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Combustion and Emissions Study

Modeling Fuels and NO_x

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Contents

Introduction.....	4
Methanol Fuel Blend Stoichiometry	4
1.1 Methodology.....	4
1.1.1 Chemical Balancing.....	4
1.1.2 Air Fuel Ratio.....	5
1.1.3 Mass Percentages.....	6
1.1.4 Enthalpies of Formation	6
1.1.5 Higher and Lower Heating Values	6
1.1.6 CO ₂ Mass	7
1.1.7 An Ideal Fuel	7
Lean NO _x Production Model	8
1.2 Methodology and Analysis	8
1.2.1 Adiabatic Flame Temperatures	8
1.2.2 The Zeldovich Model	10
E.G.R. NO _x Model	11
1.3 Method and Analysis	12
Conclusion.....	12
References	13
Appendix	14

Figure 1 – Fuel blend calculations formatted within a Microsoft Excel spreadsheet.	5
Figure 2 – Mass of air and fuel of the stoichiometric combustion of a 50:50 Methanol-Isooctane blend compared to that of isooctane and methanol.	6
Figure 3 - - Initial flame temperature Matlab script showcasing the upper and lower flame temperature finding function.	9
Figure 4 - The drop-in flame temperature with change in the fuel equivalence ratio.....	9
Figure 5 - NOx PPM against Equivalence ratio.	11
Figure 6 - The effect of EGR % on NOx PPM.....	12
Figure 7 - Isooctane calculations within Microsoft Excel.	14
Figure 8 - Methanol calculations within Microsoft Excel.	14
Figure 9 - Enthalpies of formation for various fuels. Courtesy of (McAllister, et al., 2011).....	15
Figure 10 - Enthalpies of formation for various hydrogen species including the liquid and gas states.	15
Figure 11 - Enthalpies of formation for various compounds. Imported from http://self.gutenberg.org/articles/eng/Standard_enthalpy_change_of_formation_(data_table)	15
Figure 12 - The various concentrations of pollutants evident in a spark-ignition engine according to equivalence ratio. (Heywood, 2018).....	16

Table 1 - The enthalpies of formation for various compounds and elements featured within the blended combustion mixture.....	6
Table 2 - Comparison between the mass of CO ₂ produced per kg of fuel for the pure fuels and blend.....	7

Equation 1 - Methanol and isooctane fuel blend chemical equation.....	4
Equation 2 – Carbon Count.....	4
Equation 3 - Hydrogen Count.....	4
Equation 4 - Oxygen Count.....	5
Equation 5 - Nitrogen Count.....	5
Equation 6 - Air fuel ratio.....	5
Equation 7 - Air Mass.....	5
Equation 8 - Fuel Mass.....	5
Equation 9 - Fuel mass percentage.....	6
Equation 10 - Used to find the lower and higher heating value of a methanol-isooctane blend.....	7
Equation 11 - Mass of CO ₂ per kg of fuel.....	7
Equation 12 - Method used to find the initial flame temperature from a JANAF table curve fit.....	8
Equation 13 - Burn zone temperature.....	10
Equation 14 – Gunter P. Merker Zeldovich Model (Merker, 2004).....	10
Equation 15 - kmols of mixture drawn into the cylinder based on the ideal gas law.....	10
Equation 16 - Alpha Variable formula.....	10
Equation 17 - O ₂ and N ₂ concentration calculations.....	10
Equation 18 - NO _x PPM.....	11
Equation 19 - Ideal gas law containing EGR from (Heywood, 2018).....	12

Introduction

Fuel, a commodity due to its abundance and affordability, takes on many forms. Most commonly isooctane (gasoline) and n-dodecane (diesel) are found on the floor court of a local fuel station. However other fuels exist such as methanol and ethanol, both biofuels. Each fuel has certain attributes which are evident in combustion with oxidizers.

Therefore, the initial focus will explore stoichiometry, the balancing of fuels during combustion, of alternative fuel blends particularly a 50% methanol-Isooctane blend. Identifying the benefits and variations that exist compared to that of Iso-octane.

However, the production of pollutants from combustion have played a large role in the shaping of the current state of the automobile since the enforcement of stringent laws in the 1950 and 60s during California's smog problems (Raymond, 1962).

While a broad topic spanning many papers and articles only one element will be investigated within this paper, NO_x. different from laughing gas N₂O. Both part of the nitric oxide family, laughing gas is not strongly oxidizing and thus is not classified as a nitrous gas (Dietsche & Reif, 2018). While on the other hand Nitrogen Dioxide NO₂ and Monoxide NO as well as other various dimers are strongly oxidizing and therefore known as nitrous gasses. Responsible for smog and acid rain.

The main focus will be brought on to study the impact of varying equivalence ratios, specifically when combustion grows leaner, on the production of NO_x through the development of a mathematical model in Matlab based on the Merker Zeldovich model.

Further to this a common method of reducing NO_x production, recirculated exhaust gases (EGR), will be investigated to determine the impact this system has on the reduction of NO_x parts per million.

Methanol Fuel Blend Stoichiometry

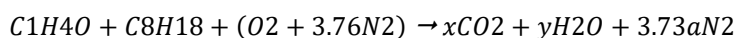
Stoichiometry is the balancing of fuel and oxidizers for complete combustion, an essential component within an internal combustion engine as it allows the mass of fuel in relation to air to be understood.

Understanding this an investigation is carried out into properties that exist within a fuel blend of 50% Iso-Octane and 50% methanol. This is done through a calculation spreadsheet within Microsoft Excel.

1.1 Methodology

1.1.1 Chemical Balancing

The fuel blend is 50% Methanol C₁H₄O and 50% IsoOctane C₈H₁₈ and is represented in the following chemical equation.



Equation 1 - Methanol and isooctane fuel blend chemical equation.

The composition of air is understood to be made up of part oxygen O₂ and nitrogen N₂ (as well argon and CO₂) which are assumed to be 20.95% and 78.09% respectively (Haynes, 2017). This produces the atmospheric ratio of 3.73.

The next step in the process is to chemically balance the equation. Assuming that the input of both isooctane and methanol on the left-hand side of the equation automatically divides the fuel balance in half. Firstly, the total carbon molecules on the left must equal those on the right as no other carbon molecules are present this produces n₁ as seen in Equation 2. Secondly, hydrogen can be found through the understanding as described by Equation 3.

$$n_1(x) = \text{Total Carbon on the left}$$

Equation 2 – Carbon Count.

$$n_2 = y/2$$

Equation 3 - Hydrogen Count.

The oxygen count is found first before the number of nitrogen molecules, following the simplified Equation 4. Lastly the nitrogen count is found through Equation 5 directly connected to the atmospheric ratio. Following this summation, the combustion is balanced.

$$n4 = \frac{(2 * n1) + n2 - 1}{2}$$

Equation 4 - Oxygen Count.

$$n3 = \text{Atmospheric Ratio} * n4$$

Equation 5 - Nitrogen Count.

Below is the chemical balancing expressed in a Microsoft Excel spreadsheet specifically calculated for the 50% methanol-isooctane fuel blend.

50% ISO-OCTANE + 50% METHANOL					
O2	20.95%	20.95	Atmospheric	Ratio	
N2	78.09%	78.09	Composition	3.73	
HC Fuel Balance $C_8H_{18}O + C_8H_{18} + a(O_2 + 3.76N_2) \rightarrow xCO_2 + (y/2)H_2O + 3.76aN_2$					
where... $a = ((2 * n1) + n2 - 1) / 2$					
			a	n4	14
Carbon (x)	9		CO2	n1	9
Hydrogen(y)	22		H2O	n2	11
			N2	n3	52.18424821
m(air)	1909.862 kg		Molecular Weight		
m(fuel)	146.274 kg				
Fuel Mass Percentage			Air		136.42
Iso-Octane	78.09 %		Carbon		12.01
Methanol	21.91 %		Hydrogen		1.01
			Oxygen		16.00
			Nitrogen		14.01
m(CO2)	396.081 kg				
CO2/kg of Fuel	2.707802 kg				
Stoich Ratio	13.05674				
LHV	39.25 MJ/kg				
HHV	42.56 MJ/kg				

Figure 1 – Fuel blend calculations formatted within a Microsoft Excel spreadsheet.

1.1.2 Air Fuel Ratio

The stoichiometric air fuel ratio describes the ratio of air mass to fuel mass to be burned for complete combustion. Lambda is another term used for comparing a current air fuel ratio against the stoichiometric ratio. If less air is present during combustion than stoichiometric the mixture is referred to as being rich. If there is a greater amount of air present than fuel the mixture is known as being lean. Equivalence ratio on the other hand describes the fuel air ratio, the inverse of lambda.

The air fuel relationship is expressed through the Equation 6.

$$\text{AirFuel Ratio} = \frac{Ma}{Mf}$$

$$Ma = \text{Air Mass (kg)}, \quad Mf = \text{Fuel Mass (kg)}$$

Equation 6 - Air fuel ratio.

The ratio is built upon the calculation of the masses of both fuel and air from the molecular weights (AMU) of each element. The mass of air and fuel are expressed in Equation 7 and Equation 8, respectively.

$$Ma = n4((\text{Oxygen AMU} * 2) + (\text{Atmospheric Ratio} * \text{Nitrogen AMU} * 2))$$

Equation 7 - Air Mass.

$$Mf = (\text{Carbon AMU} * n1) + (\text{Hydrogen AMU} * (n2 * 2)) + (\text{Oxygen AMU} * 1)$$

Equation 8 - Fuel Mass.

It is found through the calculations that the combined stoichiometric ratio of the 50% methanol-isooctane blend is 13.06. Compared to the stoichiometric air fuel ratio of isooctane at 14.93 and that of methanol at 6.39 there are considerably more less fuel to air quantity to methanol alone.

m(air)	1909.862	kg
m(fuel)	146.274	kg

Figure 2 – Mass of air and fuel of the stoichiometric combustion of a 50:50 Methanol-Isooctane blend compared to that of isooctane and methanol.

1.1.3 Mass Percentages

The mass percentage represents the concentration of an element, in this case either isooctane or methanol, within the whole blend. The mass percentage is found through the Equation 9, using fuel masses calculated from pure isooctane and methanol combustion calculations, these tables can be found in the appendix Figure 3 & Figure 4. The fuel mass of isooctane makes up the majority of the fuel blend at 78.09%. (Helmenstine, 2018)

$$\text{Fuel Mass Percentage} = \left(\frac{\text{Mass of Single Fuel}}{\text{Mass of Fuel Blend}} \right) * 100$$

Equation 9 - Fuel mass percentage.

1.1.4 Enthalpies of Formation

Enthalpies of formation describes the change in enthalpy for the formation of a molecule from its elemental state. For example, the enthalpy of formation of isooctane C_8H_{18} is -259.20 KJ (an exothermic reaction) from the base elements of carbon C and hydrogen H. The values used for further calculations are found in Table 1.

Compounds	Enthalpy of Formation (KJ/mol)
Methanol CH_3OH	-239.1
Iso-Octane C_8H_{18}	-259.20
Carbon Dioxide C	-393.50
Water H_2O (liquid)	-285.83
Water H_2O (liquid)	-241.82
Oxygen	0
Nitrogen	0

Table 1 - The enthalpies of formation for various compounds and elements featured within the blended combustion mixture.

1.1.5 Higher and Lower Heating Values

Heating values are determined by the state of the water products within the fuel at the standardised conditions of 25°C and 101.3kPa. If the water H_2O is in a gas state it is less dense and the heat released is lower denoting it as the lower heating value LHV. When the water products are in a liquid state it has additional energy present due to the latent heat of evaporation, defined as “the heat required to change one mole of liquid at its boiling point under standard atmospheric pressure.” (Singh, et al., 2011). This energy addition defines this phase as the higher heating values HHV. (McAllister, et al., 2011)

Through the understanding of Hess's law which states that regardless of the type of reaction the resultant or total change in enthalpy will still be the sum of all changes. This is based on the fact that enthalpy is a state function. Using

a data sets containing the enthalpies of formation for each individual component, featured in the appendix Figure 5,6,7 (McAllister, et al., 2011), the total LHV and HHV can be calculated for the reaction using the Equation 10, respectively.

$$LHV \left(\frac{MJ}{kg} \right) = \left((n_1 * \Delta h_{fo} \text{ of CO}_2) + (n_2 * \Delta h_{fo} \text{ of H}_2\text{O gas}) \right) - \left((\Delta H_{fo} \text{ of IsoOctane}) + (\Delta H_{fo} \text{ of Methanol}) \right) / M_f$$

$$HHV \left(\frac{MJ}{kg} \right) = \left((n_1 * \Delta h_{fo} \text{ of CO}_2) + (n_2 * \Delta h_{fo} \text{ of H}_2\text{O liquid}) \right) - \left((\Delta H_{fo} \text{ of IsoOctane}) + (\Delta H_{fo} \text{ of Methanol}) \right) / M_f$$

Equation 10 - Used to find the lower and higher heating value of a methanol-isooctane blend.

The lower and higher heating value of the fuel blend was as follows. It was found to be closer to that of isooctane than methanol.

$$LHV = 39.25 \text{ MJ/kg}$$

$$HHV = 42.56 \text{ MJ/kg}$$

1.1.6 CO2 Mass

Carbon dioxide, a by-product of the combustion process is of main concern when discussing global warming especially when in relation transportation, hence it is useful to be able to quantify the mass production of CO2 per kg of fuel burnt. This can be found through the equation 11.

$$CO_2 \text{ Mass} = n_1 * (\text{Carbon Molecular Mass} + (2 * \text{Oxygen Molecular Mass})) \quad kg$$

$$CO_2 \text{ per kg of fuel} = \frac{CO_2 \text{ Mass}}{M_f}$$

Equation 11 - Mass of CO2 per kg of fuel.

Examining the differences in the mass of CO2 produced per kg of different fuel types in Table 2. The fuel blend strikes a medium between the two fuel types as isooctane produces the highest while standalone method produces the lowest by far. Hence, the blend showcases a clear reduction in CO2 emissions from that of isooctane.

Fuel	Mass of CO2 per kg of fuel (kg)
Iso-Octane	3.08
Methanol	1.37
50:50 Methanol-IsoOctane Blend	2.70

Table 2 - Comparison between the mass of CO2 produced per kg of fuel for the pure fuels and blend.

1.1.7 An Ideal Fuel

These are believed to be the three main points relevant to this study, not touching upon volatility or safety, that stipulates an ideal fuel.

1.1.7.1 Resistance to Detonation

As cylinder pressures increase, in turn increasing the temperatures within, the requirement for fuels resistant to resist detonation (knock) is paramount. Comparing ignition temperatures methanol proves advantageous with an ignition temperature of 450°C, higher than that of Isooctane at 300°C. This higher temperature means a greater resistance to ignition from hotspots present and allows for more burn time before abnormal combustion can occur.

1.1.7.2 High Energy Content

At 44.3 MJ/kg – 47.8 MJ/kg the lower and upper heating values of Isooctane are far greater than that of methanol at 21.1 MJ/kg – 23.8 MJ/kg. Therefore, fuel consumption will have to be increased for the same power output. This is

due to the there being oxygen present in alcohol-based fuels, which does not contribute to the energy release (Dietsche & Reif, 2018). The even blend of the two fuels produce a heat release value of 39.3 MJ/kg – 42.5 MJ/kg closer to that of Isooctane.

Methanol has the disadvantage of requiring a greater percentage within a volume of air at 12%, compared to 1.6%, that of isooctane (Williams, 2018). A point to be taken into consideration when within a port injected system, as the amount of reactant to be drawn into the cylinder would be limited. This can be corrected with direct injection. The isooctane blend similar to before has properties closer to that of isooctane and the negative value of stand-alone methanol is improved upon.

1.1.7.3 Rate of Combustion

The rate of combustion is another factor to consider when discussing the ideal fuel. Reason being it affects the maximum brake torque (MBT) timing, the ideal time for ignition resulting in the best power output. The rate of fuel burning dictates this position, slow burning would result in earlier ignition causing an increase in negative work while if left unaltered would create a greater amount of burning during the expansion stroke. Both outcomes causing a reduction in break torque.

Isooctane has a burning velocity of 27.00 cm/s at an equivalence ratio of 1 while methanol burns at 32.69 cm/s, 19% faster than gasoline (Metghalchi & Keck, 1982). Therefore, the fuel blend may exhibit an improvement within burn rates over isooctane, lending itself to an ideal fuel.

Lean NOx Production Model

NOx as discussed previously is the name given for either NO or NO₂ and is a product of the reaction between nitrogen and oxygen during combustion at high temperatures. Temperatures which are evident when residual gas from the flame front is compressed during an engine cycle. When a fuel mixture is lean the flame front moves at a slower rate and allows more time for the heating of the residual gas. In this first task the effect of equivalence ratio on adiabatic flame temperatures and therefore the production of NOx will be investigated.

1.2 Methodology and Analysis

An Isooctane NOx model is developed within Matlab running on the lean side of stoichiometric.

Note from author: The reason for the change from Microsoft Excel based analysis to Matlab based was purely a choice of direction and academic learning. While competent in Excel the challenge and spur to learn Matlab would be most evoked through a learning challenge with a positive outcome. Hence the use of Matlab.

The equivalence ratio for lean combustion is calculated for a range of 0.6 to 0.95 in increments of 0.05, and from 0.95 to 1.0 in increments of 0.01. This creates the variable PHI.

1.2.1 Adiabatic Flame Temperatures

The first step is to find the adiabatic flame temperatures assuming the there is no heat transfer within the system.

The net enthalpy release of the chemical reaction is calculated for each fuel equivalence ratio. A curve fit to the 8th polynomial, which is believed to fit the curve best, is developed from JANAF thermochemical data tables (McAllister, et al., 2011) showing the corresponding temperature for the change in enthalpy for each element. This is done in order to find the exact corresponding temperature between figures. The 'find' method is used within Matlab to locate the upper and lower constituents closest to the corresponding net heat release figure. Seen in Figure 3, lines 91-99, the script for this function is shown. Therefore Equation 12 can be used to find the corresponding initial flame temperature.

Initial Flame Temperature

$$= \text{Lower Temp} + ((\text{Upper Temp} - \text{Lower Temp}) * \left(\frac{\text{Net Entalpy} - \text{Lower Heat Release}}{\text{Upper Heat Release} - \text{Lower Heat Release}} \right)) \text{ } ^\circ\text{K}$$

Equation 12 - Method used to find the initial flame temperature from a JANAF table curve fit.

```

80 load('CO2fit.mat')
81 load('H2Ofit.mat')
82 load('N2fit.mat')
83 load('O2fit.mat')
84
85 Poly_Ent_CO2 = n1.*CO2fit(Temperature); % CO2 Entropies
86 Poly_Ent_H2O = n2.*H2Ofit(Temperature); % H2O Entropy
87 Poly_Ent_O2 = n3.*O2fit(Temperature); % O2 Entropy
88 Poly_Ent_N2 = n4.*N2fit(Temperature); % N2 Entropy
89
90 Net_Heat_Release = Poly_Ent_CO2 + Poly_Ent_H2O + Poly_Ent_N2 + Poly_Ent_O2; % CO2, H2O, N2 and O2 Entropies added.

```

Flame Temp

```

91 Flame_Temp = zeros(1,13); % Empty flame temperature matrix
92
93 for i = 1:13 % Loop to find most accurate entropy for temperature range.
94
95     Upper_Temp_ind = find(Net_Heat_Release(:,i)>=Net_Enthalpy(:,i));
96     Upper_Temp = Temperature(1,Upper_Temp_ind(1,:));
97
98     Lower_Temp_ind = find(Net_Heat_Release(:,i)<=Net_Enthalpy(:,i));
99     Lower_Temp = Temperature(1,Lower_Temp_ind(end,:));
100
101     Flame_Temp(:,i) = Lower_Temp + (((Upper_Temp - Lower_Temp)*((Net_Enthalpy(:,i)-Net_Heat_Release(Lower_Temp_ind(end,:),i)))/((Net_Heat_Release(Upper_T
102 % Equations from 'flame temperature' sheet
103
104 end

```

Figure 3 -- Initial flame temperature Matlab script showcasing the upper and lower flame temperature finding function.

It is clear to see in Figure 3 that there is a drop-in flame temperature as the combustion runs leaner. The reason for this trend is that as the combustion process gets leaner there is less net heat release from the reaction, as less fuel is burned.

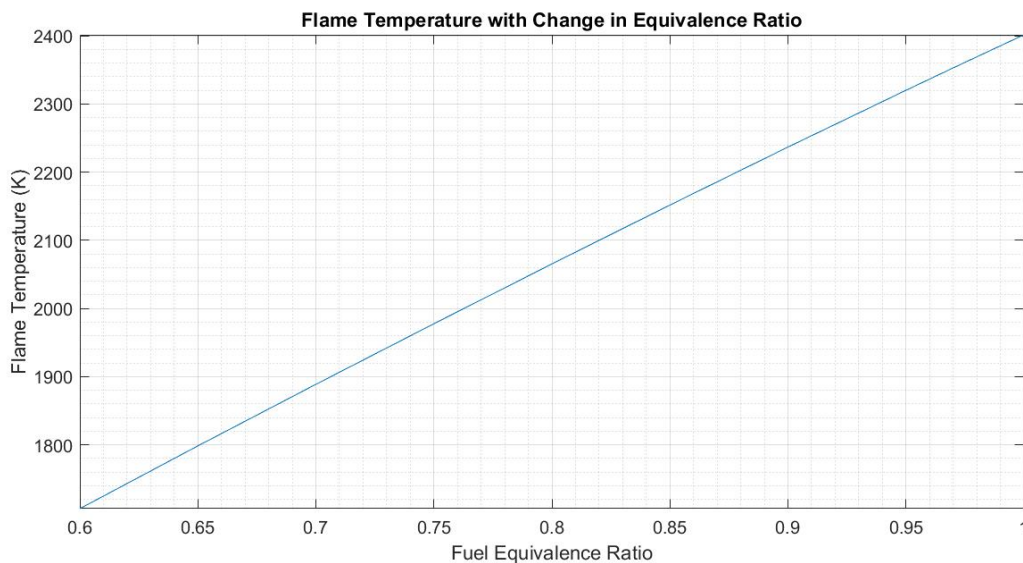


Figure 4 - The drop-in flame temperature with change in the fuel equivalence ratio.

Once the initial flame temperatures are found the actual burn zone temperatures can be calculated. A product of an increase in cylinder pressure experienced within the engine compression cycle. The increase in pressure is modelled across a range of 10 bar to 40 bar in 2 bar increments at 1° crank intervals. A polytropic index of 1.17 is assumed. Therefore, the burn zone temperature can be calculated using the Equation 12, derived from the understanding that the process is polytropic. A clear rise in temperature is evident from the pressure increase.

$$\text{Burn Zone Temperature} = \text{Flame Temperature} * \left(\frac{P_2}{P_1}\right)^{nx} \quad ^\circ K$$

$$nx = \frac{(n-1)}{n}$$

$n = \text{Polytropic Index, } P = \text{Pressure (Bar)}$

Equation 13 - Burn zone temperature.

1.2.2 The Zeldovich Model

The formation of NO_x is directly dependant on temperature, through the understanding that at high temperatures the formation of unstable radicals increases during the separation of nitrogen and oxygen molecules. Which is not the case at lower temperatures as the dissociated molecules form more stable radicals. (Williams, 2018) This formation is described by the Zeldovich mechanism.

There are various Zeldovich models developed to calculate the production of NO_x. The one focused upon in this report is the model developed by Merker as shown in Equation 14. The main difference between other models such as John B. Heywoods and McAllister models are the alteration speed coefficients for the forward reaction. (Merker, 2004)

$$\frac{d[NO]}{dt} = 4.7 * 10^{13} [N_2][O_2] * 0.5 * e^{\left(\frac{-67837}{\text{Burn Zone Temperature}}\right)} \left(\frac{\text{kmols}}{\text{m}^3}\right)$$

Equation 14 – Gunter P. Merker Zeldovich Model (Merker, 2004)

A component of Zeldovich model is the oxygen and nitrogen concentrations. As an increase in these concentrations directly impact the chances of a reaction occurring between these substances. In order to calculate the concentrations, an alpha variable must first be found using Equation 14. This determines the actual kmols of O₂ and N₂ in the complete mixture drawn into the cylinder.

For this mathematical model a theoretical engine is used, specified at a capacity of 1600cc with four cylinders, it is naturally aspirated. The engine speed it assumed constant at 1800 RPM. A volumetric efficiency of 40% is also assumed. Cylinder head volume is assumed at 40ccs.

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

Equation 15 - kmols of mixture drawn into the cylinder based on the ideal gas law.

$$\alpha = \frac{n}{\phi + 12.5(1 + 3.76)}$$

Gas Constant $R = 8314 \text{ KMOL}^{-1} \text{ K}^{-1}$, $P = 1 \text{ Bar Atmospheric}$, $V = \text{Cylinder Volume} * \text{Volumetric Efficiency}$

Equation 16 - Alpha Variable formula.

$$[O_2] = \frac{n_3 * \alpha}{\text{Cylinder Volume Head} * 10^{-6}}$$

$$[N_2] = \frac{n_4 * \alpha}{\text{Cylinder Volume Head} * 10^{-6}}$$

Cylinder Volume Head (ccs)

Equation 17 - O₂ and N₂ concentration calculations.

Once the concentrations and burn temperatures are found the NO_x production for the theoretical engine, per the various Zeldovich models, can be calculated. Following this the NO_x PPM can be found through Equation 18.

$$NO_x PPM = \left(\frac{\frac{d[NO]}{dt} * Cylinder Volume Head * 10^{-6}}{RPM * 6 * \alpha(n1 + n2 + n3 + n4)} \right) * 10^6 (PPM)$$

Equation 18 - NO_x PPM.

The results from the MATLAB lean NO_x Formation script are represented in Figure 4. The script model is validated as it shows a trend similar to that discussed by John B. Heywood, seen in Figure 12 (Heywood, 2018)(Heywood, 2018). Peak NO_x formation is evident at an equivalence ratio of 0.97 as it is believed that combustion has significantly slowed at this point for the optimal formation of unstable radicals to occur. As the equivalence ratio further decreases the NO_x production decreases, despite the increased availability of O₂ concentrations the flame temperatures are no longer high enough.

The NO_x production result in real world conditions are expected to be lower and this method is generally considered to be an overprediction as reverse reactions are not taken into consideration. (McAllister, et al., 2011)

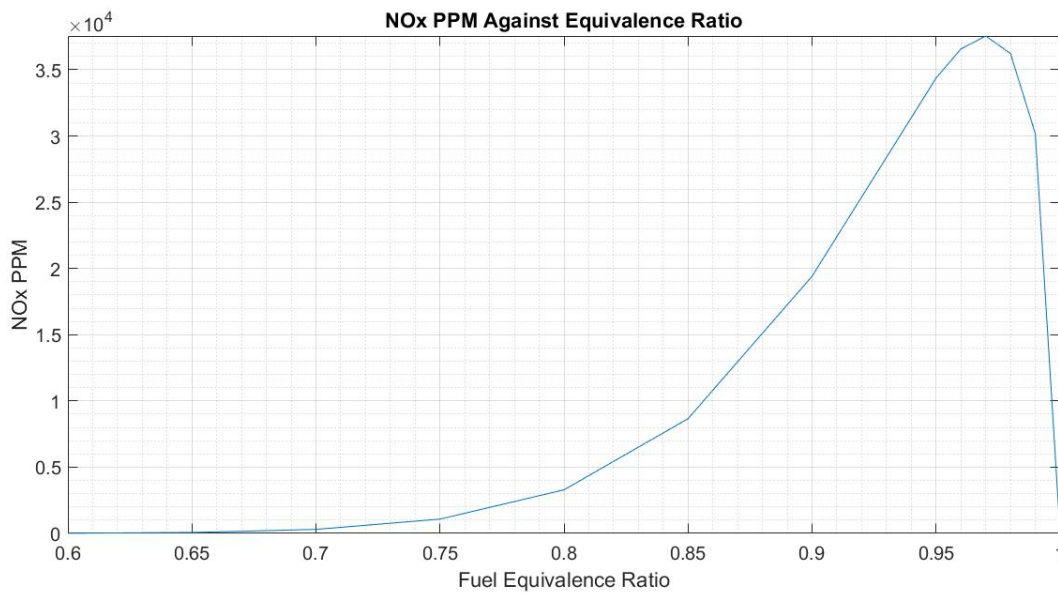


Figure 5 - NO_x PPM against Equivalence ratio.

E.G.R. NO_x Model

Exhaust gas recirculation is the re-introduction of exhaust gas, which has been cooled, into a fresh intake charge mixture through an EGR valve. (Dietsche & Reif, 2018) The principle behind this concept is to lower the in cylinder peak temperatures through increasing the mixture mass. Examining the ideal gas equation with the addition of EGR as featured in (Heywood, 2018) the affect of EGR can be shown. Pressure and volume remain the same as well as the gas constant with minor differences. The mass however increases in relation to the percentage of EGR added. A 5% EGR addition adds 5% more mass to the mixture thus creating a 5% drop in the temperatures, essential in lowering the production of the aforementioned unstable radicals.

$$PV = M_{EGR}RT_{EGR}$$

Equation 19 - Ideal gas law containing EGR from (Heywood, 2018).

1.3 Method and Analysis

The effects of EGR is studied through the use of the model previously developed for lean NO_x calculation in Matlab. A set fuel equivalence ratio is selected, 0.97, as the highest NO_x PPM was featured. The net enthalpy remains the same, as the exhaust gases have been added to both sides of the combustion equation. Only the initial flame temperatures are affected as the EGR ratio are added to the curve fit function and the remainder of the script is run without alternation. The volumetric efficiency is assumed to be the same. The O₂ and N₂ concentrations are automatically adjusted. The same theoretical engine model as before is used.

The NO_x PPM is plotted against EGR %, and the Figure 5 is produced.

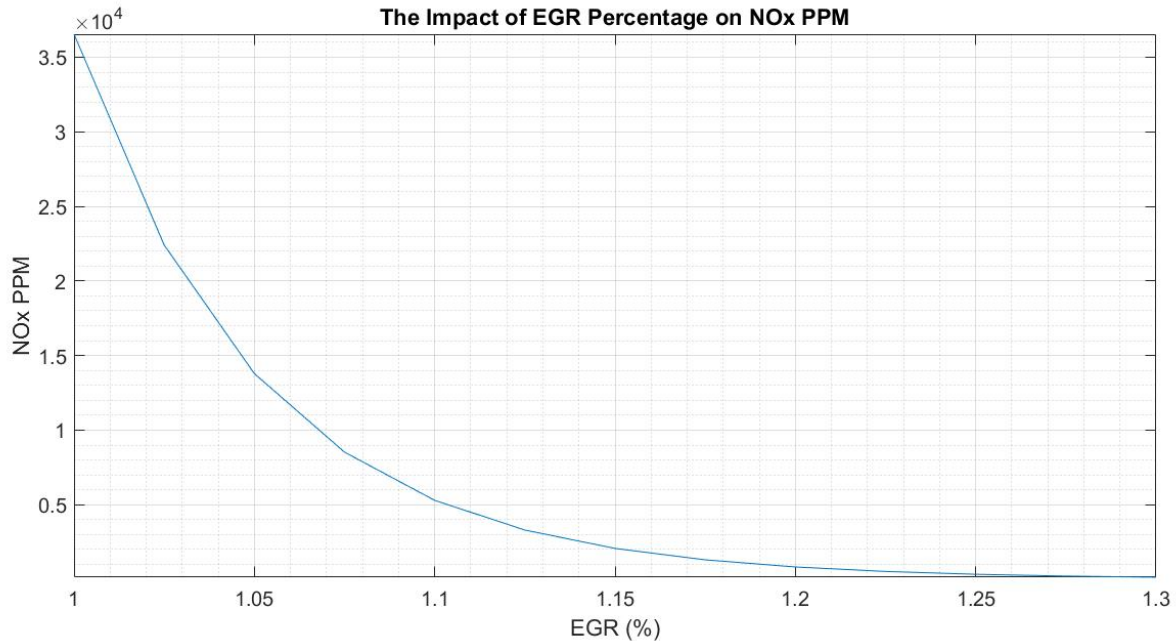


Figure 6 - The effect of EGR % on NO_x PPM.

At an equivalence ratio of 0.97 the reduction of NO_x production in relation to the addition of exhaust recirculated gases is clear. The addition of 5% EGR produces a reduction of average NO_x PPM by 62.26%. This trend is continued through with each 5% addition of EGR, a reduction of ~60% is experienced. This can be traced to the lower initial flame temperatures that it produces. At 0% EGR the burn temperature is 2344.3 °K, with 5% EGR the new flame temperature is 2254.6 °K. It proves the effectiveness of EGR addition to lower NO_x production.

Conclusion

An ideal fuel is debatable however there are a few characteristics that can be agreed upon which would make up such a substance, resistance to detonation, high energy content and a fast rate of combustion. Through the calculations carried out on a 50% methanol-Isooctane fuel blend it can be considered close to an ideal fuel with a presumed higher resistance to detonation and a rate of combustion closer to that of iso-octane, although both these elements will require further investigation and testing. The mixing of alcohols-based fuels with isooctane significantly increases the production of aldehyde emissions responsible for photochemical smog. Therefore, although exhibiting the ideal fuel properties it possesses other factors that inhibit it from being an ideal fuel in reducing emissions.

The lean NO_x model developed in Matlab has proven successful in the data produced. It has shown that the peak NO_x production for the specified engine model occurred at an equivalence ratio of 0.97. Interestingly the production of NO_x did not continue to increase in relation to the further drop in equivalence ratio despite the increase of O₂ and N₂ concentrations, the sufficient drop in temperature inhibited the further disassociation of molecules. It was accurately proven however that with a reduction in flame temperature combustion was sufficiently slowed to allow for the formation of unstable radicals. Only one iteration of the Zeldovich model was used within the Matlab model and

proved sufficient as other iterations are also believed to over predict the production of NO_x as in all instances the reverse reactions are not accounted for. The comparison of all Zeldovich model can be carried out against real data for further work. The model however was satisfactory and produced the trends exhibited in previous studies.

The increased inclusion of the EGR system on modern SI and diesel engines to reduce the production of NO_x can be understood as the effectiveness of this system is proven through the model. Reducing the flame temperatures through the addition of mass to the mixture was understood by solving the ideal gas equation. A 10% addition of EGR resulted in a 10% reduction in the flame temperatures. The effect of EGR percentages on NO_x formations was quantified and with each 5% increase in EGR into the mixture decreased the NO_x PPM production by ~60%. Resulting in an effective method at reducing NO_x production.

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Appendix

ISO-OCTANE C8H18					
O2	20.95%	20.95	Atmospheric	Ratio	
N2	78.09%	78.09	Composition	3.73	
HC Fuel Balance $C_xH_y + a(O_2 + 3.76N_2) \rightarrow xCO_2 + (y/2)H_2O + 3.76aN_2$					
where... $a = x + (y/4)$					
			a	n4	12.5
Carbon (x)	8		CO2	n1	8
Hydrogen(y)	18		H2O	n2	9
			N2	n3	46.59308
m(air)	1705.234				
m(fuel)	114.232		Molecular Weight		
			Air		136.42
m(CO2)	352.072		Carbon		12.01
CO2/kg of Fu	3.082079		Hydrogen		1.01
			Oxygen		16.00
Stoich Ratio	14.92781		Nitrogen		14.01
LHV	44.34				
UHV	47.81				

Figure 7 - Isooctane calculations within Microsoft Excel.

METHANOL CH4O					
O2	20.95%	20.95	Atmospheric	Ratio	
N2	78.09%	78.09	Composition	3.73	
HC Fuel Balance $C_xH_yO + a(O_2 + 3.76N_2) \rightarrow xCO_2 + (y/2)H_2O + 3.76aN_2$					
where... $a = ((2 \cdot n_1) + n_2 - 1)/2$					
			a	n4	1.5
Carbon (x)	1		CO2	n1	1
Hydrogen(y)	4		H2O	n2	2
			N2	n3	5.591169
m(air)	204.628				
m(fuel)	32.042		Molecular Weight		
			Air		136.42
m(CO2)	44.009		Carbon		12.01
CO2/kg of Fu	1.373479		Hydrogen		1.01
			Oxygen		16.00
Stoich Ratio	6.386244		Nitrogen		14.01
LHV	21.09				
UHV	23.83				

Figure 8 - Methanol calculations within Microsoft Excel.

Formula	Fuel	$\Delta \hat{h}^0$ (kJ/mol)
CH ₄	Methane	-74.40
C ₂ H ₂	Acetylene	8.70
C ₂ H ₄	Ethylene	52.40
C ₂ H ₆	Ethane	-83.80
C ₃ H ₈	Propane	-104.70
C ₄ H ₁₀	n-Butane	-146.60
C ₄ H ₁₀	iso-Butane	-153.50
C ₅ H ₁₂	n-Pentane	-173.50
C ₅ H ₁₂	iso-Pentane	-178.50
C ₆ H ₁₄	n-Hexane	-198.70
C ₆ H ₁₄	iso-Hexane	-207.40
C ₇ H ₁₆	n-Heptane	-224.20
C ₈ H ₁₈	n-Octane	-250.10
C ₈ H ₁₈	iso-Octane	-259.20
C ₉ H ₂₀	n-Nonane	-274.70
C ₁₀ H ₂₂	n-Decane	-300.90
C ₁₀ H ₂₂	iso-Decane	0.00
C ₁₂ H ₂₆	n-Dodecane	-350.90
CH ₄ O	Methanol	-201.50
C ₂ H ₆ O	Ethanol	-235.10
H ₂	Hydrogen	0.00

Figure 9 - Enthalpies of formation for various fuels. Courtesy of (McAllister, et al., 2011)

Selected Thermodynamic Values (at 298.15 K)*				
Species	DHf° (kJ/mol)	S° (J/K·mol)	DGf° (kJ/mol)	
Hydrogen				
H+(g)		1536.20		
H ₂ O(l)		-285.83	69.91	-237.13
H ₂ O(g)		-241.82	188.83	-228.57
H ₂ O ₂ (l)		-187.78	109.60	-120.35
Nitrogen dioxide	NO ₂	33.2		

Figure 10 - Enthalpies of formation for various hydrogen species including the liquid and gas states.

Compound	Formula	M g mol ⁻¹	Hc° kJ mol ⁻¹	Hf° kJ mol ⁻¹	Gf° kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹
Carbon monoxide	CO(g)	28.00	-283.00	-110.50	-137.23	197.60
Carbon dioxide	CO ₂ (g)	44.0	-----	-393.50	-394.40	213.60
Alkanes						
Methane	CH ₄ (g)	16.00	-890.30	-74.80	-50.80	186.20
Ethane	CH ₃ CH ₃ (g)	30.10	-1559.70	-84.70	-32.90	229.50
Propane	CH ₃ CH ₂ CH ₃ (g)	44.10	-2219.20	-104.50	-23.40	269.90
Butane	CH ₃ (CH ₂) ₂ CH ₃ (g)	58.10	-2876.50	-126.50	-15.60	310.10
Pentane	CH ₃ (CH ₂) ₃ CH ₃ (l)	72.20	-3509.10	-173.20	-9.20	261.20
Hexane	CH ₃ (CH ₂) ₄ CH ₃ (l)	86.20	-4163.00	-198.60	-4.20	295.90
Heptane	CH ₃ (CH ₂) ₅ CH ₃ (l)	100.20	-4816.00	-224.00	1.30	328.50
Octane	CH ₃ (CH ₂) ₆ CH ₃ (l)	114.20	-5470.20	-250.00	6.40	361.10
Nonane	CH ₃ (CH ₂) ₇ CH ₃ (l)	128.30	-6124.60	-274.00	11.90	393.70
Decane	CH ₃ (CH ₂) ₈ CH ₃ (l)	142.30	-6777.90	-300.90	17.40	425.90
Undecane	CH ₃ (CH ₂) ₉ CH ₃ (l)	156.30	-7430.90	-327.20	22.80	-----
Dodecane	CH ₃ (CH ₂) ₁₂ CH ₃ (l)	170.30	-8086.50	-350.90	28.40	-----
Eicosane	CH ₃ (CH ₂) ₁₈ CH ₃ (s)	282.60				
Alcohols						
Methanol	CH ₃ OH(l)		32	-726	-239.1	239.7
Ethanol	CH ₃ CH ₂ OH(l)		46.1	-1367.3	-277.1	160.7

Figure 11 - Enthalpies of formation for various compounds. Imported from [http://self.gutenberg.org/articles/eng/Standard_enthalpy_change_of_formation_\(data_table\)](http://self.gutenberg.org/articles/eng/Standard_enthalpy_change_of_formation_(data_table))

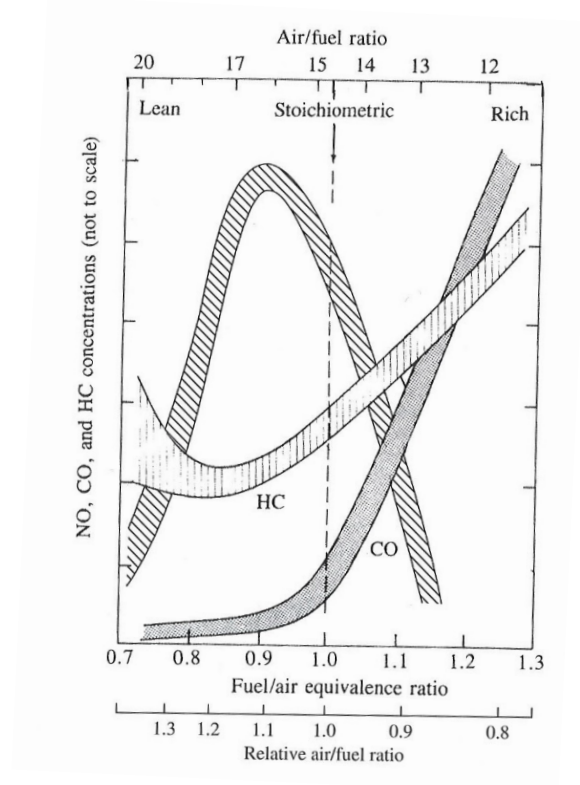


Figure 12 - The various concentrations of pollutants evident in a spark-ignition engine according to equivalence ratio. (Heywood, 2018)