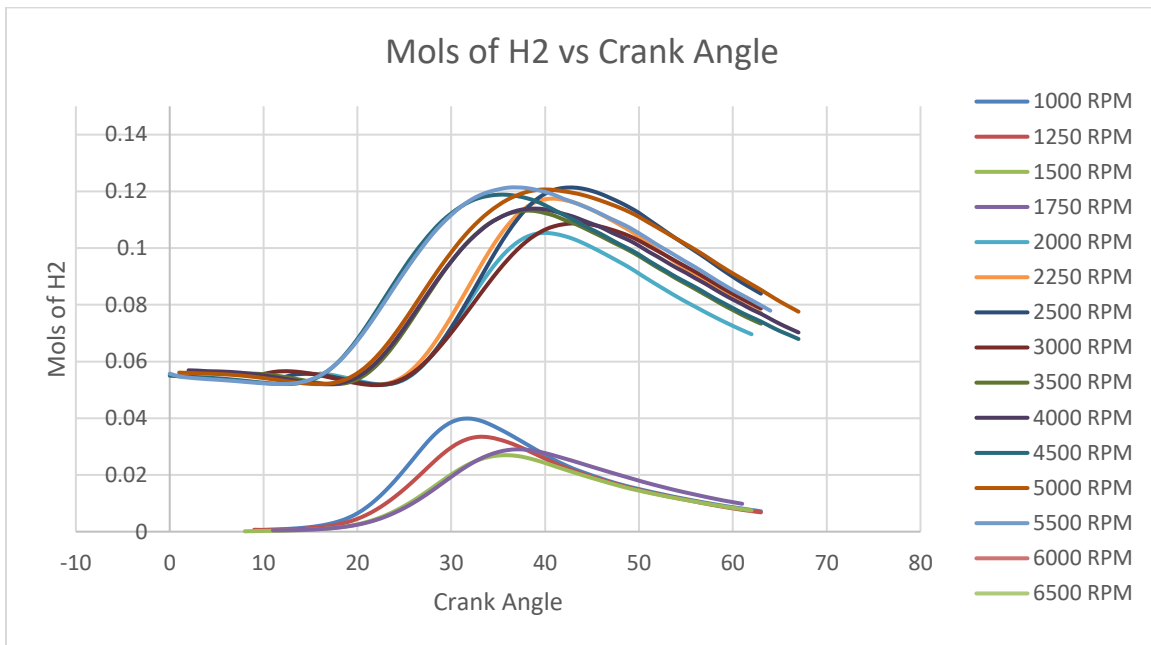


Figure 26

Figure 26 shows the same data as figure 24 just with a different scale to make the lower RPM's more viewable. We can see clearly that at the lean RPM's less hydrogen is being produced which results in less hydrogen dissociating as a result.

4.4.5. Hydroxyl Molecule

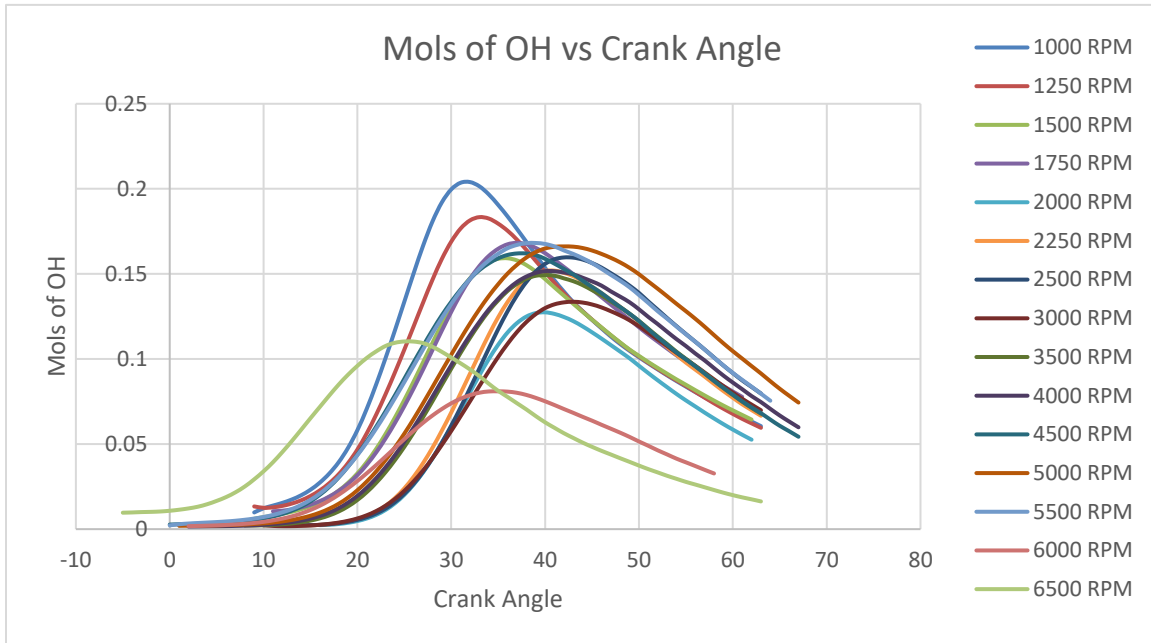


Figure 27

From the results shown in figure 27 we can see that the higher values of hydroxyl dissociation occur at lower RPM's. This occurs because the mols of hydroxyl that dissociate is governed as follows:

$$n_{10} = \frac{n_2}{KH_2O_{OH} \left(\frac{n_4}{n_T} P \right)^{\frac{1}{2}}} \quad (16.2)$$

From figure 24 we can see that at the higher RPM's there is a larger amount of hydrogen (n_4) which decrease the value of n_{10} . There are also generally higher pressures at higher RPM's shown in figure 8 which also results in a decrease in the amount of hydroxyl that dissociates.

4.5. FORMATION AND DESTURCTION OF NOX

The following figures show all the data for nitrogen oxide formation and destruction for each RPM range as well as the data taken from the Ford Fox engine. Figures 28-31 show the data for 1000-1750RPM. As we can see from these figures as well as figure 43, for these RPM's the NOx production is over being over predicted when compared to the real engine data. One reason for this is down to the rate constants being used. These rate constants have been acquired through extensive research on the rates of reactions for the formation of NOx in stoichiometric conditions. As the engine is running lean at this point the amount of oxygen available is much higher than it would be if the

combustion was stoichiometric. Because of this there is a higher concentration of oxygen then there would have been during the experiments that were carried out to acquire the rate constants used. Another reason for this could be inaccurate combustion temperatures at lower RPM's. Because the engine speed is fairly slow there is time for heat to transfer through the walls of the cylinder resulting in a lower temperature and therefore a lower production of NOx. There is also an assumption in the theoretical model that the combustion is happening completely and that no fuel is being wasted. In a real engine some fuel will come into contact ill the cylinder walls and piston head and form particulates rather than combusting to form the predicted products.

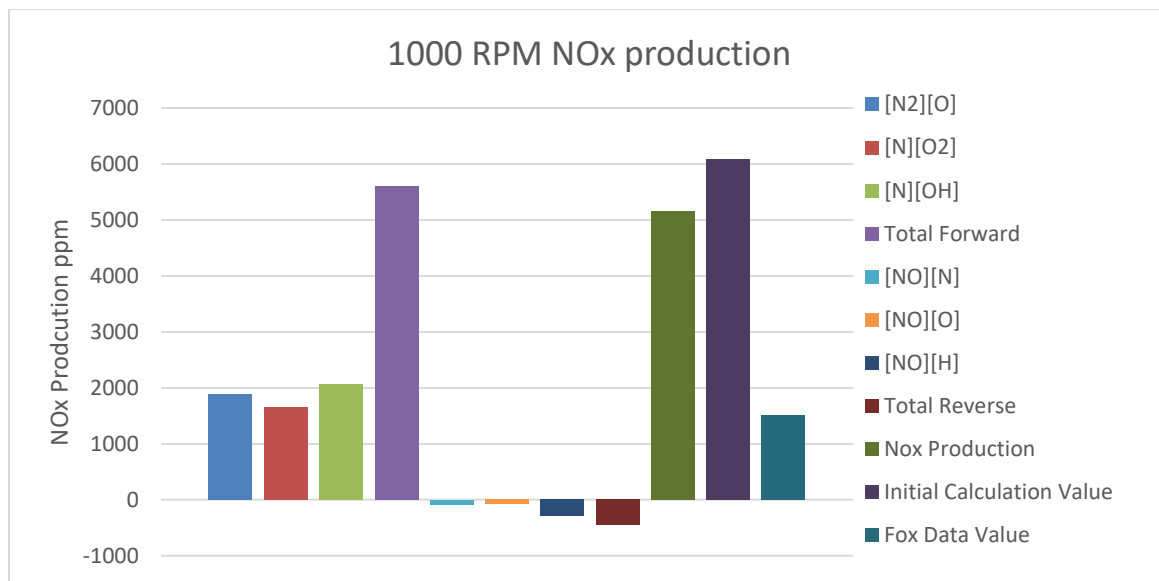


Figure 28

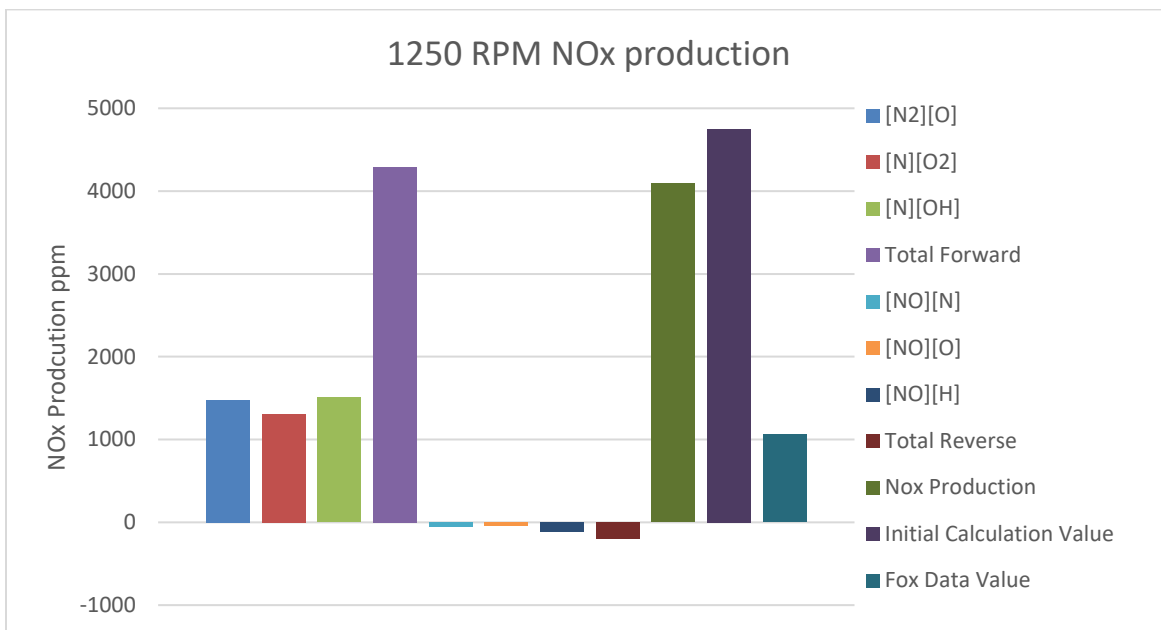


Figure 29

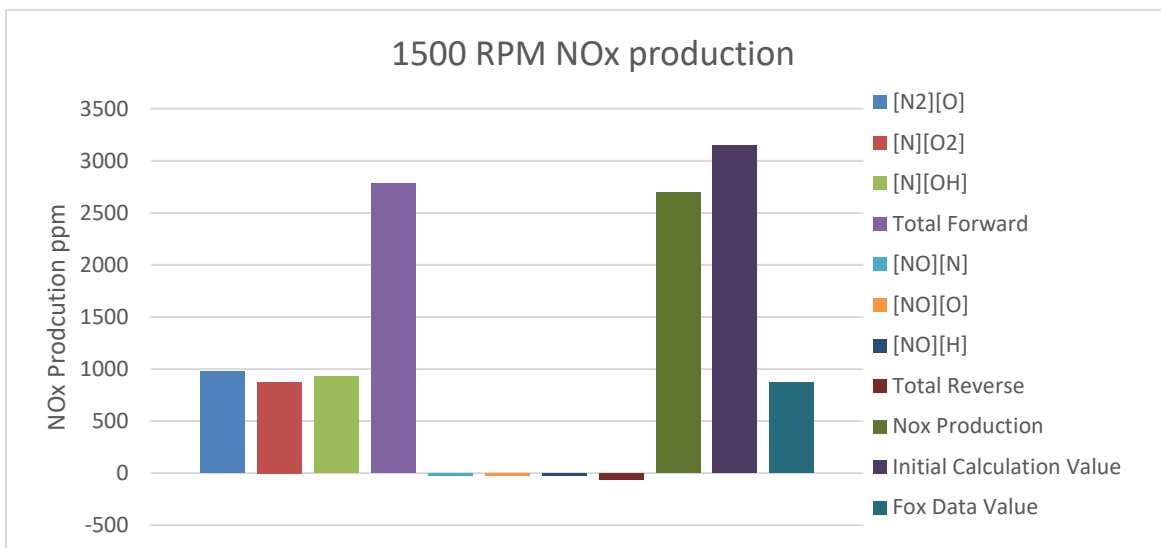


Figure 30

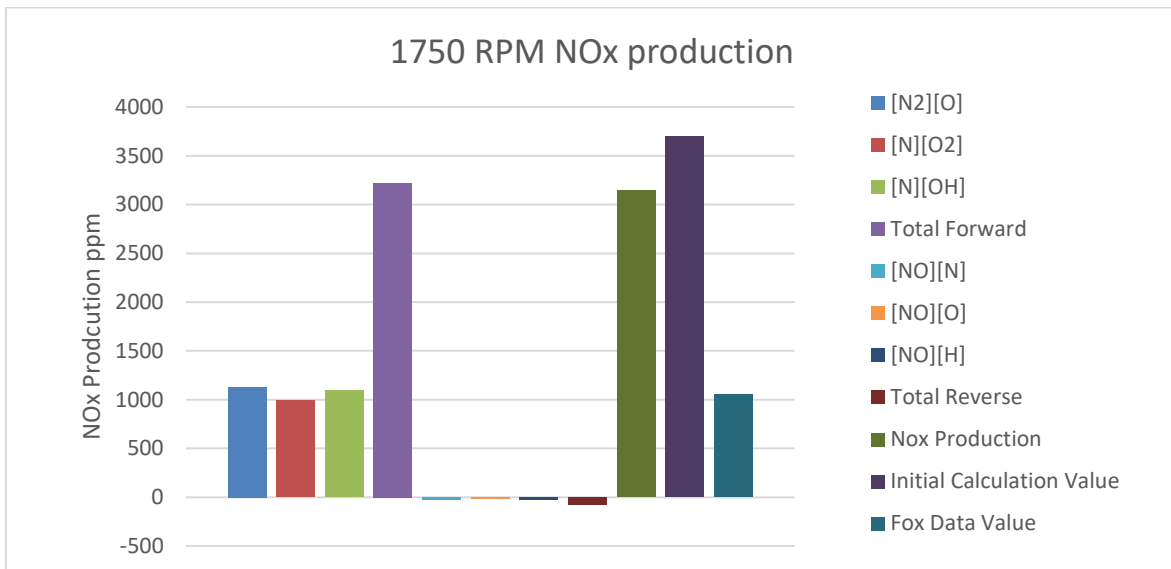


Figure 31

After these RPM's the fuel mixture becomes very close to stoichiometric and we can see that the results become more accurate in figures 35-40. Prior to this the predicted NOx is still higher, this could still be down to inaccurate combustion temperatures as the engine speed is still considered fairly slow.

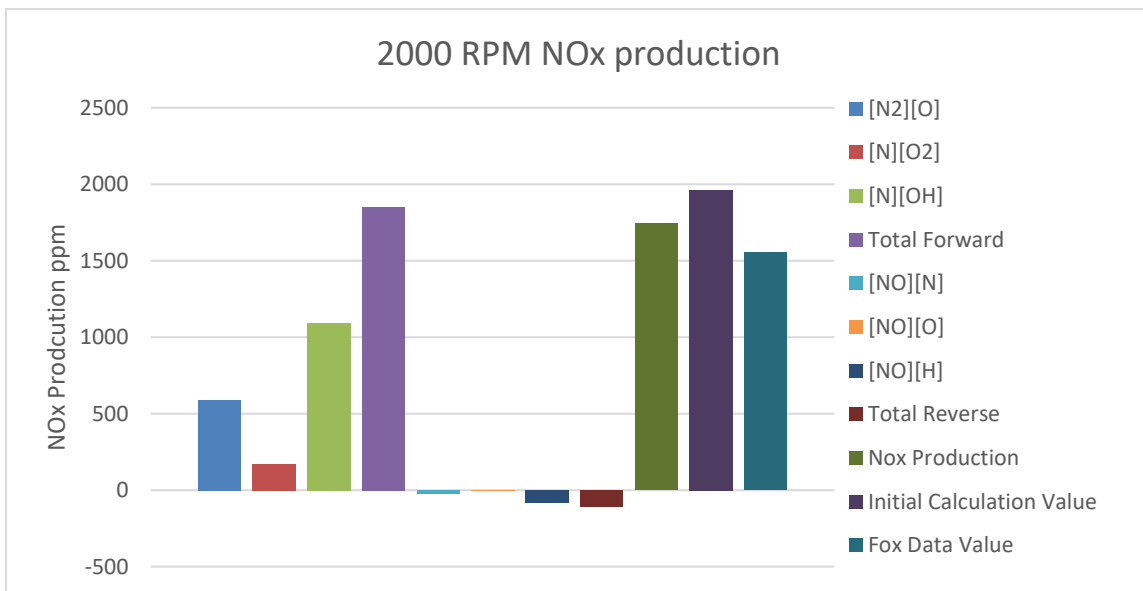


Figure 32

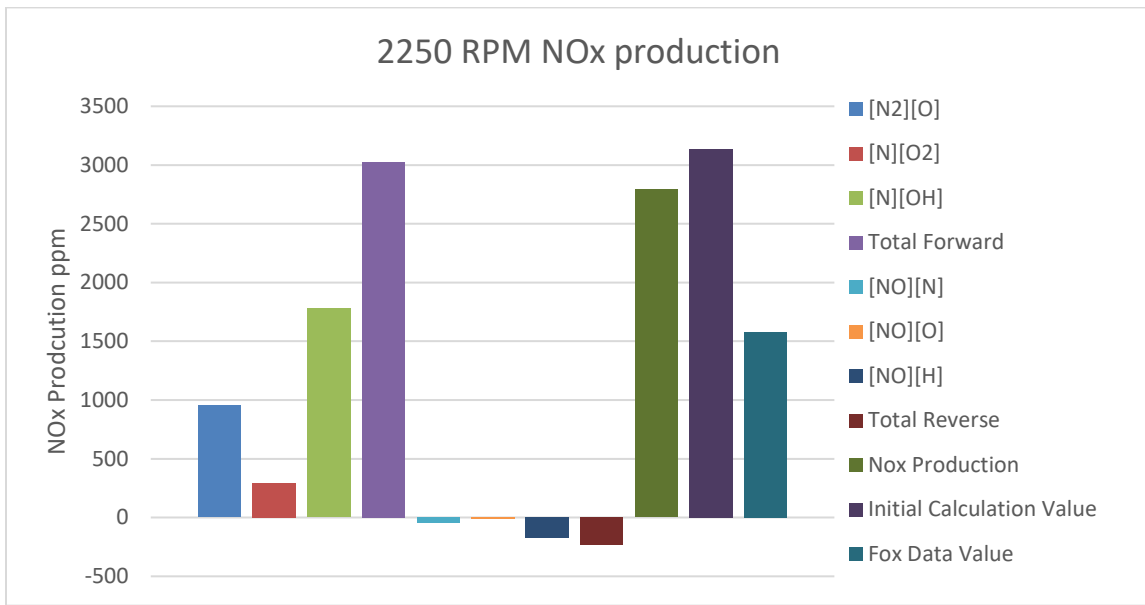


Figure 33

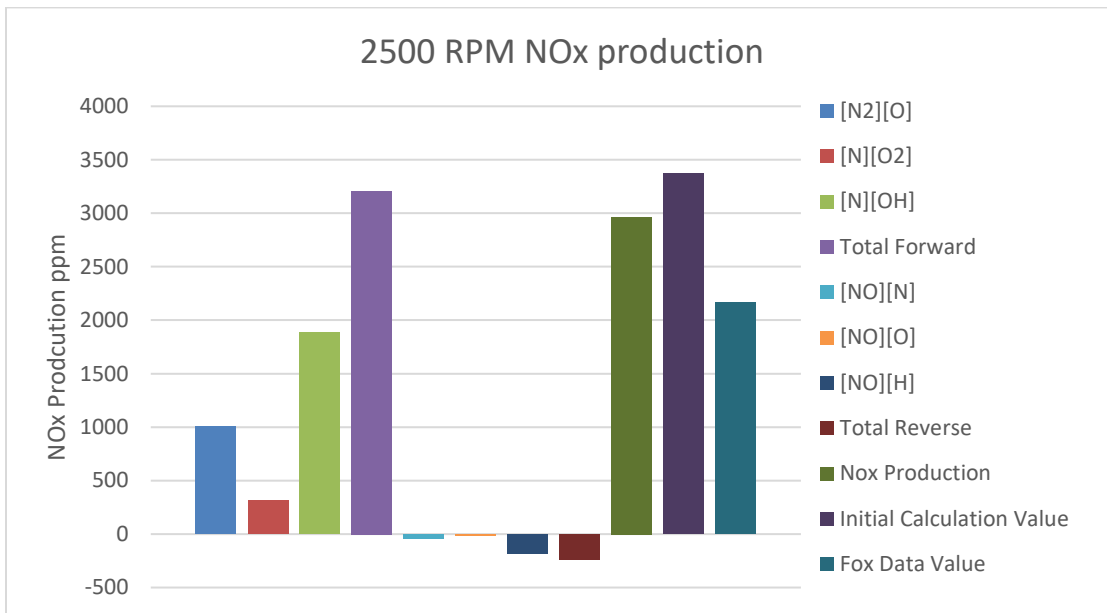


Figure 34

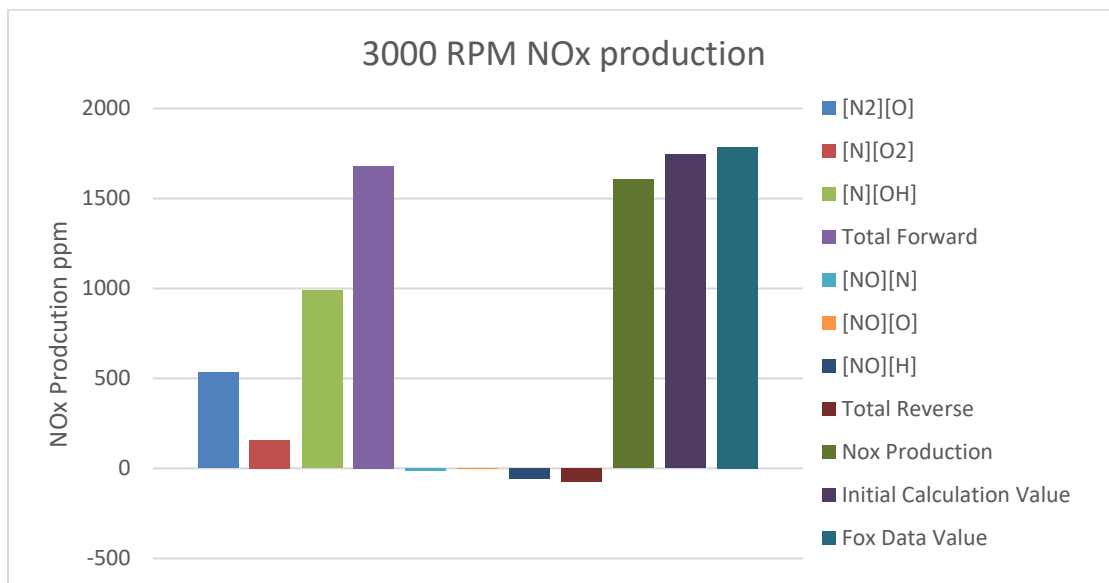


Figure 35

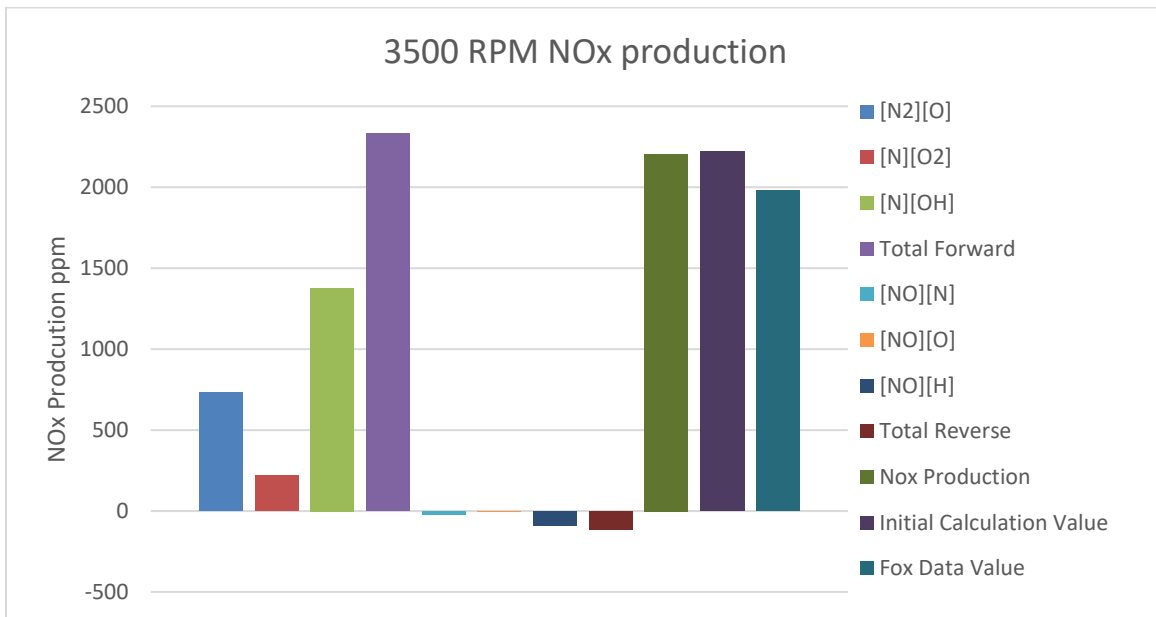


Figure 36

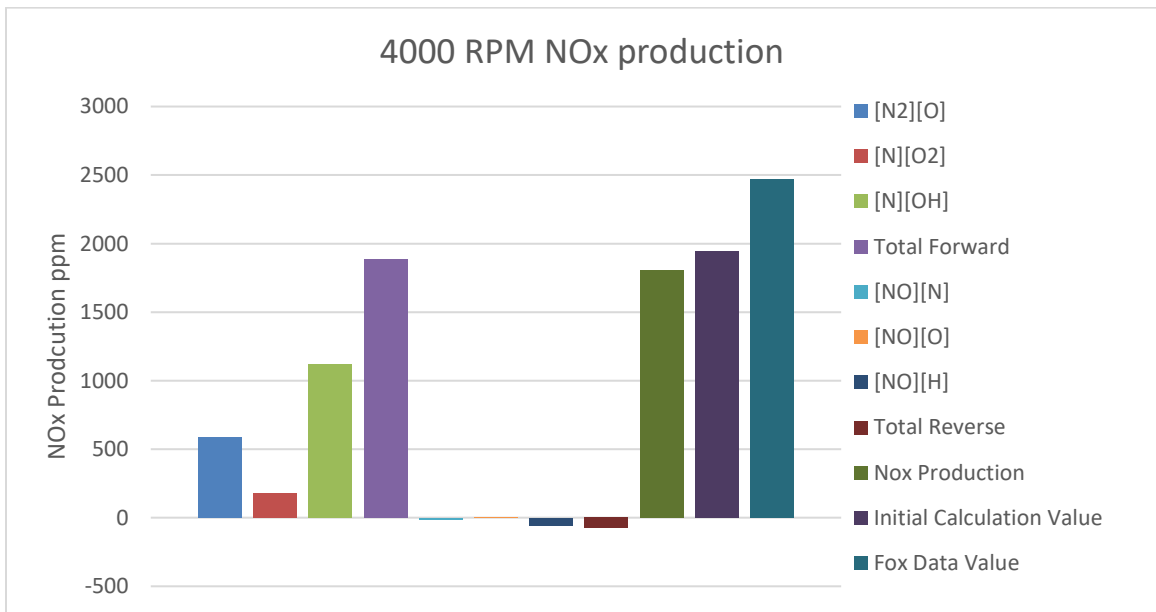


Figure 37

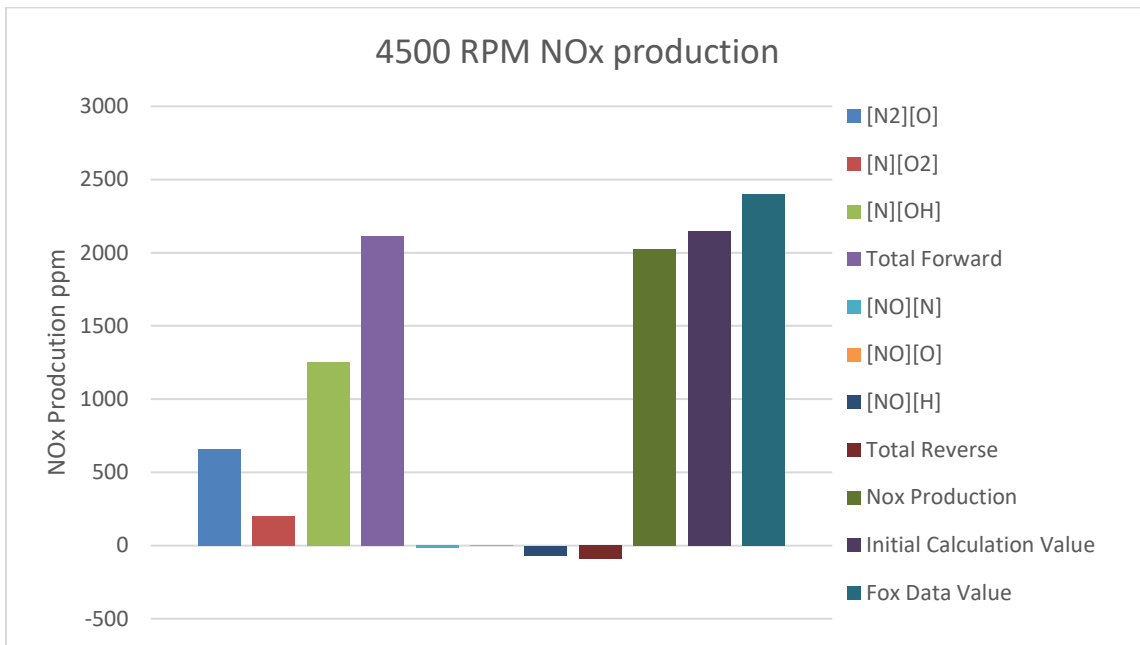


Figure 38

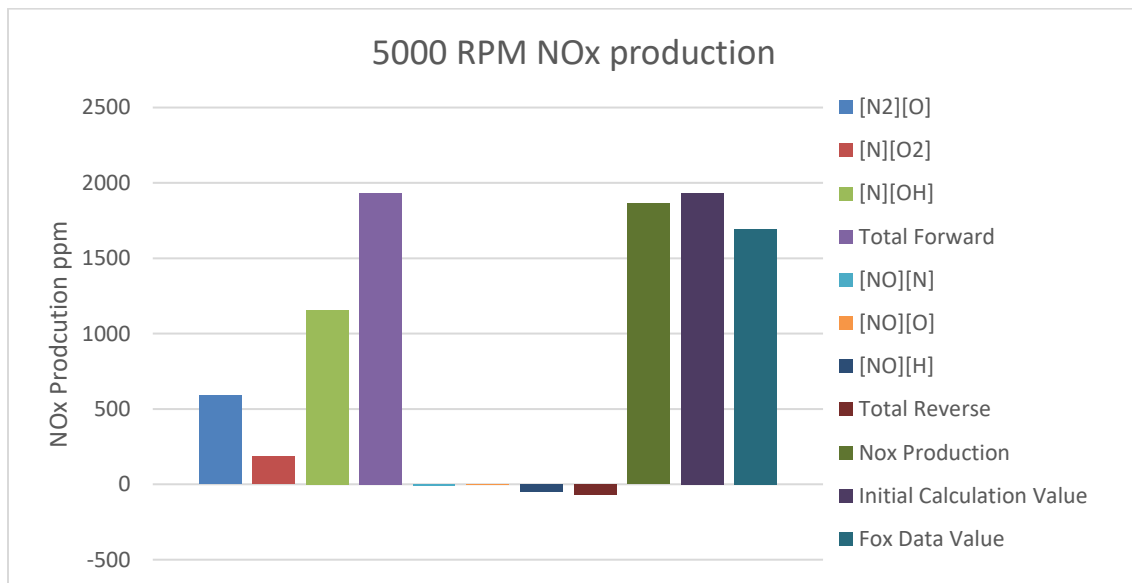


Figure 39

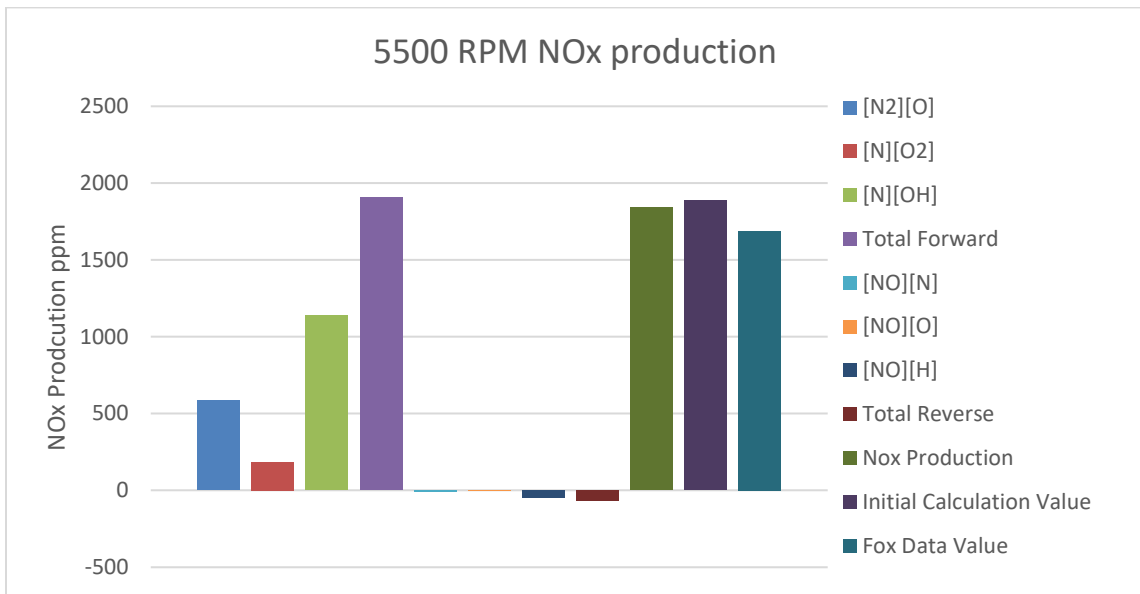


Figure 40

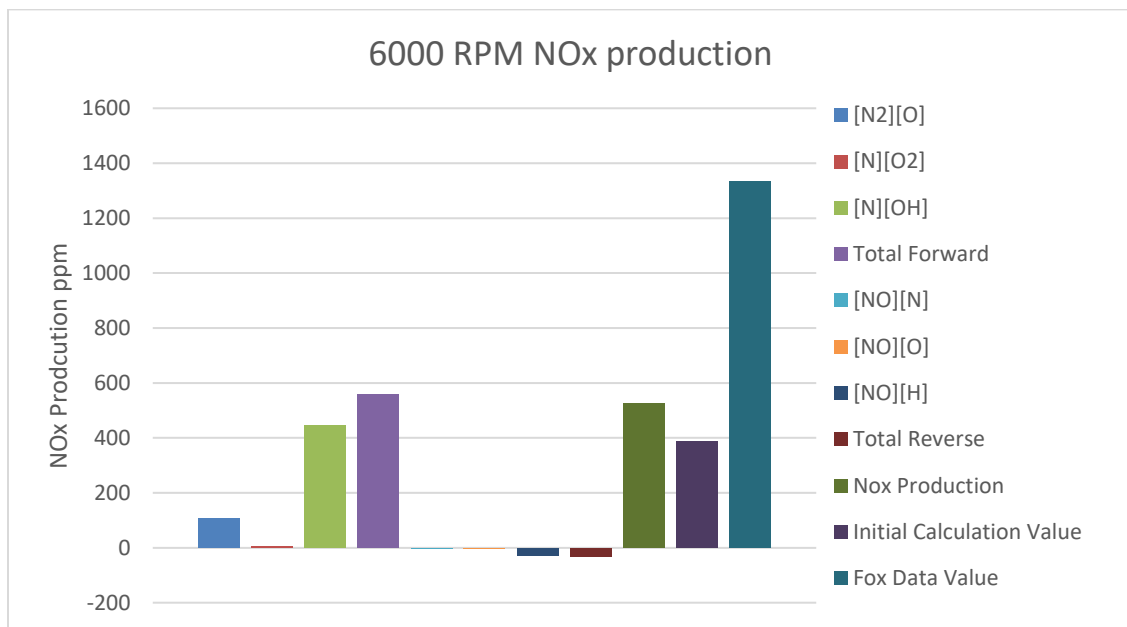


Figure 41

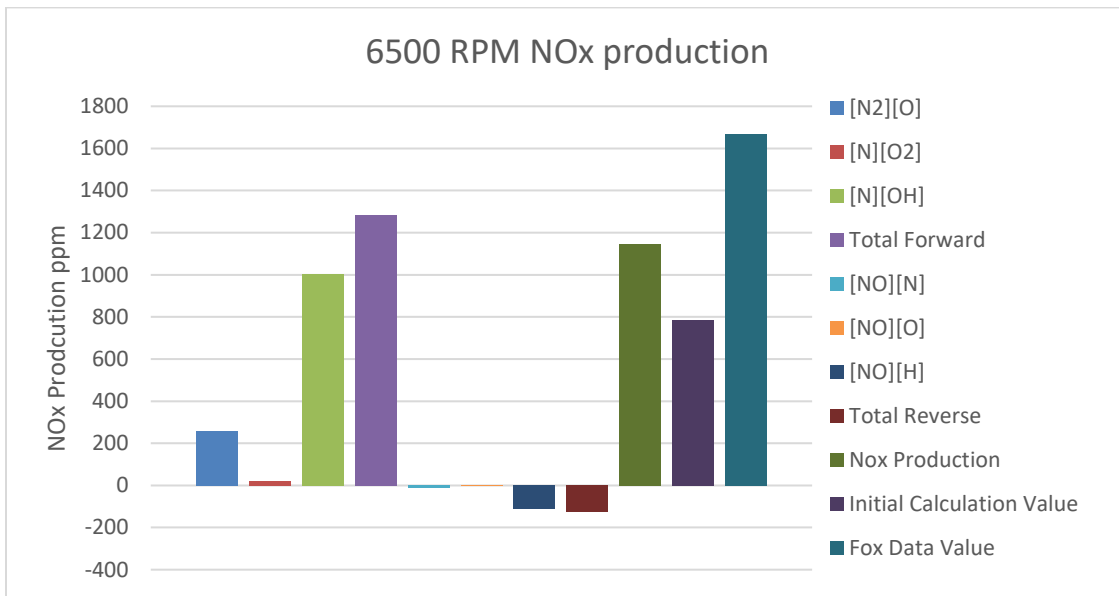


Figure 42

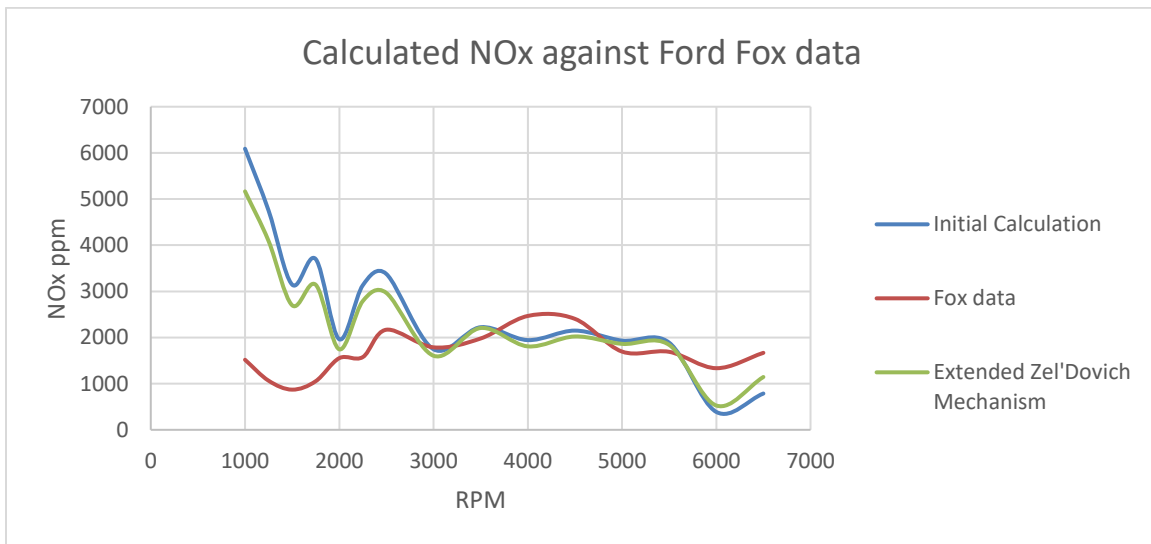


Figure 43

In figures 41 and 42 we can see an under prediction of NOx. The reason this occurs is because the model being used assumes that the mixture of fuel and air is homogenous where as in actuality this is not the case. At these two RPM's the model assumes all combustion to be rich which therefore means that oxygen molecules are only formed through the dissociation mechanisms. When the fuel is injected into the cylinder it will form both lean and rich patches. In the real engine these lean patches will lead to addition oxygen in the combustion chamber that has not been calculated in the theoretical model.

Figure 43 gives a general idea of how accurate the model is. We can see from the values between 3000 and 5500 RPM that the model is predicting fairly accurate results with the differences and error percentages shown in the figure below.

RPM	Nox from Fox Data	Theoretical Nox	Difference	error %
1000	1518	5165.563274	3647.563274	240.2874
1250	1064	4090.410615	3026.410615	284.4371
1500	871	2697.961565	1826.961565	209.7545
1750	1053	3143.278717	2090.278717	198.507
2000	1553	1743.519007	190.519007	12.2678
2250	1577	2791.297459	1214.297459	77.00047
2500	2169	2965.37987	796.3798696	36.71645
3000	1787	1605.29206	181.7079397	10.16832
3500	1979	2205.721954	226.7219543	11.45639
4000	2467	1808.342022	658.657978	26.69874
4500	2404	2023.052736	380.9472639	15.84639
5000	1695	1862.051764	167.0517642	9.855561
5500	1690	1839.989561	149.9895613	8.875122
6000	1335	527.039621	807.960379	60.52138
6500	1668	1144.644661	523.3553388	31.37622

The results with low error values can be used to compare the formation and destruction rates of the different mechanisms that are involved. From figures 35 to 40 we can see that the governing forward mechanism revolves around NO_x formation from dissociated nitrogen atoms and hydroxyl molecules as these values are the highest in all of these cases. The rate constant for this mechanism is $4.1 \times 10^{13} \text{ cm}^3/\text{mol.s}$, this rate constant is not governed by temperature and is purely based on concentrations. As hydroxyl dissociates fairly readily in combustion temperatures along with the fact that this rate constant is very large the small amount of nitrogen atoms available from dissociation makes very little difference to the rate of production. From these figures we can also see that the next highest rate of NO_x production comes from the mechanism involving dissociated oxygen atoms and nitrogen molecules. There is an abundance of nitrogen in the air inside the cylinder however this reaction is limited by the amount of dissociated oxygen. Where as the amount of oxygen has similar values to the amount of hydroxyl, the amount of dissociated oxygen atoms are roughly a power of 10 smaller. The least NO_x production comes from the mechanism that involves dissociated nitrogen and oxygen molecules this reaction produces less than half the amount of NO_x produced from the previously mentioned mechanism. This is due to the very low concentration of nitrogen atoms because of its strong bonds that provide resistance to dissociation.

These results also give us an insight into what mechanisms govern the reverse reactions. We can see from these figures that the reverse reactions occurring between NO and nitrogen or oxygen atoms are essentially negligible. The only reaction that seems cause much of a reverse reaction is the reaction involving NO and dissociated hydrogen atoms.

5. Conclusion

The aim of this dissertation was to create theoretical model for the production of NO_x during combustion. By comparing the theoretical to the real data taken from the Ford Fox engine it has been shown that the model created is accurate to a decent extent. The model created was able to predict results close to the real data values for the RPM regions that are not too rich or not too lean and in these cases the reasoning behind these inaccuracies has been covered. The accurate data sets have been used to compare the mechanisms that form and destroy NO_x during the combustion process giving an insight into the ways in which NO_x is produced. This model could be further improved to give more accurate results for NO_x production and could be used to predict NO_x emissions from data taken from other engines.

6. Further Work/ Improving the Model

There are several ways that this model could be improved. Firstly, a computation fluid dynamics model of the fuel injection could be created. This combined with a CFD model for the air flow intake and air behavior within the cylinder during the combustion process could create a multi-zone model that could predict the formation of lean and rich patches inside the cylinder. These could then be used to predict more accurate values for the production of NO_x and potentially stop the model from under predicting when the engine is running rich.

Finite element analysis could be used to calculate the heat transfer through the cylinder walls and piston to provide more accurate temperatures, this could also allow the model to be set as a running model to provide emission data as the engine heats up when it kept at a specific RPM.

To improve the issues with the rate constants when the engine is running lean new rate constants would need to be calculated. This can be done through experimentation using a combustion chamber where the conditions can be fixed.

7. References

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8. Appendix

