

University of Wales

Trinity Saint David

School of Engineering
Combustion and Emission Study:
Modeling Fuels and NO_x

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1.Introduction

The report includes the calculations, explanation, analysis and modelling of the fuels and NO_x .

The author can obtain deeper knowledge of combustion and emission mechanism and cultivate the skill of tackling with large quantities of data. In this report, lots of data need to be worked on and throughout analysis this enable the author to study the combustion chemistry and engine performance.

For the first part, a blended fuel which was given by task consists of 50% methanol and isooctane, and the calculations in the first part includes comprehensive knowledge from easy question of mass percentage to every critical knowledge points, such as Air/Fuel mass ratio (AFR), lower heating value, mass of CO_2 , etc. The explanations provide author more energy with more concentration on the definition and deep understanding of the combustion and emissions.

For the second part, a NO_x model need to be developed for isooctane with the changes of fuels equivalence ratio (φ), and the NO_x PPM can be demonstrated as a graph by coping with many relative data in excel in order to understand how the effect of φ on the production of NO_x . In addition, the author calculated and plot the graph of NO_x PPM when adding EGR level (0%-20%) to compare the value at different EGR level to find how EGR exerts the influence on the procedure of combustion.

2. Calculations and Explanations for the combustion of the fuel blend

From the known conditions in the task description, isooctane and methanol both have molar composition of 50%.

METHANOL - 50%
ISOCTANE - 50%

2.1 Calculations of the mass fraction of methanol and isooctane

Assuming the molar of the blended mixture is a mol, then the molar of the methanol and isooctane are both $0.5a$ kmol.

Mixed fuel composition and mass:

	Atomic No	Atomic Weight
H	1	1
C	6	12
O	8	16

Table 2.1 Atomic number and weight of H, C and O

$$0.5a \text{ kmol methanol}(\text{CH}_3\text{OH}) = (12+3+16+1) * 0.5a = (0.5a*32) \text{ kg}$$

$$0.5a \text{ kmol isooctane}(\text{C}_8\text{H}_{18}) = (12*8+18) * 0.5a = (0.5a*114) \text{ kg}$$

$$\therefore \text{mass percentage of methanol} = \frac{32*0.5a}{0.5a*(32+114)} = 0.219 = 21.9\%$$

$$\text{mass percentage of isooctane} = \frac{114*0.5a}{0.5a*(32+114)} = 0.781 = 78.1\%$$

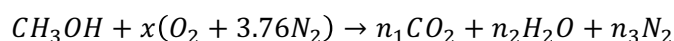
Methanol(CH_3OH)	21.9%
Isooctane(C_8H_{18})	78.1%

Table 2.2 Mass percentage of methanol & isooctane

2.2 Calculate the Air/Fuel Ratio (AFR) for the stoichiometric air fuel

$$AFR \text{ by mass} = \frac{\text{Air Mass}}{\text{Fuel Mass}}$$

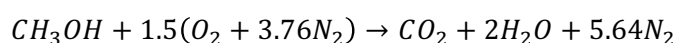
For methanol,



CxHyOz+a(02+3.76N2) → xCO2+(y/2)H2O+3.76aN2			
a=x+(y/4)-z/2			
Carbon(x)	1	a	1.5
Hydrogen(y)	4	CO2	1
Oxygen(z)	1	H2O	2
		N2	5.64

Table 2.3 The balance of equation for methanol in excel

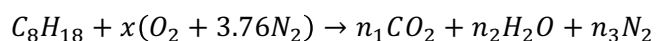
Hence the stoichiometric equation:



Air mass for methanol = $1.5(16 \times 2 + 3.76 \times 28) \times 0.5a = 205.92 \times 0.5a$ kg

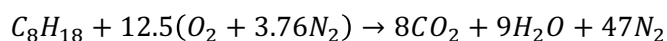
Fuel mass = $(12 + 3 + 16 + 1) \times 0.5a = 32 \times 0.5a$ kg

For isooctane,



CxHyOz+a(02+3.76N2) → xCO2+(y/2)H2O+3.76aN2			
a=x+(y/4)-z/2			
Carbon(x)	8	a	12.5
Hydrogen(y)	18	CO2	8
Oxygen(z)	0	H2O	9
		N2	47

Table 2.3 The balance of equation for isooctane in excel



Air mass for isooctane = $12.5(16 \times 2 + 3.76 \times 28) \times 0.5a = 1716 \times 0.5a$ kg

Fuel mass = $(12 \times 8 + 18) \times 0.5a = 114 \times 0.5a$ kg

Hence, total air mass = $(1716 + 205.92) \times 0.5a = 1921.92 \times 0.5a$ kg

$$\text{Total fuel mass} = (32+114) * 0.5a = 146 * 0.5a \text{ kg}$$

$$\text{AFR by mass} = \frac{1921.92 * 0.5a}{145 * 0.5a} = 13.1638$$

2.3 The lower heating value

The standard table shown below details the $\Delta \bar{h}_f^0$ for these two fuels in the blend.

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

^aGas phase specific heat evaluated at 25°C

^bHeat of vaporization at 1 atm

^cEstimated equilibrium flame temperature

^dResearch octane number

^eMotoring octane number

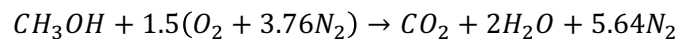
Table 2.5 The fuel database

From the table $\Delta \bar{h}_f^0$, $(CH_3OH) = -259.2 \text{ kJ/mol}$, $\Delta \bar{h}_f^0$ $(C_8H_{18}) = -201.5 \text{ kJ/mol}$.

Also, $\Delta \bar{h}_f^0$ $(CO_2) = -393.5 \text{ kJ/mol}$. Because O_2 and N_2 are pure substances in their standard state, $\Delta \bar{h}_f^0$ $(O_2) = 0 \text{ kJ/mol}$, $\Delta \bar{h}_f^0$ $(N_2) = 0 \text{ kJ/mol}$.

In order to get lower heating value in the blend, the formation of the water should be gas, because H_2O is $\Delta H = -241.8 \text{ kJ/mol}$ as a gas(g) and $\Delta \bar{h}_f^0 = 285.8 \text{ kJ/mol}$ as a liquid (l), and the lower heating value is the term used when H_2O is a gas (LHV) (Williams, 2019, pp.6-7).

For methanol



Enthalpy needed for products = $201.5 \times 0.5a$ MJ ①

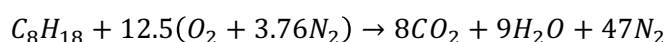
Enthalpy released from reaction = $(393.5 + 2 \times 241.8 + 0) \times 0.5a = 877.1 \times 0.5a$ MJ ②

Net enthalpy = product enthalpy – reactant enthalpy = ② - ① = $675.5 \times 0.5a$ MJ

Since the unit of the heating value is MJ/kg, the mass of methanol in the blend is $0.5a \times 32$ kmol,

The heating value of 1kg of the methanol = $\frac{675.5 \times 0.5a}{0.5a \times 32} = 21.11 \text{ MJ/kg}$

For isooctane



Enthalpy needed for products = $259.2 \times 0.5a$ MJ ③

Enthalpy released from reaction = $(393.5 \times 8 + 9 \times 241.8 + 0) \times 0.5a = 5324.2 \times 0.5a$ MJ ④

Net enthalpy = product enthalpy – reactant enthalpy = ④ - ③ = $5065 \times 0.5a$ MJ

The mass of isooctane in the blend is $0.5a \times 114$ kmol,

The heating value of 1kg of the isooctane = $\frac{5065 \times 0.5a}{0.5a \times 114} = 44.43 \text{ MJ/kg}$

Since the blend consists of methanol and isooctane, and the unit of the calculation is relative to the mass, the mass percentages of these two fuels can be used to solve the heating value of the mixed fuel.

So 1kg blended fuel releases the lower heating value = $21.11 \times 21.9\% + 44.43 \times 78.1\% = 39.32$

MJ/kg

2.4 Explain enthalpy of formation

The enthalpy of formation ($\Delta \bar{h}_f^0$) is the enthalpy change for the formation of 1mol of a compound from its component elements (Williams, 2019, pp.3).

At a certain temperature and pressure, the thermal effect of generating 1 mole of pure substance from the most stable elementary substance is called enthalpy of formation.

The value of ΔH for a reaction is relative to the physical states of reactants and products, the pressure of gases and the temperature (Williams, 2019).

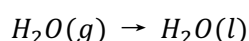
When the pressure where all gases appear is 1 atmosphere (atm) and the concentration of all species in solution (1 mol/L) is 1 M, these conditions are standard.

When a reaction happens and the component elements are at their standard condition, the enthalpies of formation under standard state are called standard enthalpies of formation.

The standard enthalpy of formation of each pure substance is zero, and pure substances must be in the standard state (Williams, 2019).

2.5 Explain the difference between higher and lower heating values

The 'Lower Heating Value' is the term used when H_2O is a gas (LHV), and the 'Higher Heating Value' is the state when H_2O is a liquid (HHV). Since the formation of liquid ($H_2O(l)$) from gaseous water ($H_2O(g)$) needs to release heat, the enthalpy change in this formation can be calculated as followed:



The enthalpy released from liquefaction = $-285.8 - (-241.8) = -44 \text{ KJ/mol}$

When H_2O is a liquid in the reaction above, the 'Higher Heating Value' is:

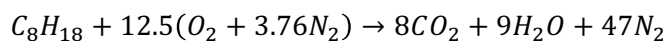
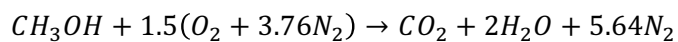
$$\text{HHV} = \frac{763.6}{32} * 0.219 + \frac{5461}{114} * 0.781 = 42.64 \text{ MJ/kg}$$

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

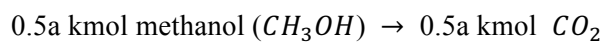
$$\text{HHV} = 42.64 \text{ MJ/kg}$$

The higher heating value include the releasing heat during a reaction from gaseous water to liquid except the heat released by fuels. Hence, HHV shows the releasing heat of the fuel during the combustion.

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



For methanol,



$$0.5a \text{ kmol methanol } (CH_3OH) = (12+3+15+1)*0.5a = 32*0.5a \text{ kg}$$

$$\text{Mass of } 0.5a \text{ kmol } CO_2 = (12+16*2)*0.5a = 44*0.5a \text{ kg}$$

So if 1kg of methanol is burned,

$$\text{Mass of } CO_2 = 44/32 = 1.375\text{kg}$$

For isooctane,

mass of CO₂ produced per kg of isooctane burned,

$$\text{Mass of } CO_2 = 44*8/114 = 3.088\text{kg}$$

Since 1kg blend has 0.219 kg methanol and 0.781 kg isooctane,

$$\text{Total mass of } CO_2 \text{ per kg fuel burned} = 1.375*0.219 + 3.088*0.781 = 2.713\text{kg}$$

2.7 Describe the properties of an “Ideal” fuel

An ‘Ideal’ fuel

An ideal fuel needs to have strong anti-knock performance.

An ideal fuel should absorb more heat to vaporise and then it can cool things down (Williams, 2019, pp.9).

Lighter fuel can lead to faster moving of the molecules, thus it can increase the speed of flame and lose less heat considering the faster combustion. (Williams, 2019, pp.9).

The value of octane rating is an indicator of the anti-knock performance of gasoline (Yan, 2017).

Higher octane rating for engine means it has a stronger anti-knock performance and it has small possibility to split considering the molecule is smaller and more stable (Williams, 2019, pp.9).

An ideal fuel need to have a good oxidation stability, copper corrosion resistance and also need to be clear and bright (Williams,2019, pp.19).

For diesel, it needs to have a low octane rating for igniting without a spark. (Williams, 2019, pp.18).

3. NO_x Model for Isooctane

From the task description, three assumptions can be shown below:

(1) The increase about cylinder pressure after combustion start is linear, and there is a 2 bar per degree from pressure at start of combustion (10 bar) up to the peak pressure (40 bar).

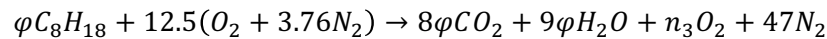
(2) It is a naturally aspirated engine which is 1600 cc four-cylinder.

(3) 1800 RPM engine speed.

(3) 40% volumetric efficiency and polytropic index for burned zone up to peak pressure is 1.17

(Williams, 2019)

3.1 Calculate flame temperature and plot a graph of NO_x PPM



$$n_3 = (25 - 16\varphi - 9\varphi)/2 = 12.5(1 - \varphi)$$

$\varphi = 0.6 \rightarrow 1.0$ (φ : equivalence ratio) means 40% $\rightarrow$ 0% lean.

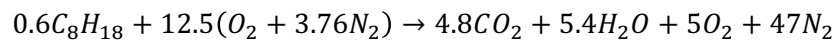
For the flame temperature, the net enthalpy needs to be calculated through the 'standard enthalpy of formation' and the flame temperature can be solved because the temperature of the products may increase to the flame front temperature through the reaction and enthalpy releasing.

The author used excel to calculate the net heat released per φ kmol of C_8H_{18} when φ grows from 0.6 to 1.0.

$\phi C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8\phi CO_2 + 9\phi H_2O + n_3 O_2 + 47N_2$					
$n_3 = (25 - 16\phi - 9\phi)/2 = 12.5(1 - \phi)$					
ϕ	CO ₂	H ₂ O	O ₂	N ₂	$\Delta H(298K)$
0.6	4.8	5.4	5	47	3039
0.65	5.2	5.85	4.375	47	3292.25
0.7	5.6	6.3	3.75	47	3545.5
0.75	6	6.75	3.125	47	3798.75
0.8	6.4	7.2	2.5	47	4052
0.85	6.8	7.65	1.875	47	4305.25
0.9	7.2	8.1	1.25	47	4558.5
0.95	7.6	8.55	0.625	47	4811.75
0.96	7.68	8.64	0.5	47	4862.4
0.97	7.76	8.73	0.375	47	4913.05
0.98	7.84	8.82	0.25	47	4963.7
0.99	7.92	8.91	0.125	47	5014.35
1	8	9	0	47	5065

Table 3.1 Net enthalpy at different ϕ in excel

(1) When $\phi=0.6$



The net enthalpy released per 0.6 kmol of $C_8H_{18} = \Delta H = 3039$ MJ

From the fuel database table, the data for CO_2 , H_2O , O_2 and N_2 can be found.

At 1600K,

enthalpy needed: $H_f = (4.8 \times 67.54 + 5.4 \times 52.94 + 5 \times 44.25 + 47 \times 41.9) = 2800.6$ MJ

At 1700K,

enthalpy needed: $H_f = (4.8 \times 73.44 + 5.4 \times 57.78 + 5 \times 47.94 + 47 \times 45.42) = 3038.964$ MJ

At 1750K,

enthalpy needed: $H_f = (4.8 \times 76.41 + 5.4 \times 60.24 + 5 \times 49.8 + 47 \times 47.19) = 3158.994$ MJ

Since the net heat (3039 MJ) is between 3038.964MJ(at 1700K) and 3158.994MJ(at 1750K),

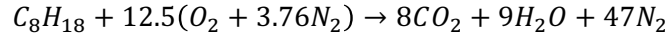
the flame front temperature can be solved as follows:

$$\frac{T - 1700}{1750 - 1700} = \frac{3039 - 3038.964}{3158.994 - 3038.964}$$

$$\frac{T - 1700}{50} = \frac{0.036}{120.03}$$

$$T = 1700.015K$$

(2) When $\varphi=1.0$



The net enthalpy released per 0.6 kmol of $C_8H_{18} = \Delta H = 5065$ MJ

At 2500K, enthalpy needed: $H_f = (8*121.94+9*99.11+47*70.64) = 5187.59$ MJ

At 2400K, enthalpy needed: $H_f = (8*115.79+9*93.74+47*70.64) = 5090.06$ MJ

At 2300K, enthalpy needed: $H_f = (8*109.66+9*88.42+47*66.99) = 4821.59$ MJ

The flame front temperature:

$$\frac{T - 2300}{2400 - 2300} = \frac{5065 - 4821.59}{5090.06 - 4821.59}$$

$$T = 2390.67K$$

(3) Flame front temperature ($\varphi=0.6 \rightarrow 1.0$)

Through calculating the two special points ($\varphi=0.6$ and 1.0), the interval of the flame front temperature can be got (from 1600K to 2400K). Using excel to calculate the specific temperature at every different value of φ (φ grows in 0.05 steps from 0.6 to 0.95 and 0.01 steps from 0.95 to 1.0), which is shown as followed.

$\varphi C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8\varphi CO_2 + 9\varphi H_2O + n_3 O_2 + 47N_2$															
$n_3 = (25 - 16\varphi - 9\varphi)/2 = 12.5(1 - \varphi)$															
φ	CO ₂	H ₂ O	O ₂	N ₂	$\Delta H(298K)/MJ$	1600K	1700K	1800K	1900K	2000K	2100K	2200K	2300K	2400K	Flame Tem/K
	8 φ	9 φ	12.5(1- φ)	47	MJ	1600	1700	1800	1900	2000	2100	2200	2300	2400	
0.6	4.8	5.4	5	47	3039	2800.618	3038.964	3279.644	3521.94	3765.896	4010.896	4257.922	4505.416	4754.368	1700.015
0.65	5.2	5.85	4.375	47	3292.25	2823.80075	3064.3785	3307.336	3551.945	3798.24275	4045.6115	4295.03675	4544.93775	4796.3295	1793.791
0.7	5.6	6.3	3.75	47	3545.5	2846.9835	3089.793	3335.028	3581.95	3830.5895	4080.327	4332.1515	4584.4595	4838.291	1885.238253
0.75	6	6.75	3.125	47	3798.75	2870.16625	3115.2075	3362.72	3611.955	3862.93625	4115.0425	4369.26625	4623.98125	4880.2525	1974.425878
0.8	6.4	7.2	2.5	47	4052	2893.349	3140.622	3390.412	3641.96	3895.283	4149.758	4406.381	4663.503	4922.214	2061.584439
0.85	6.8	7.65	1.875	47	4305.25	2916.53175	3166.0365	3418.104	3671.965	3927.62975	4184.4735	4443.49575	4703.02475	4964.1755	2146.627848
0.9	7.2	8.1	1.25	47	4558.5	2939.7145	3191.451	3445.796	3701.97	3959.9765	4219.189	4480.6105	4742.5465	5006.137	2229.736081
0.95	7.6	8.55	0.625	47	4811.75	2962.89725	3216.8655	3473.488	3731.975	3992.32325	4253.9045	4517.72525	4782.06825	5048.0985	2311.157284
0.96	7.68	8.64	0.5	47	4862.4	2967.5338	3221.9484	3479.0264	3737.976	3998.7926	4260.8476	4525.1482	4789.9726	5056.4908	2327.175405
0.97	7.76	8.73	0.375	47	4913.05	2972.17035	3227.0313	3484.5648	3743.977	4005.26195	4267.7907	4532.57115	4797.87695	5064.8831	2343.13498
0.98	7.84	8.82	0.25	47	4963.7	2976.8069	3232.1142	3490.1032	3749.978	4011.7313	4274.7338	4539.9941	4805.7813	5073.2754	2359.03633
0.99	7.92	8.91	0.125	47	5014.35	2981.44345	3237.1971	3495.6416	3755.979	4018.20065	4281.6769	4547.41705	4813.68565	5081.6677	2374.879773
1	8	9	0	47	5065	2986.08	3242.28	3501.18	3761.98	4024.67	4288.62	4554.84	4821.59	5090.06	2390.665624

Table 3.2 The flame temperature at different φ in excel

(3) Burn zone temperature

Burn zone temperature is not the same as flame front temperature, and the burn zone temperature increases as the cylinder pressure rises (Williams, 2019, pp.12). Hence the burn zone temperature can be calculated through using the ideal gas law.

$$n = \frac{C_p}{C_v}$$

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

From the assumption in the task description, $n=1.17$.

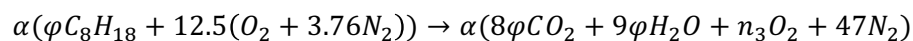
The cylinder pressure increases in a value of 2 bar per degree from 10 bar up to a peak value of 40 bar, and the crankshaft angle start at 1° with 1° intervals, thus the crankshaft angle ranges from 1° to 15° with θ increasing from 10 bar to 40 bar.

Using excel to calculate the burn zone temperature as followed:

	φ	0.6		0.65	0.7	0.75	0.8	0.85	0.9
Crankshaft angle	P	Temp(K)	Nox	Tem(K)	Tem	Tem	Tem	Tem	Tem
0	10	1700.015		1793.791	1885.23825	1974.425878	2061.58444	2146.62785	2229.736081
1	12	1745.6522		1841.94564	1935.84781	2027.429689	2116.92804	2204.25445	2289.59374
2	14	1785.19241		1883.66696	1979.69608	2073.352349	2164.8779	2254.18231	2341.454594
3	16	1820.1669		1920.5707	2018.48117	2113.972306	2207.29097	2298.34499	2387.327059
4	18	1851.5849		1953.72178	2053.32228	2150.461696	2245.39114	2338.01685	2428.53484
5	20	1880.14851		1983.86101	2084.99801	2183.63595	2280.02983	2374.08443	2465.99881
6	22	1906.36684		2011.5256	2114.07293	2214.086365	2311.82444	2407.19062	2500.386724
7	24	1930.62143		2037.11811	2140.97015	2242.256042	2341.23763	2437.81715	2532.198983
8	26	1953.20589		2060.94838	2166.01528	2268.486021	2368.6255	2466.33481	2561.820723
9	28	1974.35131		2083.26022	2189.46458	2293.044665	2394.26825	2493.03536	2589.555011
10	30	1994.24294		2104.24911	2211.52348	2316.147136	2418.39055	2518.15274	2615.644829
11	32	2013.0317		2124.07428	2232.35934	2337.96871	2441.17542	2541.87751	2640.28812
12	34	2030.84223		2142.86728	2252.1104	2358.654161	2462.774	2564.36707	2663.648377
13	36	2047.77875		2160.73804	2270.89221	2378.324515	2483.31268	2585.753	2685.862276
14	38	2063.92929		2177.77948	2288.80242	2397.082027	2502.89821	2606.14647	2707.045295
15	40	2079.36895		2194.07083	2305.9243	2415.013911	2521.62168	2625.64231	2727.295926

Table 3.3 The burn zone temperature at different cylinder pressure in excel

(3) The Zeldovich model for NO_x PPM



From the task description, the engine is assumed as a 1600cc naturally-aspirated four-cylinder engine, each cylinder must have a displacement of 400cc.(Williams)

The ideal gas law,

$$PV = nRT$$

When the cylinder is at 1 bar and 20°C, and

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

$$n = \frac{10^5 \times (400 \times 0.4) \cdot 10^{-6}}{8314 \times 293}$$

$$n = 6.57 \times 10^{-6} \text{ kmols}$$

From the balanced chemical equation, the intake of combustion blend consists of fuel and air

(Williams, 2019), so the value of n which was calculated above can be used.

$$\alpha(\varphi C_8H_{18} + 12.5(O_2 + 3.76N_2)) = 6.57 \times 10^{-6} \text{ kmols}$$

$$\alpha(\varphi + 12.5(1 + 3.76)) = 6.57 \times 10^{-6} \text{ kmols}$$

$$\therefore \alpha = \frac{6.57 \times 10^{-6}}{\varphi + 12.5(1 + 3.76)}$$

Using excel to calculate the value of the α at different fuel equivalence ratio (φ).

alpha
1.09318E-07
1.09227E-07
1.09136E-07
1.09046E-07
1.08955E-07
1.08865E-07
1.08775E-07
1.08685E-07
1.08667E-07
1.08649E-07
1.08631E-07
1.08613E-07
1.08595E-07

Table 3.4 The alpha at different φ in excel

The combustion chamber volume of 40cc considering the engine speed is 1800RPM,

$$[O_2] = \frac{n_3 * a}{40 \times 10^{-6}}$$

$$[N_2] = \frac{47 * a}{40 \times 10^{-6}}$$

$\phi C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8\phi CO_2 + 9\phi H_2O + n_3 O_2 + 47N_2$									
$n_3 = (25 - 16\phi - 9\phi)/2 = 12.5(1 - \phi)$									
ϕ	CO2	H2O	O2	N2	Enthalpy	[O2]	[N2]	alpha	Flame Tem/K
	8 ϕ	9 ϕ	12.5(1- ϕ)	47	MJ				
0.6	4.8	5.4	5	47	3039	0.01366473	0.12844842	1.09318E-07	1700.015
0.65	5.2	5.85	4.375	47	3292.25	0.0119467	0.12834165	1.09227E-07	1793.791
0.7	5.6	6.3	3.75	47	3545.5	0.01023152	0.12823505	1.09136E-07	1885.238253
0.75	6	6.75	3.125	47	3798.75	0.00851919	0.12812863	1.09046E-07	1974.425878
0.8	6.4	7.2	2.5	47	4052	0.0068097	0.12802239	1.08955E-07	2061.584439
0.85	6.8	7.65	1.875	47	4305.25	0.00510304	0.12791632	1.08865E-07	2146.627848
0.9	7.2	8.1	1.25	47	4558.5	0.00339921	0.12781043	1.08775E-07	2229.736081
0.95	7.6	8.55	0.625	47	4811.75	0.0016982	0.12770471	1.08685E-07	2311.157284
0.96	7.68	8.64	0.5	47	4862.4	0.00135834	0.12768359	1.08667E-07	2327.175405
0.97	7.76	8.73	0.375	47	4913.05	0.00101858	0.12766248	1.08649E-07	2343.13498
0.98	7.84	8.82	0.25	47	4963.7	0.00067894	0.12764137	1.08631E-07	2359.03633
0.99	7.92	8.91	0.125	47	5014.35	0.00033942	0.12762027	1.08613E-07	2374.879773
1	8	9	0	47	5065	0	0.12759917	1.08595E-07	2390.665624

Table 3.5 The calculations of [O2] & [N2] at different ϕ in excel

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

Since the engine speed is assumed to be at a constant 1800 RPM,

$$1800 \times \frac{360}{60} = ^\circ/\text{sec}$$

$$\therefore \frac{4.7 \times 10^{13} \times [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-E_A}{RT}\right)}{1800 \times 6} = \frac{\text{kmols}}{\text{m}^3 \cdot ^\circ}$$

The combustion chamber volume is 40ccs,

$$\frac{4.7 \times 10^{13} \times [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-E_A}{RT}\right)}{1800 \times 6} \cdot 40 \times 10^{-6} = \frac{\text{kmols}}{^\circ}$$

Using the equation written by Günter P. Merker from the book 'Simulating Combustion'

$$\frac{4.7 \times 10^{13} \times [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-67837}{T}\right)}{1800 \times 6} \times 40 \times 10^{-6} = \frac{\text{kmols}}{^\circ}$$

Using excel to solve the NO_x /degree with ranges of fuel equivalence ratio.

	ϕ	0.6		0.65		0.7	
Crankshaft angle	P	Temp(K)	Nox	Tem(K)		Tem	
0	10	1700.015	1.22E-14	1793.791	9.1985E-14	1885.238253	5.3258E-13
1	12	1745.652	3.47E-14	1841.946	2.4723E-13	1935.847807	1.3644E-12
2	14	1785.192	8.21E-14	1883.667	5.5894E-13	1979.696075	2.9649E-12
3	16	1820.167	1.7E-13	1920.571	1.1166E-12	2018.48117	5.7275E-12
4	18	1851.585	3.21E-13	1953.722	2.0332E-12	2053.322283	1.013E-11
5	20	1880.149	5.59E-13	1983.861	3.4457E-12	2084.998008	1.6734E-11
6	22	1906.367	9.19E-13	2011.526	5.5146E-12	2114.072935	2.6178E-11
7	24	1930.621	1.44E-12	2037.118	8.4239E-12	2140.970148	3.9176E-11
8	26	1953.206	2.16E-12	2060.948	1.238E-11	2166.015281	5.651E-11
9	28	1974.351	3.13E-12	2083.26	1.7613E-11	2189.464577	7.9032E-11
10	30	1994.243	4.41E-12	2104.249	2.4372E-11	2211.523476	1.0765E-10
11	32	2013.032	6.05E-12	2124.074	3.2929E-11	2232.359339	1.4334E-10
12	34	2030.842	8.14E-12	2142.867	4.3573E-11	2252.110398	1.8711E-10
13	36	2047.779	1.07E-11	2160.738	5.6614E-11	2270.892214	2.4004E-10
14	38	2063.929	1.39E-11	2177.779	7.238E-11	2288.802422	3.0326E-10
15	40	2079.369	1.77E-11	2194.071	9.1215E-11	2305.924298	3.7791E-10

0.97		0.98		0.99		1	
Tem		Tem		Tem		Tem	
2343.135	1.894E-10	2359.036	1.8792E-10	2374.88	1.61E-10	2390.666	0
2406.037	4.0372E-10	2422.365	3.9853E-10	2438.634	3.4E-10	2454.843	0
2460.535	7.5386E-10	2477.233	7.4104E-10	2493.871	6.29E-10	2510.447	0
2508.741	1.2804E-09	2525.766	1.2542E-09	2542.729	1.06E-09	2559.631	0
2552.044	2.0259E-09	2569.363	1.9783E-09	2586.619	1.67E-09	2603.813	0
2591.413	3.0339E-09	2609	2.9545E-09	2626.522	2.48E-09	2643.98	0
2627.55	4.3487E-09	2645.382	4.2246E-09	2663.148	3.54E-09	2680.85	0
2660.98	6.0148E-09	2679.039	5.8304E-09	2697.031	4.88E-09	2714.959	0
2692.109	8.0769E-09	2710.378	7.8137E-09	2728.581	6.53E-09	2746.718	0
2721.253	1.0579E-08	2739.721	1.0216E-08	2758.121	8.52E-09	2776.454	0
2748.67	1.3566E-08	2767.324	1.3078E-08	2785.909	1.09E-08	2804.427	0
2774.567	1.708E-08	2793.396	1.644E-08	2812.157	1.37E-08	2830.849	0
2799.115	2.1164E-08	2818.111	2.0342E-08	2837.037	1.69E-08	2855.895	0
2822.459	2.5861E-08	2841.613	2.4823E-08	2860.697	2.06E-08	2879.712	0
2844.719	3.1213E-08	2864.024	2.9922E-08	2883.259	2.48E-08	2902.424	0
2865.999	3.7259E-08	2885.449	3.5675E-08	2904.828	2.95E-08	2924.136	0

Table 3.7 The calculations of NO_x /degree at different ϕ in excel

The value of NO_x for every cycle can be worked out by the summation of NO_x over x degrees of combustion.

$$\sum_{x_{soc}}^{x_{eoc}} \left(\frac{4.7 \times 10^{13} \times [N_2][O_2]^{\frac{1}{2}} \cdot \exp\left(\frac{-E_A}{RT}\right)}{1800 \times 6} \times 40 \times 10^{-6} \right) = kmols/cycle$$

PPM means NO_x parts per million, and it is the ratio of NO_x /cycle as a percentage of one million exhaust gas particles. (Williams,2019, pp 6).

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

$$\text{Total exhaust kmols} = \alpha(8\phi + 9\phi + n_3 + 47)$$

Also, using excel to calculate the PPM at different φ .

kmols/cycle			6.98E-11		3.72508E-10		1.59766E-09		5.68051E-09
Total exhaust kmols			6.8E-06		6.81849E-06		6.83738E-06		6.85624E-06
		0.6	10.26136	0.65	54.63206205	0.7	233.6655206	0.75	828.5156514
	1.71427E-08		4.42571E-08		9.70241E-08		1.6864E-07		1.7872E-07
	6.87507E-06		6.89387E-06		6.91264E-06		6.9314E-06		6.9389E-06
0.8	2493.461442	0.85	6419.768214	0.9	14035.74907	0.95	24330.1572	0.96	25769.8382
								0.97	26351.3797
	1.7588E-07		1.461E-07		0				
	6.9426E-06		6.946E-06						
0.98	25333.1819	0.99	21033.843	1	0				

Table 3.8 The calculations of NO_x PPM at different φ in excel

When reaction at $\varphi = 0.97$, PPM has the largest value of 26351.3797 which means at this state the rate of NO_x produced is highest.

The author used excel to plot the graph of NO_x PPM as followed:

From the graph below, when φ is at lower value, although it has more and higher concentration of N_2 and O_2 for producing NO_x , the N and O molecules dissociate slowly considering the low burn and flame temperature. And the curve shows that PPM has an increasing trend up to 26351.3797(at $\varphi = 0.97$) and then drops down to 0(at $\varphi = 1$).

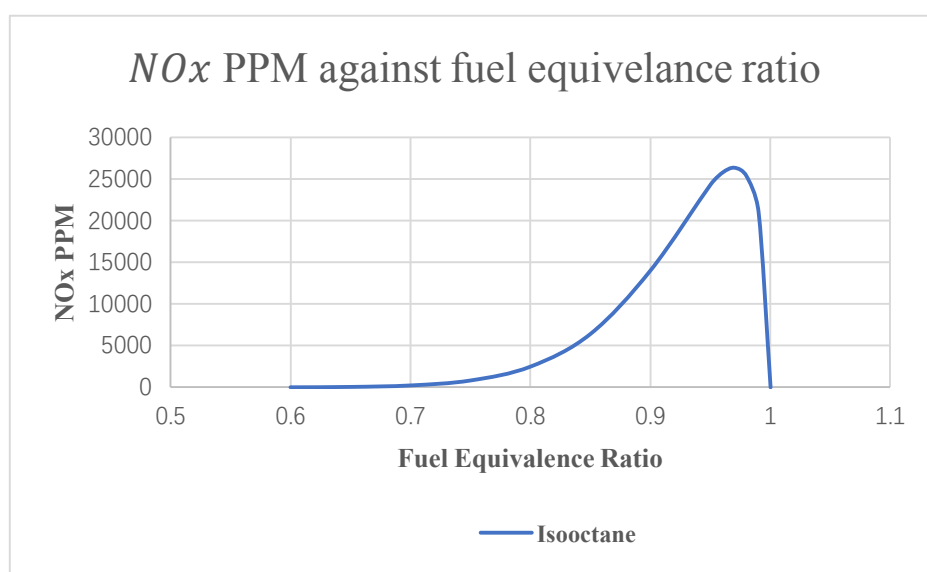


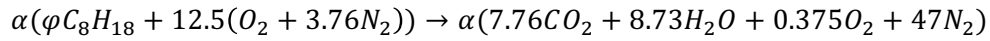
Figure 3.1 NO_x PPM @fuel equivalence ratio

3.2 The effect on PPM when EGR is applied

For the EGR valve, the recirculated gas adds extra mass to the combustion mixture and also decreases the burn zone temperature considering the ideal gas law, thus the production of NOx reduced (Williams,2019, pp 8).

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

For $\phi = 0.97$,



Since EGR levels are assumed up to 20%, the author choosed the level of 10%, 15%, 20% to calculate the effect.

Recalculating isooctane equation after adding EGR, the modulus of the products can be worked out:

	0%	5%	10%	15%	20%
CO2	7.76	8.148	8.536	8.924	9.312
H2O	8.73	9.1665	9.603	10.0395	10.476
O2	0.375	0.39375	0.4125	0.43125	0.45
N2	47	49.35	51.7	54.05	56.4

Table 3.9 The modulus of the products at different EGR level in excel

The net enthalpy does not change because of the balance among the equation.

The volumetric efficiency is still assumed as 40%, hence, the value of n does not change. And

the value of [N] & [O] will change as the modulus of products changes.

ϕ	EGR	[O2]	[N2]
0.97	0	0.001018584	0.12766248
	5%	0.001069513	0.1340456
	10%	0.001120442	0.14042872
	15%	0.001171371	0.14681185
	20%	0.0012223	0.15319497

Table 3.10 The value of [O2]&[N2] at $\phi = 0.97$ in excel

And the flame temperature may change,

EGR	2000K	2100K	2200K	2300K	Flame Tem/K
0					2343.13498
5%	4205.52505	4481.18024	4759.19971	5037.7708	2255.22838
10%	4405.78815	4694.56977	4985.82827	5277.66465	2175.06196
15%	4606.05124	4907.95931	5212.45682	5517.55849	2101.67183
20%	4806.31434	5121.34884	5439.08538	5757.45234	2033.88063

Table 3.11 The flame temperature at different EGR level in excel

Also, using the same method by excel to get the burn zone Temperature at different bar from 10bar to 40bar.

		0	5%	10%	15%	20%
Crankshaft angle	P	Tem	Tem	Tem	Tem	Tem
0	10	2343.13498	2255.22838	2175.06196	2101.67184	2033.88063
1	12	2406.03685	2315.77038	2233.45188	2158.09159	2088.48051
2	14	2460.53522	2368.22416	2284.04109	2206.97383	2135.78602
3	16	2508.74065	2414.62108	2328.78874	2250.21163	2177.62914
4	18	2552.04416	2456.29998	2368.98609	2289.05265	2215.21731
5	20	2591.41345	2494.19227	2405.53142	2324.36489	2249.39052
6	22	2627.55025	2528.97334	2439.07613	2356.77774	2280.75788
7	24	2660.9804	2561.1493	2470.10834	2386.76287	2309.77581
8	26	2692.10863	2591.1097	2499.00374	2414.6833	2336.79564
9	28	2721.25342	2619.16108	2526.05797	2440.82467	2362.0938
10	30	2748.6701	2645.54918	2551.50805	2465.41603	2385.89194
11	32	2774.56669	2670.47421	2575.54708	2488.64394	2408.37062
12	34	2799.11499	2694.10154	2598.33453	2510.66251	2429.67896
13	36	2822.45863	2716.56941	2620.00374	2531.60056	2449.94163
14	38	2844.71897	2737.99461	2640.66734	2551.56694	2469.26398
15	40	2865.9995	2758.47677	2660.42142	2570.65448	2487.73584

Table 3.12 The burn zone temperature at different EGR level in excel

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

For NO_x kmols/cycle, the author calculated it by adding the kmols/° from 0° to 15°.

		0		5%		10%		15%		20%	
Crankshaft angle	P	Tem	Nox/degree	Tem	Nox/degree	Tem	Nox/degree	Tem	Nox/degree	Tem	Nox/degree
0	10	2343.13498	1.89395E-10	2255.22838	6.59254E-11	2175.06196	2.33279E-11	2101.671835	8.39156E-12	2033.88063	3.05024E-12
1	12	2406.03685	4.0372E-10	2315.77038	1.44736E-10	2233.45188	5.27214E-11	2158.091591	1.95128E-11	2088.48051	7.29503E-12
2	14	2460.53522	7.53856E-10	2368.22416	2.76922E-10	2284.04109	1.03312E-10	2206.973833	3.9146E-11	2135.78602	1.49787E-11
3	16	2508.74065	1.28044E-09	2414.62108	4.80171E-10	2328.78874	1.8281E-10	2250.211626	7.06629E-11	2177.62914	2.75757E-11
4	18	2552.04416	2.02593E-09	2456.29998	7.73441E-10	2368.98609	2.99684E-10	2289.052651	1.17856E-10	2215.21731	4.67831E-11
5	20	2591.41345	3.03393E-09	2494.19227	1.17664E-09	2405.53142	4.63017E-10	2324.364888	1.84876E-10	2249.39052	7.44968E-11
6	22	2627.55025	4.34871E-09	2528.97334	1.71039E-09	2439.07613	6.82393E-10	2356.777743	2.76185E-10	2280.75788	1.12789E-10
7	24	2660.9804	6.01483E-09	2561.1493	2.39579E-09	2470.10834	9.67792E-10	2386.762873	3.96504E-10	2309.77581	1.63888E-10
8	26	2692.10863	8.07684E-09	2591.1097	3.25429E-09	2499.00374	1.32951E-09	2414.683297	5.50774E-10	2336.79564	2.30161E-10
9	28	2721.25342	1.05791E-08	2619.16108	4.30756E-09	2526.05797	1.7781E-09	2440.824675	7.44124E-10	2362.0938	3.14094E-10
10	30	2748.6701	1.35655E-08	2645.54918	5.57735E-09	2551.50805	2.32428E-09	2465.416032	9.81838E-10	2385.89194	4.18279E-10
11	32	2774.56669	1.70795E-08	2670.47421	7.08546E-09	2575.54708	2.97892E-09	2488.643943	1.26933E-09	2408.37062	5.45404E-10
12	34	2799.11499	2.1164E-08	2694.10154	8.85362E-09	2598.33453	3.75299E-09	2510.66251	1.61211E-09	2429.67896	6.98233E-10
13	36	2822.45863	2.58612E-08	2716.56941	1.09035E-08	2620.00374	4.65752E-09	2531.60056	2.0158E-09	2449.94163	8.79604E-10
14	38	2844.71897	3.12125E-08	2737.99461	1.32565E-08	2640.66734	5.70356E-09	2551.566939	2.48606E-09	2469.26398	1.09241E-09
15	40	2865.9995	3.72587E-08	2758.47677	1.5934E-08	2660.42142	6.90218E-09	2570.65448	3.02863E-09	2487.73584	1.33961E-09
		0		5%		10%		15%		20%	
kmol/cycle			1.82848E-07		7.61962E-08		3.22021E-08		1.38018E-08		5.96865E-09

Table 3.13 The NO_x/degree at different EGR level in excel

Hence, the values of NO_x PPM with adding EGR level from 0 to 20% are shown in the table below:

	0	5%	10%	15%	20%
kmol/cycle	1.82848E-07	7.61962E-08	3.22021E-08	1.38018E-08	5.96865E-09
total exhaust kmols	6.93886E-06	7.28581E-06	7.63275E-06	7.97969E-06	8.32664E-06
PPM	26351.33486	10458.16916	4218.938849	1729.616521	716.8141755

Table 3.14 The NO_x PPM at different EGR level in excel

The author plots a graph of NO_x PPM at $\phi = 0.97$ against EGR level from 0% to 20% of the air + fuel contents. As the graph shown below, it shows a decreasing trend when EGR level grows.

For adding 5% EGR,

$$\frac{PPM@0EGR - PPM@5\% EGR}{PPM@0EGR} = \frac{26351.33486 - 10458.16916}{26351.33486} \times 100\% = 60.31\%$$

For adding 20% EGR,

$$\frac{PPM@0EGR - PPM@20\% EGR}{PPM@0EGR} = \frac{26351.33486 - 716.814}{26351.33486} \times 100\% = 97.28\%$$

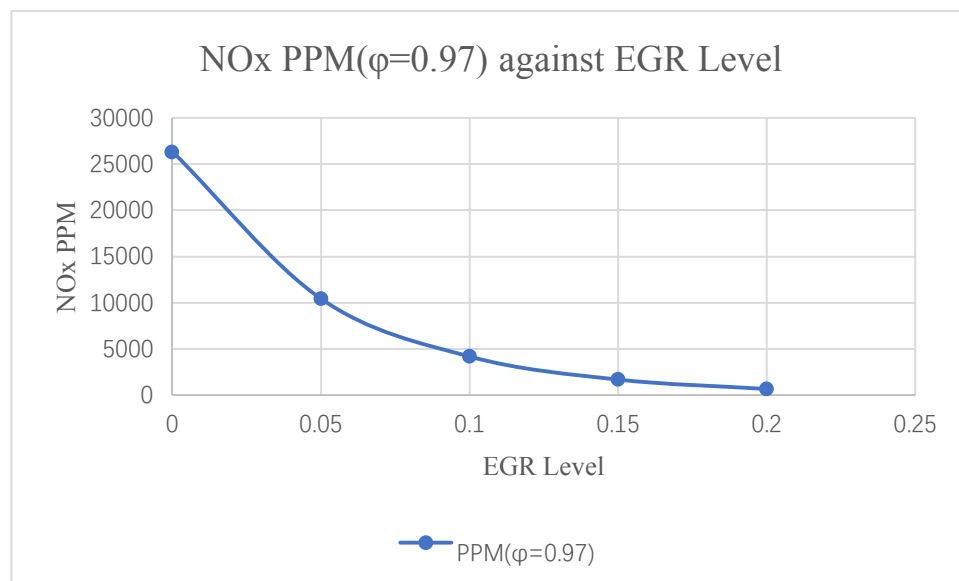


Figure 3.2 The NO_x PPM ($\phi = 0.97$) against EGR level

Hence, when adding 5% EGR level it can reduce 60% NO_x parts per million and when adding 20% EGR, the percentage can reach 97.28% which means adding EGR can efficiently lead to lower NO_x PPM produced.

4. Conclusion

In this report, the author calculated and set a NO_x model for a blended mixture which consists of 50% molar of methanol and isooctane. For the calculations, the author worked out the mass percentage, air/fuel mass ratio for combustion, lower heating value of the blend, mass of CO_2 and relative calculations of NO_x PPM by using Fuel Database and EXCEL. For the explanations on some terms, the author read some contexts in class and searched some articles online to solve these questions. Furthermore, when plotting the graphs of the NO_x PPM at different ϕ and at different EGR levels, conclusions can be drawn that the graph of NO_x PPM at different ϕ has a turning point at $\phi = 0.97$ which has the largest number. And when adding 5% EGR level, the NO_x PPM can reduce by 60%.

Reference

Williams, O.(2019). Combustion. The United Kingdom: University of Wales Trinity Saint

David.

Williams, O.(2019). Enthalpy and Fuels. The United Kingdom: University of Wales Trinity

Saint David.

Williams, O.(2019). Flame Temperatures. The United Kingdom: University of Wales Trinity

Saint David.

Williams, O.(2019). Zeldovich Model. The United Kingdom: University of Wales Trinity Saint

David.

Fu, Y. (2017, Dec). Automobile Engine Principle. China Machine Press.

Short, Daniel Z. "Components of Particle Emissions from Light-Duty Spark-Ignition Vehicles with Varying Aromatic Content and Octane Rating in Gasoline." *Environmental Science & Technology* 49.17 (2015): 10682-0692. Web.