

Combustion Analysis
And NOx Prediction For Ford GDI Engine

Major Project
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Preface

This dissertation is based on internal combustion engine analysis. I would like to thank my supervisor, Malcolm Donald for the good advice, supports and many helps throughout the process of the project.

Contents

Chapter 1 Introduction.....	9
Chapter 2 Thermodynamics of combustion.....	9
2.1 Ideal gas law.....	9
2.2 First law of thermodynamics.....	10
2.2.1 Internal energy.....	10
2.2.2 Enthalpy.....	11
2.2.3 Specific heat.....	12
2.2.4 Gamma.....	13
2.3 Combustion stoichiometry.....	13
2.3.1 Air-fuel ratio.....	14
Chapter 3 Thermodynamic analysis of engine processes.....	15
3.1 Compression process.....	15
3.1.1 Unburned temperature from IVC to SOC.....	16
3.2 Combustion process.....	16
3.3.1 Two-zone combustion model.....	16
3.3.2 Burned and unburned mixture states.....	17
3.3.2.1 Unburned temperature during combustion.....	17
3.3.2.2 Burned temperature during combustion.....	18
3.4 Expansion process.....	19
3.5 Exhaust process.....	19
3.5.1 Exhaust emissions.....	20
Chapter 4. FOX engine data analysis.....	20
4.1 Engine data.....	20
4.1.1 1L Fox engine specifications.....	20
4.2 Engine measured data.....	20
4.2.1 Measured operating data.....	20
4.2.1.1 Total mixture mass calculation.....	21
4.2.1.2 Unburned and burned mixture properties calculation.....	21
4.2.2 Measured NOx data.....	23
4.3 Cylinder-pressure data analysis.....	23
4.3.1 Cylinder pressure volume diagrams analysis.....	23
4.3.1.1 Pressure VS crank angle graph.....	23
4.3.1.2 logPressure VS logvolume graph.....	24
4.3.1.3 Polytropic index graph.....	24
4.3.1 SOC and EOC.....	25
4.3.1.1 Pressure due to combustion.....	26
4.3.1.2 Determination of SOC and EOC.....	26
4.3.1.3 Extra pressure problem at SOC.....	30
4.3.1.3.1 Polytropic index problem.....	31
4.3.1.3.2 Accuracy of SOC point.....	32
4.3.1.3.3 Cylinder pressure data sampling problem.....	34
4.3.2 Combustion duration.....	36

4.3.3 Ignition delay.....	37
4.3.4 Mass fraction burned.....	38
4.3.4.1 Mass fraction burned methods.....	38
4.3.4.1.1 Rassweiler and Withrow method.....	38
4.3.4.1.2 Wiebe Function method.....	40
4.3.4.1.2.1 Representative mass fraction graph.....	40
4.3.4.1.2.2 Wiebe function.....	41
4.3.4.2 MFB results analysis.....	41
4.3.4.2.1 Rassweiler and Withrow method results.....	41
4.3.4.2.2 Wiebe Function result.....	42
4.4 Burned Temperature.....	43
4.4.1 Burned Temperature calculation.....	43
4.4.2 Burned temperature graph.....	44
Chapter 5 Combustion and dissociation.....	44
5.1 Dissociation.....	44
5.2 Equilibrium model of combustion.....	45
5.3 Combustion product calculation.....	47
5.3.1 K_{CO_2} and K_{H_2O}	47
5.3.2 Molars of combustion products.....	49
5.3.3 Polynomial method for calculating n_5	49
Chapter 6 NOx prediction.....	50
6.1 NOx model literature review.....	50
6.2 Kinetics of NO formation.....	51
6.2.1 Thermal NO.....	51
6.2.2 Determining O radical concentration.....	53
6.2.3 NO formation rates	59
6.3 NOx calculation.....	60
6.4 NOx prediction results.....	62
6.5 NO model sensitivity analysis.....	62
6.5.1 $n_5(O_2)$ calculation method.....	63
6.5.2 Different [O] concentration method.....	64
6.5.3 Different first forward speed.....	65
6.5.5 Different lambda data.....	65
6.5.5 Burned temperature sensitivity analysis.....	66
6.5.5.1 Polytropic index sensitivity analysis.....	66
6.5.4.2 MFB sensitivity analysis.....	67
6.6 NO model limitations.....	68
6.6.1 1-zone combustion model limitation.....	68
6.6.2 Cylinder pressure data analysis limitations.....	68
6.6.3 Extended-Zeldovich mechanism limitation.....	69
7. Conclusion.....	69

Bibliography.....	70
Appendix A Chemical equilibrium.....	75
Appendix B Heat release model.....	77
Appendix C $PV^\gamma = C$	78
Appendix D Unburned temperature during combustion.....	79
Appendix E Dissociation constants.....	80
Appendix F Unburned and burned gamma.....	80
Appendix F.1 Unburned gamma.....	80
Appendix F.2 Burned gamma.....	81
Appendix G MFB - heat release method application.....	81
Appendix H Dissociated specific heat.....	82
Appendix I Specific heat and Gamma graph.....	85

Symbols

Nomenclature

$a_s : [/]$	stoichiometric molar air/fuel ratio
$A : [m^2]$	Area across which heat transfer occurs
$C : [/]$	Constant
$C_n : [kJ / kg \cdot K]$	specific heat
$C_p : [kJ / kg \cdot K]$	specific heat capacity at constant pressure
$C_v : [kJ / kg \cdot K]$	specific heat capacity at constant volume
$f : [/]$	residual mass fraction
$G : [kJ]$	Gibbs function (free energy)
$h_q : [kW / m^2 K]$	heat transfer coefficient
$H : [kJ]$	enthalpy
$k : [cm, mol, s]$	rate coefficient of the reaction
$K [/]$	equilibrium constant
$M : [kg / kmol]$	molar weight
$N_{total} : [/]$	total number of moles
$n : [/]$	polytropic index of the process
$p : [pa]$	cylinder pressure
$R : [kJ kg / K]$	gas constant
$S : [kJ / K]$	entropy
$t : [sec]$	time

$T:[K]$	temperature
$U:[kJ]$	internal energy
$\nu:[/]$	coefficient
$V:[m^3]$	volume

Subscripts

b	indicates properties or value for the burned products zone
e	equilibrium
f	fuel
g	gas
ht	heat transfer
i	inlet
m	mean
u	indicates properties or value for the unburned reactants zone
r	residual

Notations

[]	concentration, $kmol/m^3$
-----	---------------------------

Abbreviations

AFR	air fuel ratio
BDC	bottom dead center
BTDC	before top dead center
CA	crank angle
cc	combustion chamber
DI	direct injection
DISI	direct injection spark ignition
EGR	exhaust gas recirculation
EV	exhaust valve
EVC	exhaust valve close
EVO	exhaust valve open
FEM	finite element method
HCCI	homogeneous charge compression ignition
hrr	heat release rate
ID	injection duration
IGD	ignition delay

IND	injection delay
ip	injection pump
IP	injection process
IT	ignition time
ITDC	ignition top dead center
IV	intake valve
IVC	intake valve close
IVO	intake valve open
MFB	mass fraction burned
OHC-equ	oxygen-hydrogen-carbon-equilibrium
rg	residual gas
SOC	start of combustion
SOI	start of injection
TDC	top dead center

Chapter 1 Introduction

Motor vehicles have become one of the main sources of air pollution worldwide. With the increasing concerns about the air pollution problems, the automotive industry is facing the challenge of improving engine performance with less emissions. The main emissions from gasoline engine are nitrogen, water, carbon dioxide, unburned hydrocarbons, nitrogen oxides and carbon monoxide. In this dissertation, the nitrogen oxides is mainly investigated and calculated using the cylinder pressure-volume data provided by Ford Motor company.

The NO model is based on the 2-zone combustion model and extended-Zeldovich mechanism. The 2-zone thermodynamic model assumes there are two zones - burned zone and unburned zone. The first law of thermodynamics is applied to solving the thermodynamic states and properties of unburned and burned mixture. The extended-Zeldovich mechanism is used for NO_x prediction. The NO formation including the [O] concentration determination and reaction speeds are investigated and researched. To modify the predicted NO_x results, the NO sensitivity analysis is implemented as well.

This dissertation aims to predict NO_x from the basic thermodynamic principles. In addition to the NO_x prediction, the combustion process is analyzed based on the cylinder pressure-volume data, which includes the determination of SOC and EOC, MFB and burned temperature.

Chapter 2 Thermodynamics of combustion

2.1 Ideal gas law

A ideal gas is defined to obey the relationship

$$PV = RT$$

Where P and T are the absolute pressure and absolute temperature respectively, and R is the particular gas constant. The particular gas constant is dependent on the molecular weight of the gas as follows:

$$R_i = R_u / m_i [=] J / kg \cdot K$$

Where the i denotes the species of interest, and R_u is the universal gas constant,

defined by $R_u = 8314 J / kmol \cdot K$.

Kinetic theory predicts that $Pv = RT$, first, when the molecules comprising the system are infinitesimally small, hard, round spheres occupying negligible volume and, second, when no forces exist among these molecules except during collisions. Qualitatively, these conditions imply a gas at low density.

Alternative forms of the ideal-gas equation of state are presented as follows.
First, by recognizing that the specific volume is the reciprocal of the density ($v = 1/\rho$), we get $P = \rho RT$

Second, expanding the definition of specific volume ($v = V/M$) yields
 $PV = MRT$

Third, expressing the mass in terms of the number of moles and molecular weight of the particular gas of interest ($M = Nm_i$) yields

$$PV = NR_u T \text{ (Turns, S. R., 2006).}$$

2.2 First law of thermodynamics

The first law of thermodynamics is based on the conservation of energy. The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one to another, but cannot be created or destroyed. The first law states that the change in the internal energy of a closed system is equal to the amount of heat supplied to the system, subtract the amount of work done by the system on its surroundings (Turns, S. R., 2006). For fuel combustion in engine, the first law of thermodynamics can be stated as the heat coming from burning fuel partly makes combustion mixture hotter and partly pushes the piston down.

Taking ΔU as a change in internal energy, then the internal energy is expressed as:

$$\Delta U = Q - W \quad (2.1)$$

Where Q denotes the net quantity of heat released from fuel burning, and W denotes the net work done by the system.

2.2.1 Internal energy

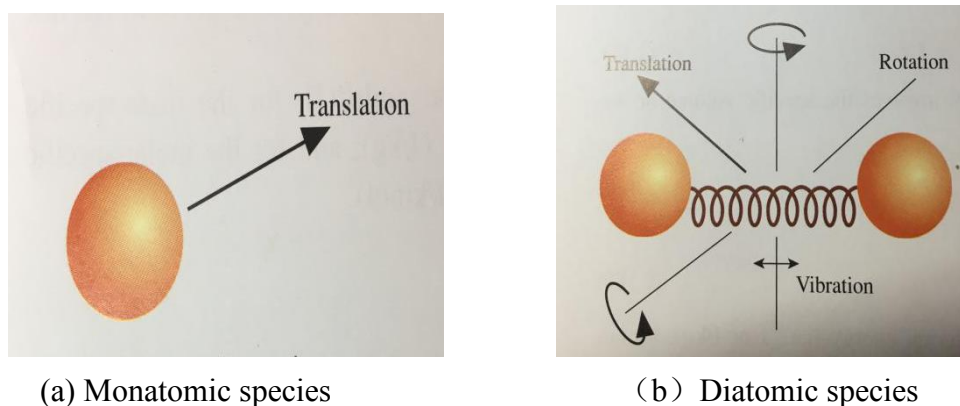


Figure 2.1:

(a) The internal energy of a monatomic species consists only of translational (kinetic) energy. (b) A diatomic species internal energy results from

translation together with energy from vibration (potential and kinetic) and rotation (kinetic) (Turns, S. R., 2006).

Internal energy is defined as the energy associated with the motions of the microscopic system. For simple monatomic gases (e.g., *He*) internal energy is associated only with the translational kinetic energy of the atoms. A gas is assumed to be modeled as a collection of point-mass hard spheres that collide elastically, the translational kinetic associated with n particles is equal to:

$$U_{trans} = n \frac{1}{2} M_{molec} \bar{v}^2 \quad (2.2)$$

Where $\bar{v}^2$ is the mean-square molecular speed. Based on kinetic theory, the translational kinetic energy can be related to temperature as

$$U_{trans} = n \frac{3}{2} k_B T \quad (2.3)$$

Where k_B is the Boltzmann constant,

$$k_B = 1.3806503 \times 10^{-23} \text{ J / K} \cdot \text{molecule}$$

And T is the absolute temperature in kelvins. [By comparing equation (2.2) and (2.3), the microscopic interpretation of temperature can be written as $T = M_{molec} \bar{v}^2 / (3k_B)$.]

For molecules, internal energy is stored in vibrating molecules bonds and rotation of the molecule about two or more axes, in addition to the translational kinetic energy. Figure 2.1b illustrates this model of a diatomic species.

Generally, the internal energy is expressed

$$U = U_{trans} + U_{vib} + U_{rot} \quad (2.4)$$

Where U_{vib} is the vibrational kinetic and potential energy;

U_{rot} is the rotational kinetic energy.

The amount of energy that is stored in each mode depends on temperature. (Turns, S. R., 2006).

2.2.2 Enthalpy

Enthalpy is a measurement of energy in a thermodynamic system, which is the thermodynamic quantity equivalent to the total heat content of a system. The equation of enthalpy is expressed as the internal energy U of the system plus the product of pressure P and volume V .

$$H = U + PV$$

The unit of enthalpy is in consistent with the internal energy.

The standard enthalpy of formation is defined as the change in enthalpy when one mole of a substance in the standard state (1 atm of pressure and 298.15 K) is formed from its pure elements under the same conditions. It is a measure of the energy released or consumed when one mole of a substance is created under standard conditions from its pure elements. The symbol of the standard enthalpy of formation is $\Delta \tilde{h}_f^\circ$

Where Δ = A change in enthalpy;

$^\circ$ = A degree signifies that it's a standard enthalpy change;

f = The f indicates that the substance is formed from its elements

(Turns, S. R., 2006).

2.2.3 Specific heat

There are two specific heats of a mixture, the specific heat at constant volume (C_v) and the specific heat at constant pressure (C_p). For the ideal gas, the specific heats are influenced by the temperature of the gas. This is due to specific heats relationship to internal energy, which can be stored in three methods in a molecule; rotational, vibration and translational. As the temperature increases the vibrational and rotational components of energy storage increase (Turns, S.R., 2006).

From the first law of thermodynamic, there is

$$dQ = dU + PdV$$

For constant volume:

$$dV = 0, \text{ then } PdV = 0, \text{ Therefore } dQ = dU$$

From the internal energy equation $dQ = m \cdot C_v \cdot dT$

For 1kg mass of gas and 1K temperature increase, there is $dQ = C_v$

Thus, the specific heat at constant volume is defined as the enthalpy required for increasing 1k of 1 kg gas/mixture.

For constant pressure:

$$\text{Similarly } dQ = dU + PdV$$

According to the ideal gas law, there is $PV = mRT$

By differentiation, it becomes $dPV + PdV = mRdT$

At constant pressure $dPV = 0$, then we get $PdV = mRdT$

Then the heat release rate is equal to

$$dQ = dU + PdV = m \cdot C_v \cdot dT + mRdT = m \cdot (C_v + R) \cdot dT$$

For 1kg mass of gas and 1K temperature increased, there is

$$dQ = C_p = C_v + R$$

Thus, the specific heat at constant pressure is defined as the energy required for increasing 1K of 1 kg/mixture.

The relationship between the two specific heats is defined as

$$C_p = C_v + R$$

Which can also be defined in terms of molar specific heats;

$$\tilde{C}_p = \tilde{C}_v + \tilde{R}$$

Where $\tilde{C}_p$ - Molar specific heat at constant pressure.

$\tilde{C}_v$ - Molar specific heat at constant volume

$\tilde{R}$ - Universal gas constant

2.2.4 Gamma

Gamma (ratio of specific heats) is used to calculate the temperature rise of an adiabatic process, which is defined as:

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

As the relationship between specific heat at constant pressure and specific at constant volume has been proved, which is $C_p = C_v + R$, then γ can also be written as:

$$\gamma = \frac{C_p}{C_v} = \frac{C_v}{C_v} + \frac{R}{C_v} = 1 + \frac{R}{C_v} = \gamma$$

Similarly, molar ratio of specific heats is

$$\frac{\tilde{C}_p}{\tilde{C}_v} = \gamma = 1 + \frac{\tilde{R}}{\tilde{C}_v}$$

2.3 Combustion stoichiometry

Generally, fuels are burned with air in engines. In combustion, oxygen is the reactive component of air. It is usually regarded as consisting of 21% oxygen and 79% nitrogen. Therefore, for each mole of oxygen in the air, there exists:

$$\frac{N_2 \%}{O_2 \%} = \frac{0.79}{0.21} = 3.76 \text{ moles of atmospheric nitrogen.}$$

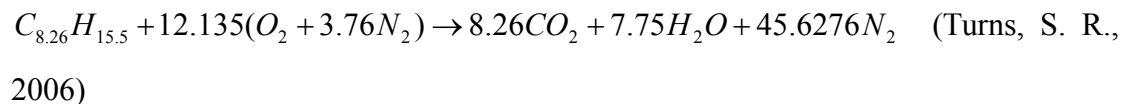
For simplicity, the chemical formula of the air can be written as $O_2 + 3.76N_2$ (Heywood, J. B., 1988).

The stoichiometric quantity of air is defined as the amount needed to completely burn a given quantity of fuel. If more than a stoichiometric quantity of air is supplied, the mixture is called fuel-lean; supplying less than the stoichiometric air produces a fuel-rich mixture. For a stoichiometric mixture, all the fuel and oxidizer are consumed to form products when combustion is finished.

For air/fuel mixture burning, air contains nitrogen, but when the products are at low temperatures the nitrogen is not significantly affected by the reaction. Therefore,

assuming that the fuel (gasoline: $C_{8.26}H_{15.5}$) reacts to form an ideal set of products

such as H_2O , CO_2 , and N_2 , and the stoichiometric reaction is expressed as



2.3.1 Air-fuel ratio

In practice, fuels are often burned with an amount of air different from the stoichiometric ratio. With less than the stoichiometric air requirement, there is insufficient oxygen to oxidize fully the C and H of fuel to CO_2 and H_2O . The

products will be a mixture of CO_2 and H_2O with carbon monoxide CO and

hydrogen H_2 (as well as N_2).

Considering the composition of the combustion products is different for fuel-lean and fuel rich mixtures, and the stoichiometric fuel/air ratio depends on fuel composition, the ratio of the actual fuel/air ratio to the stoichiometric ratio or its inverse is a more informative parameter for defining mixture composition. The fuel/air equivalence ratio ϕ ,

$$\phi = \frac{(F/A)_{actual}}{(F/A)_s}$$

The inverse of ϕ , the relative air/fuel ratio λ ,

$$\lambda = \phi^{-1} = \frac{(F/A)_{actual}}{(F/A)_s}$$

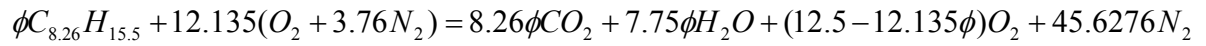
For fuel-lean mixtures: $\phi < 1, \lambda > 1$

For stoichiometric mixtures: $\phi = \lambda = 1$

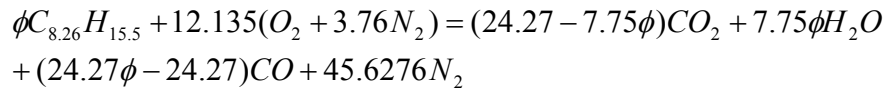
For fuel-rich mixtures: $\phi > 1, \lambda < 1$ (Heywood, J. B., 1988).

Applying the air/fuel ratio ϕ to the reaction equation, it can briefly be divided into two type of reactions.

For fuel-lean mixtures burning, there are extra oxygen produced. $\phi < 1$



For fuel-rich mixtures burning, there are additional CO produced. $\phi > 1$



However, at the beginning of the ignition, an ignitable mixture must be present at the spark plug. Mixtures that are too lean or too rich do not ignite. For gasoline fuel, the ignition boundaries lie in the area from $0.6 \leq \lambda \leq 1.6$ (Heywood, J. B., 1988).

Chapter 3 Thermodynamic analysis of engine processes

3.1 Compression process

Both the intake and exhaust valves are closed during the compression stroke then the the cylinder is assumed to be a closed system. When piston is moving forward, cylinder volume decreases, and the pressure is raised as the gas is compressed. Considering the high speed of the engine the duration of compression is short and negligible heat is lost to the cylinder wall. Relatively little energy is dissipated due to internal friction of the gas (Kuo, P. S., 1996). In general, the mixture behavior is usually described by polytropic model (Klein, M., & Eriksson, L., 2005).

$$pV^{n_c} = C \tag{3.1}$$

Where p is cylinder pressure, in pa;

V is cylinder volume, in m^3 ;

n_c is the compression polytropic exponent;

C is a cycle-to-cycle dependent constant.

3.1.1 Unburned temperature from IVC to SOC

Based on ideal gas law $pV = mRT$

After inlet valve is closed, the mixture mass in cylinder is considered to be constant, then the unburned temperature from IVC to SOC is

$$pV = mRT \Rightarrow T = \frac{pV}{mR}$$

$$\text{At crank angle of } \theta, T_\theta = \frac{p_\theta V_\theta}{mR_u} \quad (3.2)$$

Where R_u is unburned gas constant.

The unburned mixture is assumed to be air and fuel, then the unburned gas constant is obtained by

$$R_u = \frac{R}{\text{Molar-weight}_{air+fuel}}$$

3.2 Combustion process

For a conventional SI engine, the fuel and air are mixed together in the intake system, inducted through the intake valve into the cylinder, where mixing with residual gas takes place, and then compressed. Under normal operating conditions, combustion is initiated to the end of the compression at the spark plug by an electric discharge. Following inflammation, a turbulent flame develops, propagate through the premixed fuel, air, burned gas mixture until it reaches the combustion chamber walls, and then extinguishes and the combustion is finished (Heywood, 1988).

3.3.1 Two-zone combustion model

The 2-zone combustion model described by Al-Himyary and Karim has been applied for the combustion analysis in this report due to its simple formulation, good computational efficiency and low calculation time. This model calculates mixture temperature during combustion based on cylinder pressure data and then predicts NOx emission level (Chindaprasert, N., 2007).

In the two-zone model, the working fluid is assumed to consist of two zones, an unburned zone and a burned zone. These zones are actually two distinct thermodynamic systems with energy and mass interactions between themselves and their common surroundings, the cylinder walls. The first law of thermodynamics is

applied for solving basic thermodynamic properties, and the burned gas are assumed in chemical equilibrium during combustion(Heywood, 1989).

Assumptions for a typical two zone model:

1. The burned and unburned zones are ideal gases of different properties(Ramos, 1986).
2. The unburned zone is assumed to consist of a premixed fuel-air mixture. Though this may not be exact for diesel combustion, it is more realistic for SI engine combustion(Heywood, 1989).
3. No heat transfer from the burned to the unburned zone and vice versa.
4. Total volume of the two zones are equal to the cylinder volume.
5. Pressure in both the zones is the same(Wu, 2013).
6. The work required to transfer fluid from the unburned zone to the burned zone is negligible.

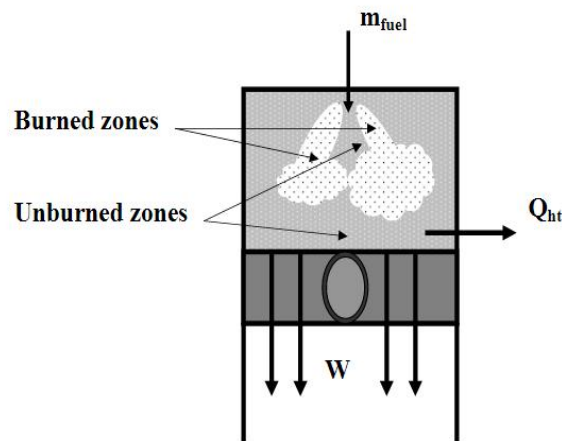


Figure 3.1 Two zone combustion models depicting the associated energy and mass transfers

3.3.2 Burned and unburned mixture states

Combustion occurs through a flame propagation process, thus the mixture state change and the motion of the burned and unburned gas are much complicated than the ideal cycle analysis. Without combustion, the mixture pressure and temperature change as a result of changes in volume due to piston movement. During combustion, the cylinder pressure increases due to the heat release from the fuel burning. The thermodynamic states and compositions of the burned gas and unburned gas are calculated and discussed in this part(Heywood, 1989).

3.3.2.1 Unburned temperature during combustion

The unburned temperature during combustion is calculated based on the assumption

that the heat losses to the walls of the combustion chamber from the unburned gas and the heat transfer from the flame are equal. The the instantaneous T_{ub} is calculated with the expression of an isentropic compression:

$$T_{ub} = T_{ub-1} \times \left(\frac{p_{\theta}}{p_{\theta-1}} \right)^{\left(\frac{\gamma_u - 1}{\gamma_u} \right)} \quad (3.3)$$

Where p_{θ} , T_{ub} , $p_{\theta-1}$ and $T_{\theta-1}$ are the cylinder pressures and temperatures at the current angle and at the previous angle respectively, γ_u is the ratio of specific heats of the unburned mixture (Guardiola, C., & López, J. J., 2011).

And for the unburned temperature at SOC

$$T_{ub-soc} = T_{ub(soc-1)} \times \left(\frac{p_{soc}}{p_{soc-1}} \right)^{\left(\frac{\gamma-1}{\gamma} \right)}$$

$$\text{Where } T_{ub(soc-1)} = \frac{p_{soc-1} V_{soc-1}}{m R_u}$$

3.3.2.2 Burned temperature during combustion

For 2-zone combustion model, the burned and unburned gases are assumed to be different ideal gases, each with constant specific heats, which are:

$$p v_b = m_b R_b T_b \quad (3.4) \quad u_b = c_{v,b} T_b + h_{f,b} \quad (3.5)$$

$$p v_u = m_u R_u T_u \quad (3.6) \quad u_u = c_{v,u} T_u + h_{f,u} \quad (3.7)$$

$$m = m_b + m_u = MFB \times m + (1 - MFB)m \quad (3.8)$$

Where V is the cylinder volume;

m is the mass of the cylinder contents (air and fuel);

v is the specific volume;

MFB is the mass fraction burned;

U_0 is the internal energy of the cylinder contents at some reference point θ_0

u is the specific internal energy; (Heywood, 1988)

From eq(3.6), the unburned gas temperature is also expressed as:

$$T_u = \frac{p V_u}{m_u R_u} \quad (3.9)$$

Where m_u is unburned mixture mass, which is approximated as:

$$m_u = (1 - MFB) \times m_{total}$$

R_u is unburned mixture gas constant.

Combining eq(3.6) and (3.3), then the unburned volume is obtained by

$$V_u = \frac{T_u m_u R_u}{p} \quad (3.10)$$

Where $T_{ub} = T_{ub-1} \times \left(\frac{p_{\theta}}{P_{\theta-1}}\right)^{\frac{\gamma_u-1}{\gamma_u}}$.

And the burned volume is equal to

$$V_b = V - V_u$$

Therefore the burned temperature in cylinder is achieved by

$$T_b = \frac{pV_b}{m_b R_b} \quad (3.11)$$

Where $m_b = MFBm$ and R_b is the burned mixture gas constant.

The burned temperatures during combustion will be applied for predicting NOx emission level.

3.4 Expansion process

After combustion, the pressure of the burned gases drives the piston down, does work by turning the crankshaft and in turn provides power to the vehicle. During expansion, the heat transferred to the cylinder liner is quite small compared to the work done, energy lost to internal friction of the mixture is minimal(Klein, M., & Eriksson, L., 2005).

The gas behavior is also described by polytropic model, which is:

$$pV^{n_e} = C$$

Where n_e is the expansion polytropic exponent.

3.5 Exhaust process

Exhaust valve opening (EVO) occurs before BDC. At this point, cylinder pressure is much greater than the exhaust system pressure. The higher pressure in the cylinder helps push the burned gases out of the cylinder. The process by which the pressure aids in the expulsion of burned gases is called blowdown(Kuo, P. S., 1996).

3.5.1 Exhaust emissions

For the complete combustion of the fuel hydrocarbons, the exhaust gases usually include oxygen (O_2), nitrogen (N_2), carbon dioxide and steam. However, for incomplete combustion, carbon monoxide, unburned hydrocarbons, nitrogen oxides and particulate matter also appear in exhaust gases. In this report, the nitrogen oxides emission level is mainly investigated and calculated.

Chapter 4. FOX engine data analysis

4.1 Engine data

The two generation Ford GDI engines are provided for investigating combustion parameters and predicting NOx emission level in this dissertation - 1.5L turbocharged engine and 1L Fox engine. In this report, the 1L Fox engine is mainly used for NOx prediction and the 1.5L turbocharged engine is used to help analyze the combustion parameters

4.1.1 1L Fox engine specifications

The 1L Fox engine specifications are shown in table 4.1.

Table 4.1 Engine specifications

Ford Fox 1.0 GDI	
Cylinders	3 in line
Displacement	999cc
Bore	71.9mm
Stroke	82.0mm
Compression	10.0:1

(Ford Motor company, 2012)

4.2 Engine measured data

The provided measured engine data has two aims - for the following NOx calculation and for examining the predicted NOx level.

4.2.1 Measured operating data

For the following calculation, necessary measured information for the Fox engine is provided, which includes: Fuel mass (kg/h); Air Fuel Ratio (measured); Lambda (measured); Residual gas (%). Then based on 2-zone combustion model, thermodynamic properties of unburned and burned zones are calculated

4.2.1.1 Total mixture mass calculation

Using provided fuel mass data to calculate total mixture (fuel and air) mass in cylinder, the calculation process is shown as follows:

$$\text{Fuel mass kg/min} = \text{fuel mass kg/h} \div 60$$

$$\text{Fuel mass kg/rev} = \text{fuel mass kg/min} \div \text{RPM}$$

$$\text{Fuel mass kg/cylinder} = \text{fuel mass kg/rev} \div 1.5 \text{ (3cylinders)}$$

$$\text{Air mass kg/cylinder} = \text{fuel mass kg/cylinder} \times \text{Air-fuel ratio}$$

$$\text{Mixture mass kg/cylinder} = (\text{Air mass} + \text{Fuel mass}) \times (1 + \text{rri}\%)$$

Table 4.2 gives the results of mixture mass for fox engine for all rpm range.

Table 4.2 Mixture mass for all RPM range

rpm (full load)	Fuel kg/h	Fuelmass kg/mim	Fuel mass kg/rev	Fuel mass kg/cylinder	air fuel ratio	air mass kg/cylinder	rr i w%	mixrure mass
1000	3.24	0.054	0.000054	0.000036	15.19	0.00054684	0. 5	0.000585754
1250	5.22	0.087	0.0000696	0.0000464	15.89	0.000737296	0. 2	0.000785263
1500	7.52	0.125333333	8.35556E-05	5.57037E-05	16.43	0.000915212	0. 1	0.000971886
1750	9.39	0.1565	8.94286E-05	5.9619E-05	14.79	0.000881766	0. 4	0.00094515
2000	11.35	0.189166667	9.45833E-05	6.30556E-05	14.28	0.000900433	0. 8	0.000971197
2250	12.92	0.215333333	9.57037E-05	6.38025E-05	14.19	0.000905357	0. 8	0.000976913
2500	14.34	0.239	0.0000956	6.37333E-05	14.25	0.0009082	1	0.000981653
3000	18.08	0.301333333	0.000100444	6.6963E-05	13.58	0.000909357	1. 5	0.000990965
3500	18.92	0.315333333	9.00952E-05	6.00635E-05	13.96	0.000838486	1. 7	0.000913825
4000	21.54	0.359	0.00008975	5.98333E-05	13.89	0.000831085	2. 2	0.000910519
4500	22.34	0.372333333	8.27407E-05	5.51605E-05	13.7	0.000755699	2. 7	0.000832752
5000	25.55	0.425833333	8.51667E-05	5.67778E-05	13.21	0.000750034	3. 1	0.000831823
5500	26.61	0.4435	8.06364E-05	5.37576E-05	13.13	0.000705837	3. 3	0.000784661
6000	27.62	0.460333333	7.67222E-05	5.11481E-05	12.9	0.000659811	3. 6	0.000736554
6500	25.11	0.4185	6.43846E-05	4.29231E-05	13.02	0.000558858	4. 1	0.000626455

4.2.1.2 Unburned and burned mixture properties calculation

The fuel is given as gasoline ($C_{8.26}H_{15.5}$), and based on the provided lambda data, the burning reaction (ignoring the dissociation of combustion products at high temperature) can be expressed as:

For fuel-lean mixtures burning: $\phi < 1, \lambda > 1$

$$\phi C_{8.26}H_{15.5} + 12.135(O_2 + 3.76N_2) + rri\%[8.26\phi CO_2 + 7.75\phi H_2O + (12.135 - 12.135\phi)O_2 + 45.6276N_2] \rightarrow (1 + rri\%)[8.26\phi CO_2 + 7.75\phi H_2O + (12.135 - 12.135\phi)O_2 + 45.6276N_2]$$

Thus the molar weight for reactant mixtures is:

$$\frac{[8.26 \times \phi \times 44(CO_2) + 7.75 \times \phi \times 18(H_2O) + 28(N_2) \times 12.135 \times 3.76 + 32(O_2) \times (12.135 - 12.135\phi)] \times rri\% + \phi \times 114.62(C_{8.26}H_{15.5}) + 12.135 \times 122.24(O_2 + 3.76N_2)}{\phi + 12.135 \times (1 + 3.76) + rri\%(8.26\phi + 7.75\phi + 12.135 - 12.135\phi + 45.6276)}$$

And the molar weight for product mixtures:

$$\frac{8.26 \times \phi \times 44(CO_2) + 7.75 \times \phi \times 18(H_2O) + 28(N_2) \times 12.135 \times 3.76 + 32(O_2) \times (12.135 - 12.135\phi)}{8.26\phi + 7.75\phi + 12.135 - 12.135\phi + 45.6276}$$

For fuel-rich mixtures burning: $\phi > 1, \lambda < 1$

$$\phi C_{8.26}H_{15.5} + 12.135(O_2 + 3.76N_2) + rri\%[(24.27 - 16.01\phi)CO_2 + (24.27\phi - 24.27)CO + 7.75\phi H_2O + 45.6276N_2] \rightarrow (1 + rri\%)[(24.27 - 16.01\phi)CO_2 + (24.27\phi - 24.27)CO + 7.75\phi H_2O + 45.6276N_2]$$

Thus, the molar weight for reactant mixtures:

$$\frac{[(24.27 - 16.01\phi) \times 44(CO_2) + (24.27\phi - 24.27) \times 28(CO) + 7.75\phi \times 18(H_2O) + 28(N_2) \times 12.135 \times 3.76] \times rri\% + \phi \times 114.62(C_{8.26}H_{15.5}) + 12.135 \times 122.24(O_2 + 3.76N_2)}{\phi + 12.135 \times (1 + 3.76) + rri\%(24.27 - 16.01\phi + 24.27\phi - 24.27 + 7.75\phi + 45.6276)}$$

And the molar weight for product mixtures:

$$\frac{(24.27 - 16.01\phi) \times 44(CO_2) + (24.27\phi - 24.27) \times 28(CO) + 7.75\phi \times 18(H_2O) + 28(N_2) \times 12.135 \times 3.76}{24.27 - 16.01\phi + 24.27\phi - 24.27 + 7.75\phi + 45.6276}$$

Assuming the reactants are in the unburned zone and products are in the burned zone, then with above calculated molar weight for reactants and products mixture the unburned and burned gas constants are achieved. The results of unburned and burned gas constant are generated in Table 4.3.

Table 4.3 Unburned and burned gas constant

lambda	1/lambda	molar weight for mixture (reactant)	molar weight for mixture (products)	Ru/J/kmol K	R unburned	R burned
1.04	0.961538462	30.23781975	28.88511772	8314	274.9536861	287.8298811
1.09	0.917431193	30.17875754	28.88318262	8314	275.4917922	287.849165

1.13	0.884955752	30.13339741	28.88175092	8314	275.906493	287.863434
1.02	0.980392157	30.26619157	28.8859416	8314	274.6959418	287.8216717
0.98	1.020408163	30.3163549	28.77222829	8314	274.2414129	288.9591976
0.98	1.020408163	30.3163549	28.77222829	8314	274.2414129	288.9591976
0.98	1.020408163	30.31313347	28.77222829	8314	274.270557	288.9591976
0.93	1.075268817	30.37741323	28.4701553	8314	273.6901901	292.0251019
0.96	1.041666667	30.32966949	28.65416431	8314	274.1210221	290.1497985
0.95	1.052631579	30.33486624	28.59377096	8314	274.0740617	290.7626283
0.94	1.063829787	30.3396208	28.53244193	8314	274.0311112	291.3876078
0.91	1.098901099	30.37413816	28.34261807	8314	273.7197005	293.3391679
0.9	1.111111111	30.38434076	28.27732009	8314	273.6277895	294.0165466
0.89	1.123595506	30.39224668	28.21096967	8314	273.5566109	294.7080549
1	1.123595506	30.38096397	28.21096967	8314	273.6582028	294.7080549

4.2.2 Measured NOx data

The measured NOx data is provided for examining the accuracy of the predicted NOx emission, and through comparing the predicted data with measured data, the improvements of NO model are investigated and discussed.

4.3 Cylinder-pressure data analysis

The cylinder-volume data of 1L Fox engine is mainly used for the calculations and analysis.

4.3.1 Cylinder pressure volume diagrams analysis

Generally, the pressure volume analysis is mainly based on 3 graphs - pressure VS crank angle, log pressure VS log volume and polytropic index graphs.

4.3.1.1 Pressure VS crank angle graph

The Pressure VS crank angle graph is easy to identify crank angle-based events such as valve openings and closings, and ignition. Moreover, the crank angle axis is linear with respect to time (Kuo, P. S., 1996).

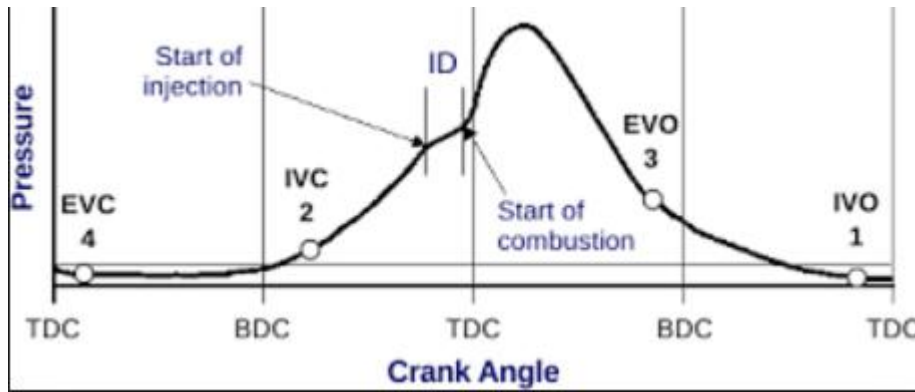


Figure 4.1 Pressure VS crank angle graph

4.3.1.2 logPressure VS logvolume graph

From the graph, the compression and expansion process are linear before combustion begins and after combustion ends, with slopes equal to the polytropic compression and expansion coefficients respectively. The compression and expansion processes are exponential on an analogue pressure VS volume plot. A second contribution of plotting log pressure versus log volume is that the pumping loop is considerably expanded (Randolph, A. L., 1994).

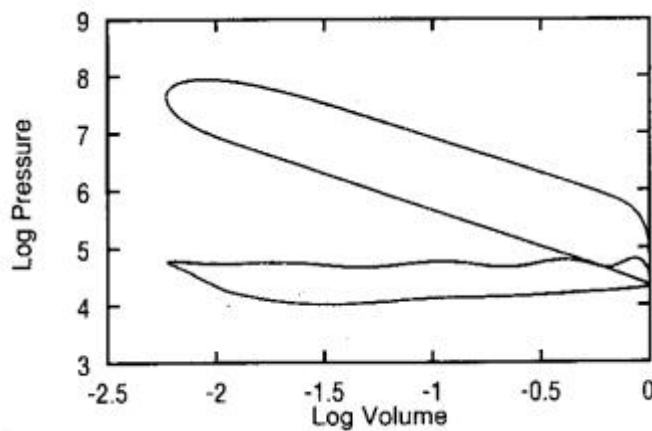


Figure 4.2 logPressure VS logvolume graph

4.3.1.3 Polytropic index graph

The compression of the unburned zone prior to combustion and the expansion after the end of combustion are close to adiabatic, and the further studies by Lancaster et al and Caris et al show that these processes are closer determined by a polytropic relationship. Currently the polytropic model is applied for compression and expansion processes.

According the polytropic relationship:

$$\begin{aligned}
pV^n &= C \\
\Rightarrow p_1V_1^n &= C; p_2V_2^n = C \\
\Rightarrow \ln p_1V_1^n &= \ln p_2V_2^n \Rightarrow \ln p_1 + n \ln V_1 = \ln p_2 + n \ln V_2 \\
\Rightarrow n &= \frac{\ln p_2 - \ln p_1}{\ln V_1 - \ln V_2}
\end{aligned}$$

Therefore, the equation of polytropic index is given by

$$n = \frac{\ln P_2 - \ln P_1}{\ln V_1 - \ln V_2}$$

The polytropic index graph is shown as follows

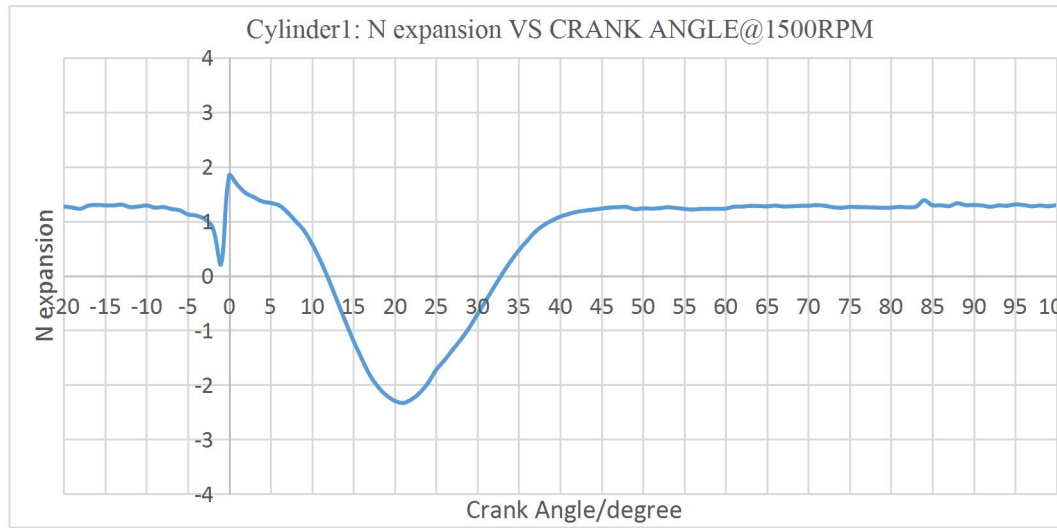


Figure 4.3 Polytropic index graph

Looking at figure 4.3, it can be observed that at TDC and BDC there are anomalies. The noise on the graph is caused by the $\ln V_1 - \ln V_2$ tending to zero. (Brunt & Pond, 1997)

4.3.1 SOC and EOC

Considering the pressure change during combustion is due to two main parts: combustion and piston movement, thus theoretically, from the pressure change point of view, the first point of appearing pressure change due to combustion is defined as SOC, and the last point of having pressure change due to combustion is defined as EOC. However, in practice, only using pressure due to combustion to determine SOC and EOC is not accurate enough since the polytropic index is not absolutely constant during compression and expansion processes and is also not reliable around TDC. Therefore, a combined method for determining SOC and EOC is applied in this report.

4.3.1.1 Pressure due to combustion

As the pressure change during combustion is caused by change in volume and combustion, which can be expressed as:

$$\Delta p_{total} = \Delta p_v + \Delta p_c$$

Where Δp_v is the incremental change in pressure due to piston motion and Δp_c is the incremental change in pressure due to combustion.

In employing the polytropic relationships, the cylinder pressure without combustion could be predicted as:

$$p_{\theta+1} = p(\theta) \left(\frac{V(\theta)}{V(\theta+1)} \right)^n$$

Where n represents a polytropic index (note: n is taken as compression polytropic index before TDC while expansion polytropic index after TDC).

$p(\theta), V(\theta), V(\theta+1)$ are the pressure and volume at crank angle of θ and $\theta+1$.

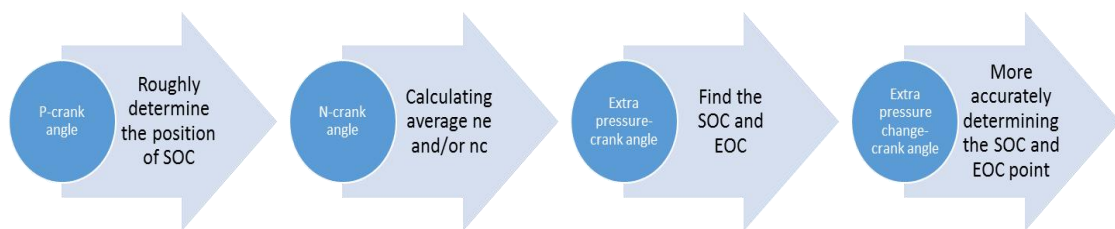
Then the pressure due to combustion at crank angle of $\theta+1$ is obtained by

$$\Delta p_{c-\theta+1} = p_{\theta+1} - p_{\theta+1}'$$

The pressure due combustion will be an important criterion to determine SOC and EOC (Klein, M., & Eriksson, L., 2005).

4.3.1.2 Determination of SOC and EOC

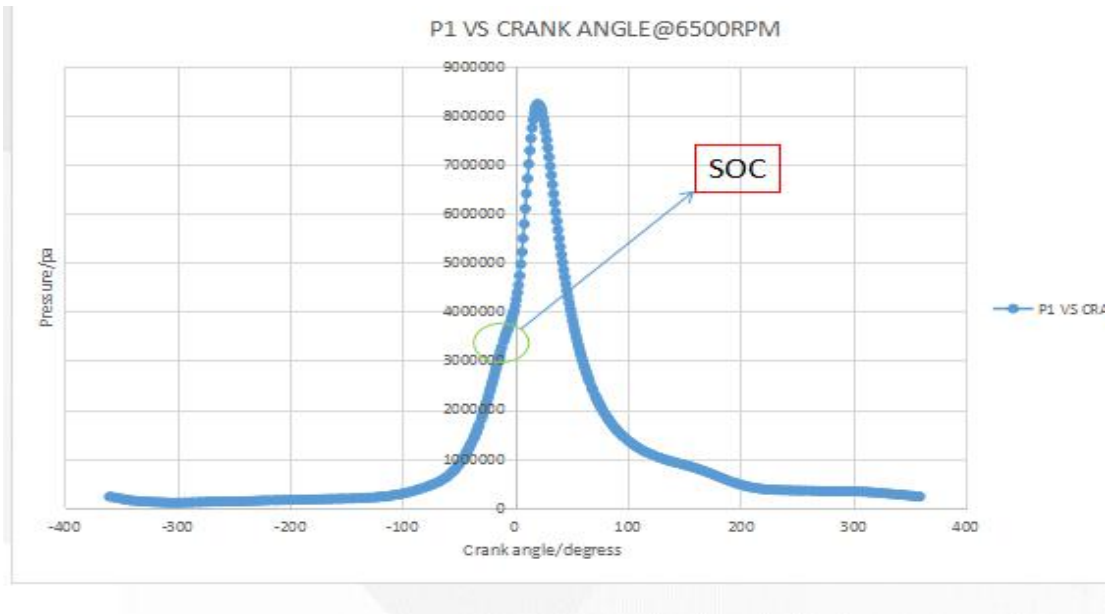
For determining SOC and EOC, general analysis process is shown as follows:



Step 1: P-crank angle diagram :roughly determining the location of SOC (before TDC, around TDC or after TDC)

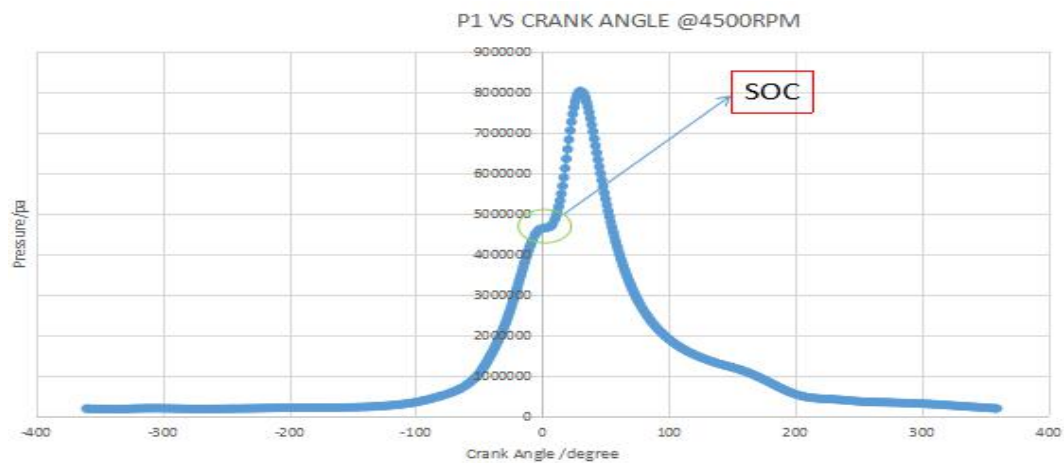
a. SOC before TDC

For SOC before TDC, the pressure relatively increases compared without combustion. Figure shows at 6500rpm, the SOC appears before TDC.



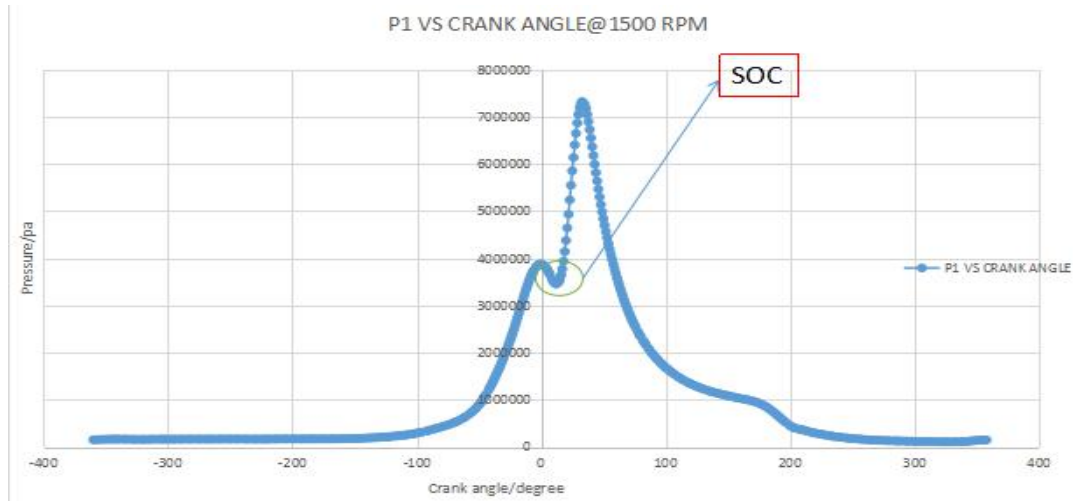
b. SOC at/around TDC

For SOC at/ around TDC, there is a obvious pressure change around TDC. For example, at 4500rpm, the SOC is roughly determined at TDC.



c. SOC after TDC

For SOC after TDC, the pressure decreases firstly due to expansion and then increases due to combustion.



Step 2: N-crank angle diagram: calculating average n_e and n_c

For most rpm range, the soc occurs after TDC, therefore the expansion polytropic index will be applied for calculating the pressure rise due to combustion. But at 6500rpm, the SOC occurs before TDC, then the compression polytropic index is applied for the extra pressure calculation.

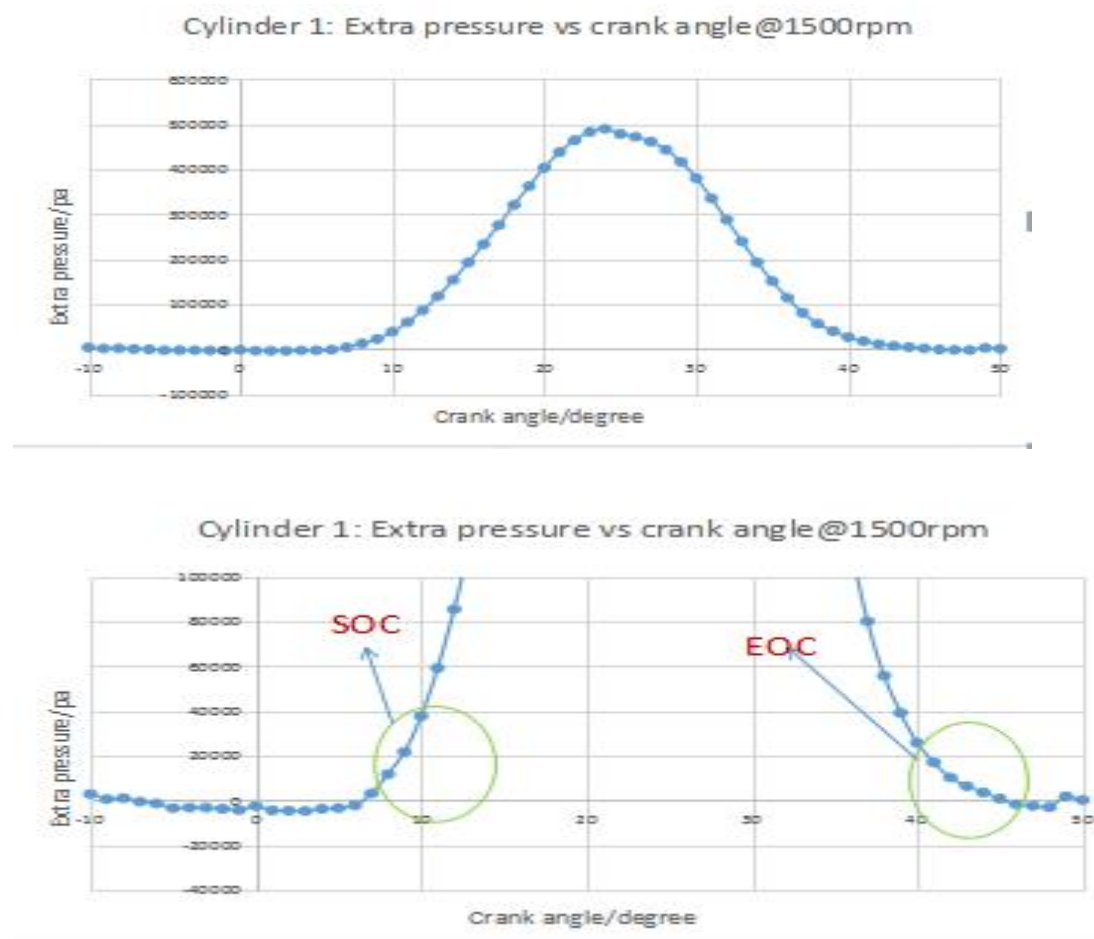
Table 4.4 Polytropic index of three cylinders

RPM	Cylinder 1		Cylinder 2		Cylinder 3	
	Nc	Ne	Nc	Ne	Nc	Ne
1000	/	1.2513	/	1.0784	/	1.2422
2000	/	1.2349	/	1.0696	/	1.213
3000	/	1.2207	/	1.1381	/	1.2214
3500	/	1.2365	/	1.0288	/	1.2332
4000	/	1.2174	/	1.0288	/	1.2332
4500	/	1.2063	/	1.0384	/	1.2071
5000	/	1.2034	/	1.0855	/	1.1905
5500	/	1.218	/	1.0194	/	1.2221
6000	/	1.2335	/	1.0565	/	1.2098
6500	1.2888	1.1855	1.2463	0.9942	1.2611	1.1456

From the table, there is a trouble with cylinder that the polytropic index is relatively small. Based on the heat release model (Appendix E), The polytropic index n is comparable to the average value of γ_u (which is around 1.3) for the unburned mixture during the compression process prior to combustion. However considering the heat transfer to the cylinder walls, the polytropic index is greater than γ_b for the burned mixture during expansion (Heywood, 1988). The γ_b is definitely over than 1, but for cylinder 2, at 6500rpm, the n_e is less than 1, this will be discussed in the following sensitivity analysis.

Step 3 : Extra pressure VS crank angle diagram to determining SOC and EOC

Looking at extra pressure diagram, the extra pressure for compression and expansion process is supposed to be near zero or relatively small, then the SOC occurs at the point where extra pressure is suddenly increases, and the EOC appears at the point where extra pressure suddenly decreases.



However, in reality, it is quite difficult to decide which point is SOC and EOC.

Therefore there is a added step 4 of combined method applied for helping determine the SOC and EOC accurately.

Step 4: A combined method to determine the SOC and EOC accurately

A combined method of real cylinder pressure change VS crank angle, extra pressure change VS crank angle, extra pressure VS crank angle and polytropic index VS crank angle is applied to determine the SOC and EOC.

Table 4.5 shows the signs of SOC and EOC

Graph / data	SOC after TDC	SOC at/around TDC	SOC before TDC	EOC
Real cylinder pressure change VS crank angle	●	●		✧
Extra pressure change VS crank angle	■	■	■	✧
Extra pressure VS crank angle	◆	◆	◆	✧
Polytropic index VS crank angle	❖		❖	✧

For SOC, there are the following signs:

- real cylinder pressure change: the real cylinder pressure change begins to decrease.
- extra pressure change : the extra pressure change begins to increase.
- ◆ extra pressure: the extra pressure begins to increase
- ❖ polytropic index : the polytropic index begins to decrease

For EOC, there are the following signs:

- ✧ real cylinder pressure change: the real cylinder pressure change tends to be constant.
- ✧ extra pressure change : the extra pressure change begins to decrease.
- ✧ extra pressure: the extra pressure begins to decrease.
- ✧ polytropic index : EOC occurs at the polytropic index tends to be stable.

4.3.1.3 Extra pressure problem at SOC

Theoretically, at the SOC, the extra pressure is definitely positive due to combustion. However, in the excel work, at the degree of SOC, the extra pressure appears to be negative. For example:

1768.531	5172.997	1280.08
-1652.85	1508.382	-6203.19
1776.585	5153.264	-674.029
3189.109	2521.785	2714.265
-107.302	-275.073	-841.895
4072.192	8069.829	4478.912
11333.11	14539.21	14326.92
15956.89	16237.4	17200.17
23088.52	25560.68	28681.18
38559.3	40501.42	44958.55
50164.92	51421.66	57295.62

@4500rpm

soc:0 degree

-793.2957055	-15154.7	-11742.5
-11229.44746	-13500.4	-25681
-4344.298837	3123.107	-3422.51
4963.171559	14780.45	13830.73
9425.042829	2262.878	24777.74
5273.334827	-13029.7	-4183.87
-2568.08619	-394.793	-2535.51
20648.79918	26805.5	35406.52
26678.61891	25976.26	46375.2
50627.43081	30068.36	66276.14
39435.64806	17127.9	35776.31
64931.9399	64878.64	85746.98

@6500rpm

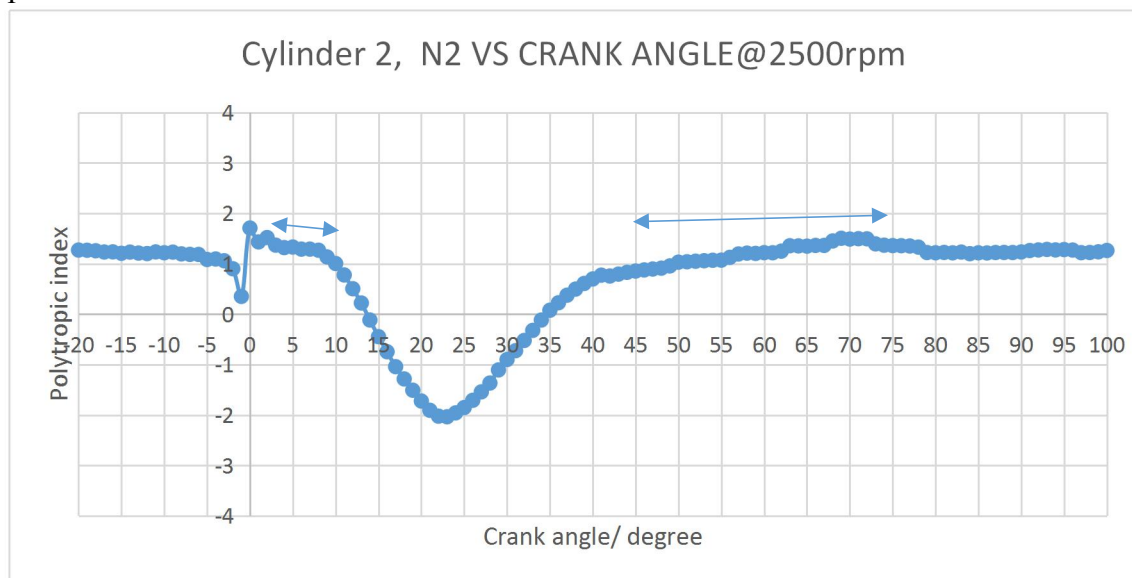
soc:-6 degree

To analyze why the extra pressure at SOC is negative, the following three possible reasons are discussed: polytropic index problem, accuracy of SOC point and cylinder pressure data sampling problem.

4.3.1.3.1 Polytropic index problem

From 1000rpm to 3500rpm, the SOC is after TDC, and around 8 degree.

Comparing the Polytropic index at (or around) SOC with that in the expansion process.



The Average n (from 50 to 55 degree):1.0505

The n close to the SOC is 1.26.

The negative value of extra pressure at SOC is probably because the polytropic index used in calculation of extra pressure is much lower than the polytropic index before SOC. For example:

$$\Delta p = p_2 - p_{2n} = p_1 \left(\frac{V_1}{V_2} \right)^{1.26} - p_1 \left(\frac{V_1}{V_2} \right)^{1.05} < 0$$

(In expansion, $V_1/V_2 < 1$)

Solution: Trying the polytropic index closing to SOC

For example: for cylinder 2 at 2500rpm, changing the polytropic index from average expansion coefficient(0.76) to expansion coefficient closing to SOC(1.22), then the extra pressure at SOC is shown to be positive.

-4097.65	-22606.3	-4945.8	-4581.78	-4646.544681	-4021.08
-4581.78	-26371.9	-4021.08	-4449.4	-3261.6116	-3360.34
-4449.4	-28004	-3360.34	2431.47	-2890.143351	1165.347
2431.47	-30975.9	1165.347	8114.11	-136.4048805	8259.557
8114.11	-31256	8259.557	15974.73	6286.057624	15253.84
15974.73	-27033.3	15253.84	25290.78	18902.36379	26987.43
25290.78	-16388.8	26987.43	41117.47	37483.61373	41885.33
41117.47	-98.1957	41885.33	57148.49	57988.98607	61363.87
			77845.52	86752.17131	82589.13

While for cylinder 2 at 2500rpm, changing the polytropic index from 1.0505 to 1.269, the extra pressure at SOC still show to be negative. Then the second problem - accuracy of SOC is discussed.

-3830.13	-12758.4	-6111.925273	-3786.14	-2867.1	-6111.93
-3431.44	-12384.6	-5957.308829	-3381.36	-1123.99	-5957.31
2192.46	-14076.7	-2401.371656	2249.251	-1299.5	-2401.37
8118.916	-14156.8	2651.134473	8181.86	-7.52691	2651.134
14889.04	-5909.62	9297.732058	14956.51	9226.417	9297.732
26811.26	3280.955	19909.92939	26882.82	19308.75	19909.93
41480.89	21345.62	35010.63631	41557.18	38400.49	35010.64
60395.42	44743.67	53016.4107	60475.15	62546.6	53016.41

4.3.1.3.2 Accuracy of SOC point

As the determination of SOC is based on the great extra pressure change, which appears from one degree to the next degree for the given fox data. However, If the determined SOC is at 6 degree, is that any possibility the real SOC happens at 6.2 ? Then at 6 degree, the extra pressure can be a very small negative value due to the variation of polytropic index in the expansion. Especially for SOC around TDC (from 4000rpm to 6000rpm), it is difficult to use polytropic index around SOC to adjust extra pressure value.

Solution: Improving the accuracy of SOC point

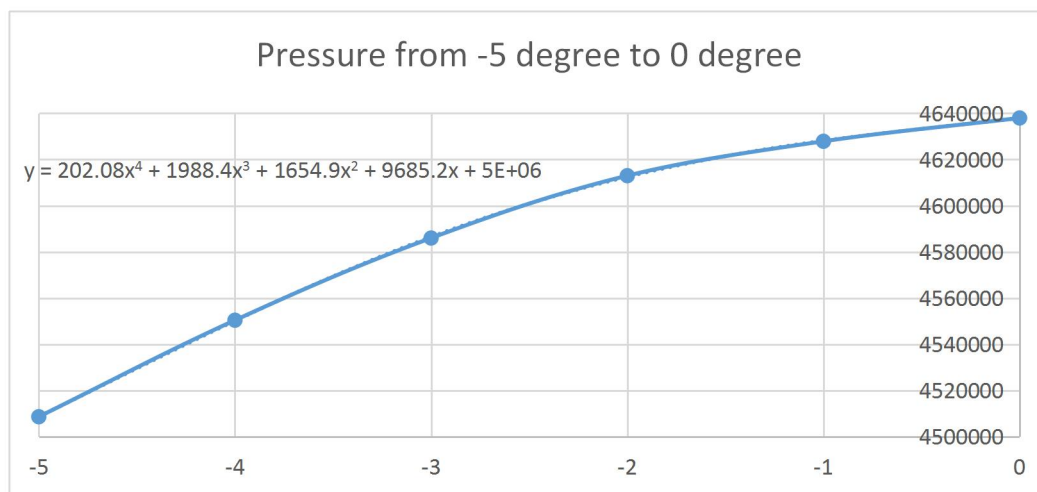
Looking at the extra pressure data at 4500rpm, where the SOC is determined at -1 degree.

1776.585	5153.264	-674.029
3189.109	2521.785	2714.265
-107.302	-275.073	-841.895
4072.192	8069.829	4478.912
11333.11	14539.21	14326.92
15956.89	16237.4	17200.17
23088.52	25560.68	28681.18
38559.3	40501.42	44958.55

Making an assumption that the the **real** SOC appears between -1 and 0degree

To prove this assumption, the following steps

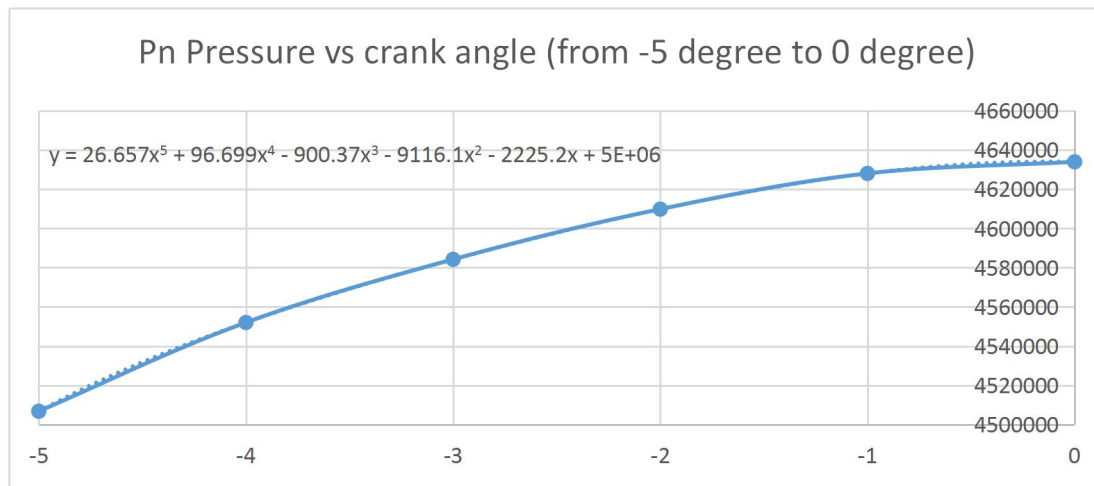
Step 1:Plot the pressure data graph from -5 degree to 0 degree, then add the trendline with polynomial equation.



The polynomial equation for pressure in relation to crank angle is:

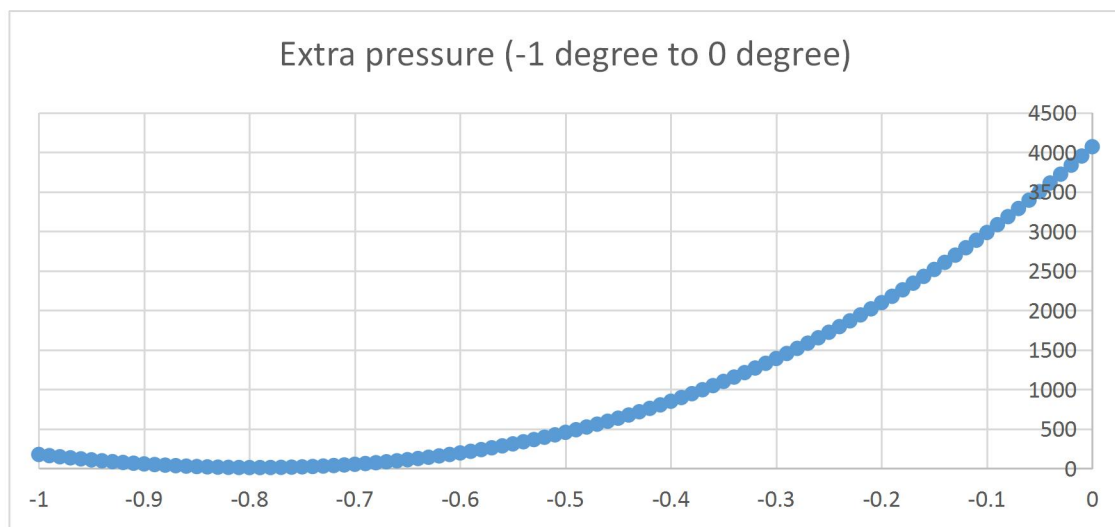
$$y_1 = 202.08x^4 + 1988.4x^3 + 9685.2x + 4638000$$

Step 2: Plot the Pn pressure data graph from -5 degree to 0 degree, then add the trend line with polynomial equation as well.



The polynomial equation for pressure without combustion in relation to crank angle is:
 $y_2 = 26.657 \cdot x^5 + 96.699 \cdot x^4 - 9116.1 \cdot x^3 - 2225.2 \cdot x + 4638000$

Step 3: Based on step 1 and step 2, then the polynomial equation of extra pressure in relation to the crank angle is obtained by: $y = y_1 - y_2$, then calculate the extra pressure per 1/100 degree from -5 to 0 degree. Especially looking at the extra pressure from -1 degree to 0 degree.



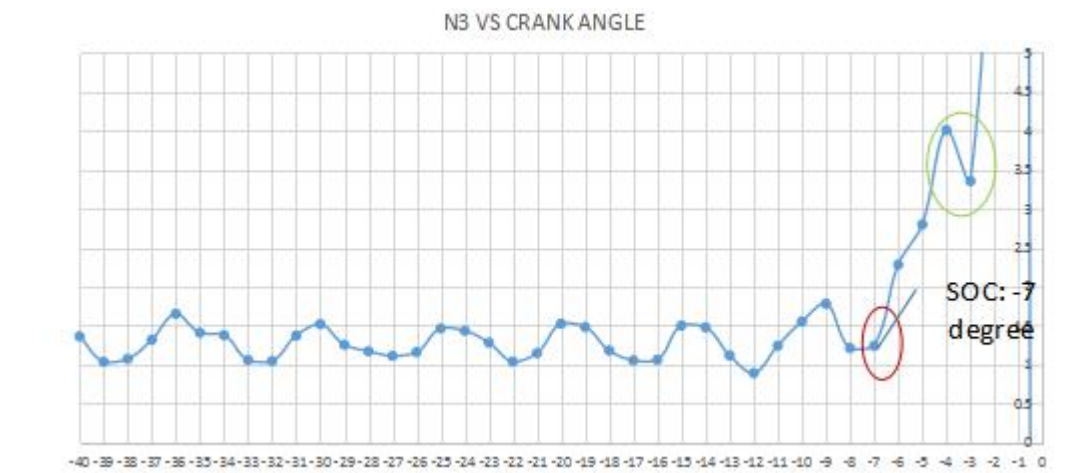
From the graph. The real SOC appearing between -1 degree and 0 degree can be proved.

Thinking about another possibility: if determined SOC (after TDC) is 6 degree, the real SOC occurs at 5.9. there is not enough time for combustion to increase the pressure greatly, the extra pressure at SOC may still be a negative value due to the variation of polytropic index per degree.

4.3.1.3.3 Cylinder pressure data sampling problem

Polytropic index varies during compression and expansion. Probably due to cylinder

pressure sampling, the cylinder pressure data selected for per degree is random. For fox engine data, at 6500rpm, the polytropic index of cylinder 3 VS crank angle is shown as follows.



Average polytropic index (from -20 to -7): 1.2948;
Average polytropic index (from -20 to -7): 1.3055;
Average polytropic index (from -20 to -7): 1.3324;
SOC polytropic index: 1.2377; And It is quite strange that after SOC, there is a drop from -4 to -3.

Figure 4.4 shows the possible cylinder pressure sampling errors.

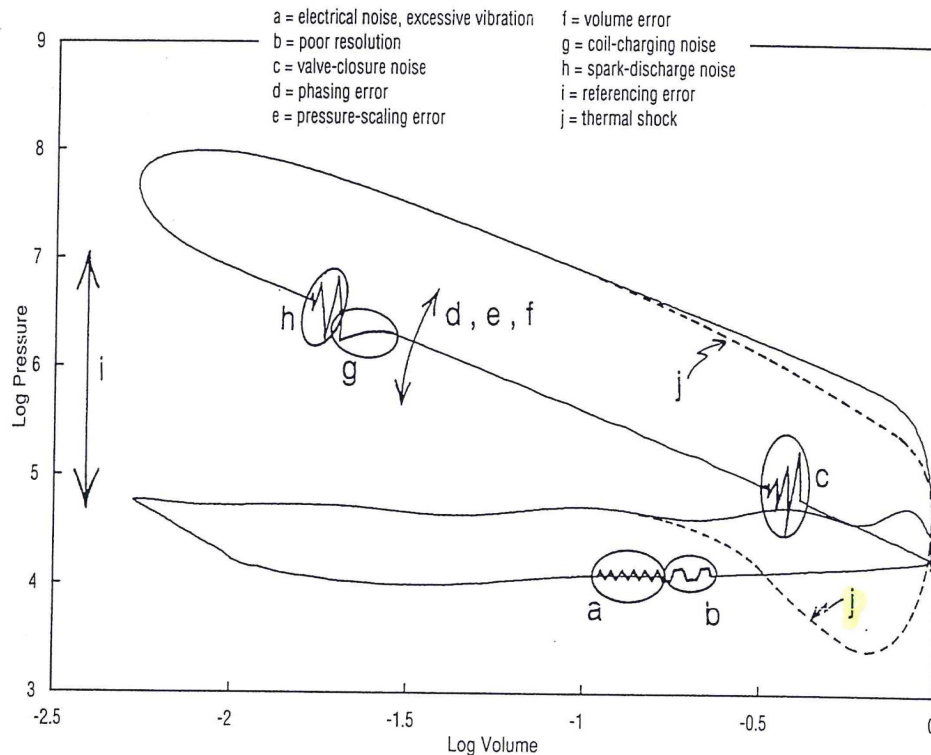
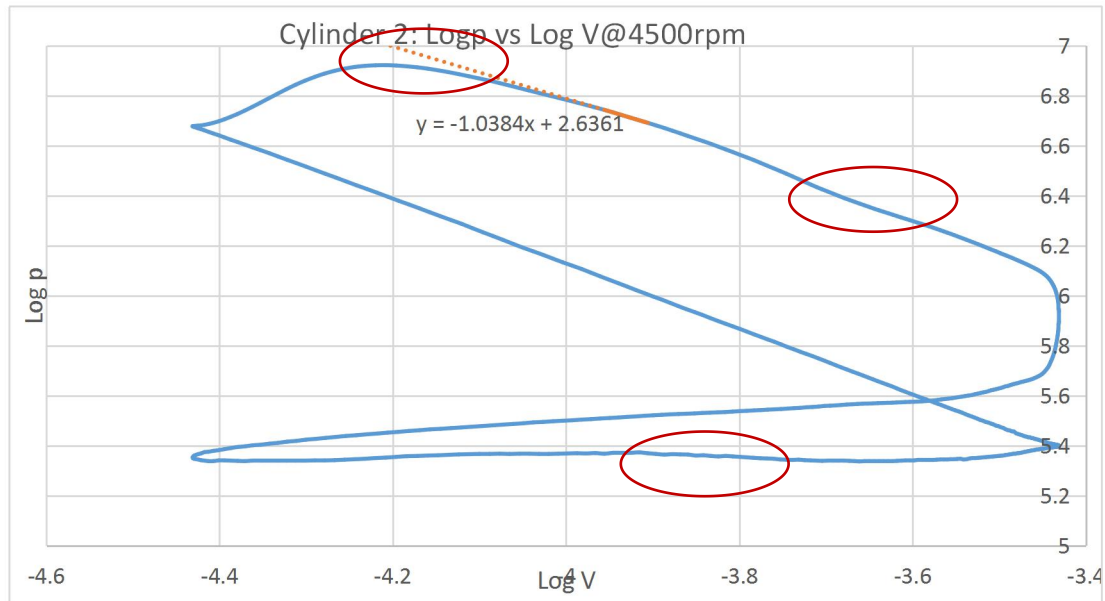


Figure 4.4 Example of several types of cylinder-pressure measurement error.

Similar pressure measurement errors are shown in the cylinder 2 at 4500rpm.

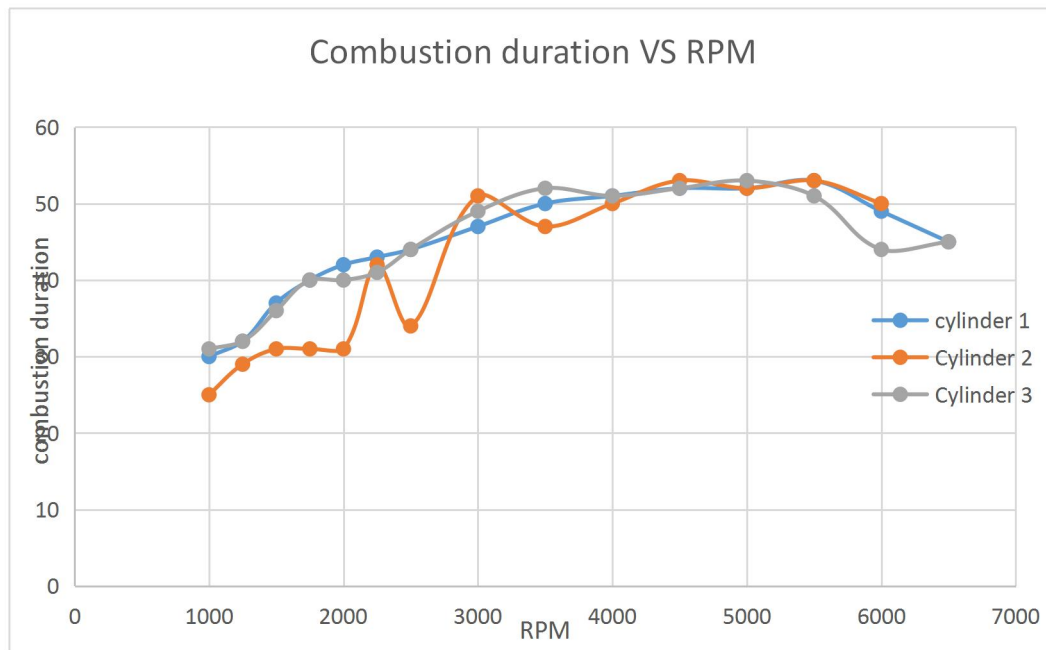


4.3.2 Combustion duration

The SOC, EOC, and combustion duration of 3 cylinders for all rpm are generated in table 4.6.

Table 4.6 SOC, EOC, and combustion duration of 3 cylinders

RPM	Cylinder 1			Cylinder 2			Cylinder 3			Air fuel ratio
	SOC	EOC	Combustion duration	SOC	EOC	Combustion duration	SOC	EOC	Combustion duration	
1000	9	38	30	10	34	25	9	39	31	0.962
1250	8	39	32	9	37	29	8	39	32	0.917
1500	8	44	37	9	39	31	8	43	36	0.885
1750	7	46	40	10	40	31	8	47	40	0.98
2000	9	50	42	11	41	31	10	49	40	1.02
2250	8	50	43	10	51	42	9	49	41	1.02
2500	8	51	44	11	44	34	8	51	44	1.02
3000	6	52	47	7	57	51	5	53	49	1.075
3500	4	53	50	5	51	47	3	54	52	1.042
4000	2	52	51	2	51	50	2	52	51	1.053
4500	-1	50	52	-1	51	53	-1	50	52	1.064
5000	0	51	52	0	51	52	0	52	53	1.099
5500	-2	50	53	-2	50	53	-1	49	51	1.11
6000	0	48	49	0	49	50	0	43	44	1.124
6500	-6	38	45	/			-6	38	45	1.124



Based on the table and graph, the following conclusions are drawn:

- The cylinder 2 has a relatively shorter combustion duration comparing with cylinder 1 and cylinder 3 at low engine speed; At medium engine speed, the three cylinders own a quite similar combustion duration; Cylinder 3 has a
- In general, the combustion duration increases with the faster engine speed because for the same time the engine rotates more degrees. However, from the graph, the combustion combustion decreases at high rpm because the combustion duration decreases with an increase in equivalence ratio. For cylinder 2, there is a abnormal rise appearing at 2500 and 3000rpm which is probably due to the pressure data problem.

4.3.3 Ignition delay

The ignition delay data is collected in table 4.7.

Table 4.7 Ignition delay

RPM	Spark advance	SOC	Ignition delay
1000	-5.7	9	3.3
1250	-5	8	3
1500	-2.9	8	5.1
1750	-3.6	7	3.4
2000	-4.2	9	4.8

2250	-3.1	8	4.9
2500	-3.2	8	4.8
3000	-0.1	6	5.9
3500	3	3	6
4000	5.3	2	7.3
4500	7.6	0	7.6
5000	4.9	0	4.9
5500	7.5	-2	5.5
6000	9.5	0	9.5
6500	14.5	-6	8.5

4.3.4 Mass fraction burned

4.3.4.1 Mass fraction burned methods

4.3.4.1.1 Rassweiler and Withrow method

Rassweiler and Withrow (1938) procedure is widely used due to its relative simplicity and computational efficiency. This procedure calculates mass fraction burned based on heat release model.

Mass fraction burned is an evaluation of the fraction of the heat released from the fuel burning to the total energy produced at the end of the combustion.

By definition, there is:

$$MFB = \frac{\sum_{soc-\theta} dQ_R}{\sum_{soc-eoc} dQ_R}$$

According to the first law of thermodynamics, there is

$$dQ = dU + pdV$$

$$dU = m \cdot C_v \cdot dT$$

$$dQ = mC_v dT + pdV$$

Then based on ideal gas law, we have

$$pdV + Vdp = mRdT \Leftrightarrow \frac{pdV + Vdp}{R} = mdT$$

For constant-volume burning, $dV = 0$, then

$$dQ = mC_v dT + pdV = mC_v dT = C_v \cdot \frac{Vdp}{R}$$

Therefore the mass fraction burned is equal to:

$$MFB = \frac{\sum_{soc-\theta} (C_v \cdot \frac{Vdp}{R})}{\sum_{soc-eoc} (C_v \cdot \frac{Vdp}{R})} = \frac{\sum_{soc-\theta} (C_v \cdot Vdp)}{\sum_{soc-eoc} (C_v \cdot Vdp)} \quad (4.1)$$

Based on the equation (4. 1), there are three methods for MFB estimation suggested.

Method 1: Extra pressure method

Assuming the pressure change during combustion Δp consists of two parts: pressure rise due to combustion Δp_c and pressure change due to volume Δp_v , and the pressure rise due to combustion is in proportion to the heat added to the cylinder during the crank angle interval, the mass fraction burned at the end of the i^{th} interval can be expressed as:

$$MFB = \frac{m_b(i)}{m_b(total)} = \frac{\sum_0^i \Delta p_c}{\sum_0^N \Delta p_c}$$

(Asgari, O., Hannani, S. K., & Ebrahimi, R., 2012).

Method 2 : $V\Delta p_c$ represents heat release

Assuming the constant specific heat of the mixture during combustion, then according to the equation (4.3.1), the mass fraction burned can be calculated by:

$$MFB = \frac{\sum_{soc-\theta} (Vdp)}{\sum_{soc-eoc} (Vdp)} = \frac{\sum_{soc-\theta} V\Delta p_c}{\sum_{soc-eoc} V\Delta p_c}$$

Method 3: Improved heat release MFB method

$$dQ = C_v \cdot \frac{Vdp}{R}$$

Considering specific heat at constant changes during combustion

$$\gamma = 1 + \frac{\tilde{R}}{\tilde{C}_v}, \text{ then } \frac{1}{\gamma - 1} = \frac{\tilde{C}_v}{\tilde{R}}$$

$$\text{Therefore } dQ = C_v \cdot \frac{Vdp}{R} = \frac{Vdp}{\gamma - 1}$$

The mass fraction burned is calculated by

$$MFB = \frac{\sum_{soc-\theta} \frac{V\Delta p_c}{\gamma_{av} - 1}}{\sum_{soc-eoc} \frac{V\Delta p_c}{\gamma_{av} - 1}}$$

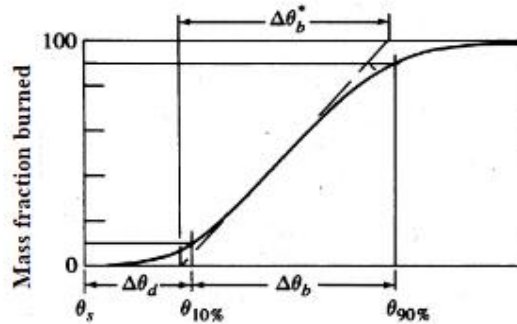
Where γ_{av} is the average γ_{av} during combustion, $\gamma_{av} = (1 - MFB)\gamma_u + MFB\gamma_b$

A big problem of applying this method is figuring out γ_b , which is dependent on burned temperature, while the equation of burned temperature includes mass fraction burned. A possible solution of applying method 3 is discussed in Appendix.

4.3.4.1.2 Wiebe Function method

4.3.4.1.2.1 Representative mass fraction graph

Mass fraction burned for a engine cycle is defined as a normalized quantity with a scale of 0 to 1, which describes the process of chemical energy release in relation to crank angle. Figure 1 shows the flame development stages based on mass fraction burned VS crank angle graph.



Flame development angle $\Delta\theta_d$: crank angle interval during which flame kernel

develops after spark ignition;

Rapid burning angle $\Delta\theta_b$: crank angle required to burn most of mixture;

Overall burning angle: sum of flame development and rapid burning angles.

4.3.4.1.2.2 Wiebe function

The Wiebe function curve has a characteristic S-shaped curve and is commonly used to estimate the mass fraction burned as a function of engine position during combustion. The Wiebe function is expressed as:

$$MFB = \{1 - \exp[-a(\frac{\theta - \theta_0}{\Delta\theta})^{m+1}]\}$$

Where θ_0 is the angle of SOC;

$\Delta\theta$ is the combustion duration(Mendera, K. Z., 2002).

The constants a and m are determined experimentally. Experimentally were detected values of coefficients of Wiebe function, which are listed in table 1. These coefficient values can be regarded as normal and depend mainly on used fuel in engine(Lotus Engineering Software).

Table. 4.8: Experimentally determined values of the Wiebe function coefficients

Fuel	Coefficient a	Coefficient m
gasoline	10	2
diesel	6.9	0.5
methane	5	2.2
methanol	10	2

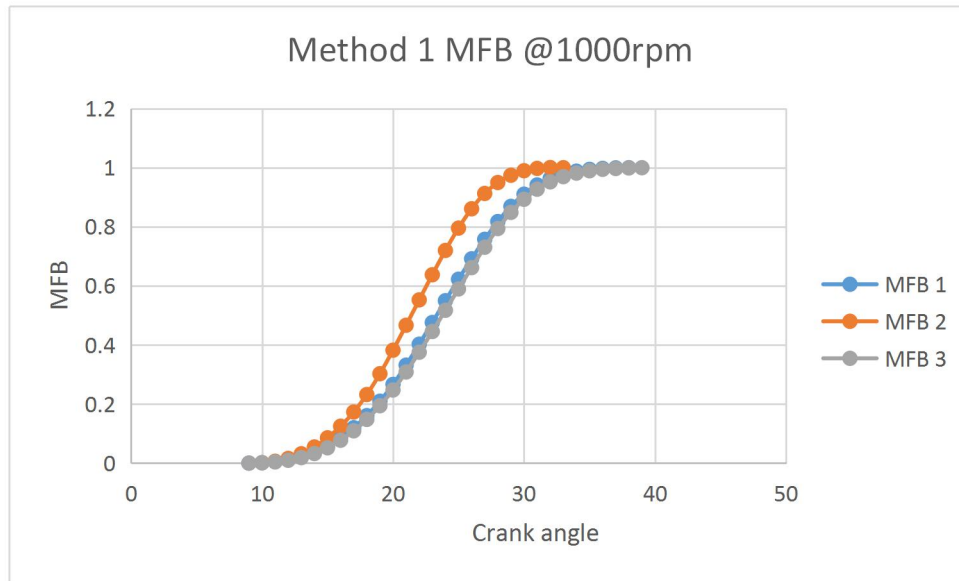
The advantage of Wiebe function is avoiding polytropic index variation problem, However the disadvantage is the complicated computation concerning for each cycle the m and a are different. For simplicity, in this report, the a general Wiebe function based on experimentally determined gasoline values is applied:

$$MFB = \{1 - \exp[-10(\frac{\theta - \theta_0}{\Delta\theta})^3]\}$$

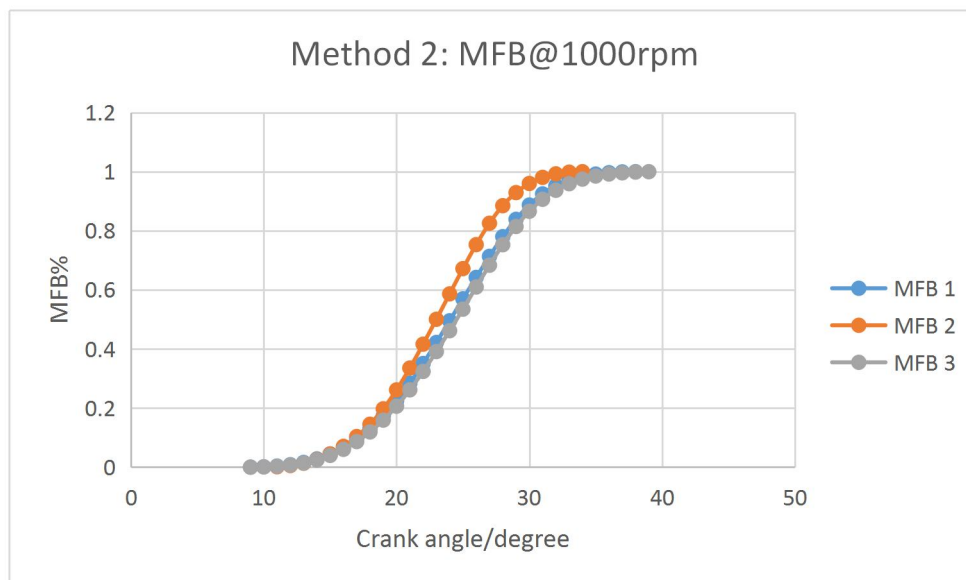
4.3.4.2 MFB results analysis

4.3.4.2.1 Rassweiler and Withrow method results

Method 1 results:

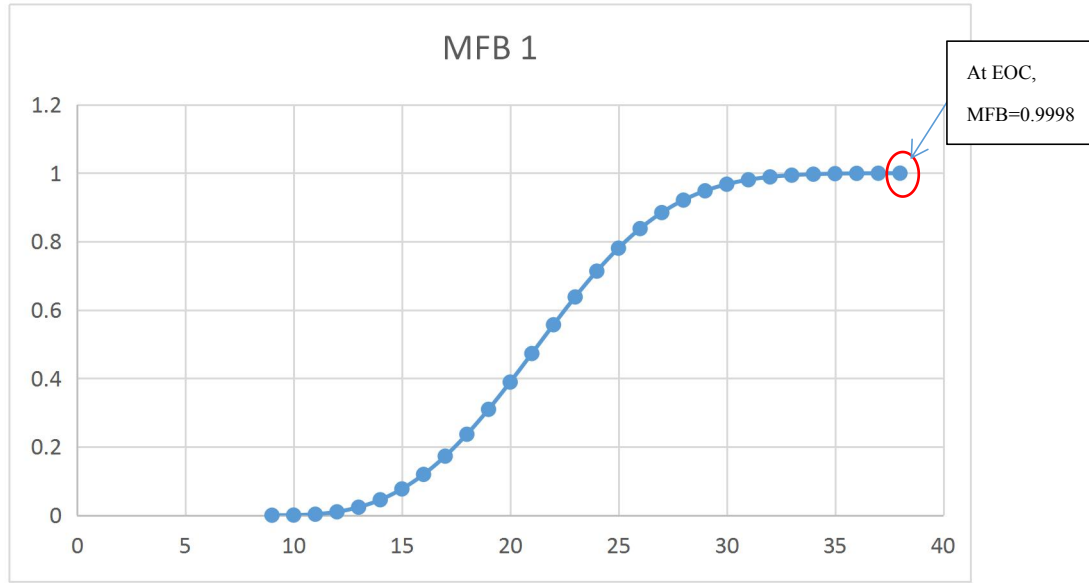


Method 2 results:



From the method 1 and method 2 graphs, both of them look similar with the representative MFB graph and comparing burning rates of three cylinders, the cylinder 2 seems to be the fastest one at 1000rpm. In this report, the method 2 is used for the following burned temperature calculations.

4.3.4.2.2 Wiebe Function result



The Wiebe function method shows a perfect MFB graph, but as this is a rough Wiebe function applied for calculating MFB, the MFB at SOC is zero while at EOC it is not 1. Therefore the Wiebe function cannot be used for MFB calculation in this report.

4.4 Burned Temperature

4.4.1 Burned Temperature calculation

The unburned volume is equal to

$$V_u = \frac{T_u m_u R_u}{p}$$

Where $m_u = (1 - MFB)m$

$$T_{ub} = T_{ub-1} \times \left(\frac{p_\theta}{P_{\theta-1}} \right)^{\left(\frac{\gamma_u - 1}{\gamma_u} \right)}$$

And then the burned volume is obtained by:

$$V_b = V - V_u$$

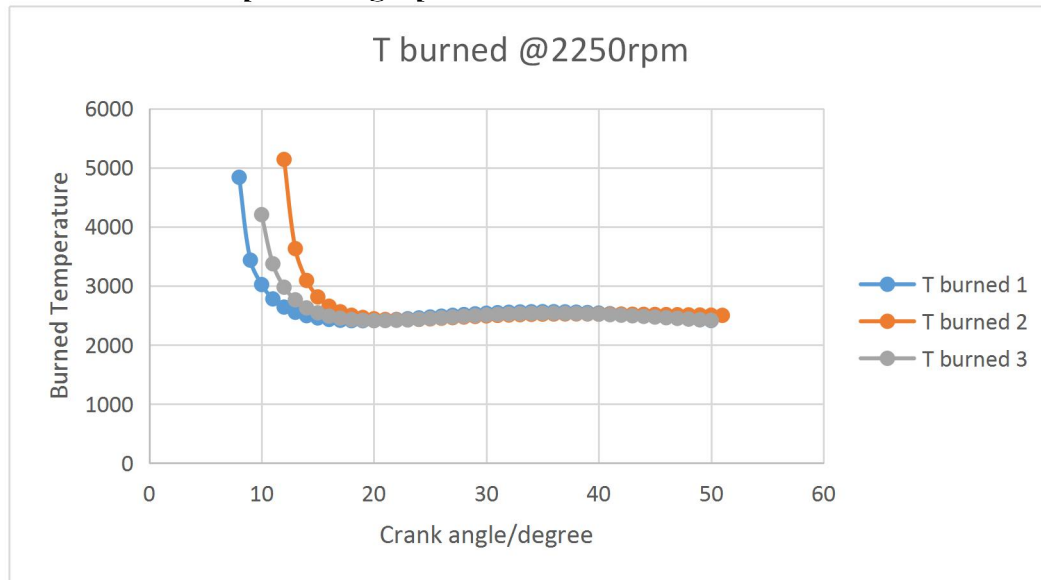
Therefore the burned temperature is calculated by:

$$T_b = \frac{p V_b}{m_b R_b}$$

Where $m_b = MFBm$

Note: m is the total mixture mass which is calculated in table 4.2. R_u is calculated in table 4.3.

4.4.2 Burned temperature graph



From the burned temperature graph, it is obvious that for the first degrees of combustion, it predicts a much higher burned temperature, which is caused by the equation of burned temperature.

$$T_b = \frac{pV_b}{m_b R_b} = \frac{pV_b}{MFB \cdot mR_b}$$

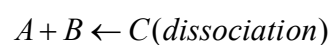
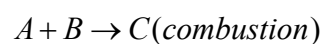
At beginning of combustion, the burned volume and MFB are both quite small. However, when the MFB is much smaller than V_b , the calculation result show a high burned temperature.

From the graph, cylinder 2 has relatively higher burned temperatures comparing with cylinder 1 and cylinder 3 considering it has a relatively faster burning rate and a shorter combustion duration.

Chapter 5 Combustion and dissociation

5.1 Dissociation

When temperatures are above about 1800K, the thermal agitation of combustion products is such that they begin to dissociate back towards their reactant materials, giving reversibility to the combustion reaction, thus



At a sustained high temperature, therefore, a condition of dynamic equilibrium exists with rates of combustion and dissociation exactly equal, thus the reactants and

products coexist in proportions that maintain constant. These proportions can be determined by partial equilibrium constants at the given temperature.

The rates of such reactions at given temperatures can be determined by experiment, and are found to be proportional to the instantaneous concentration of each material raised to some power, that is:

Forward reaction rate: $k_f[A]^a[B]^b$

Reverse reaction rate: $k_r[C]^c$

Where $[X]$ is instantaneous molar concentration of material X;

k is the rate constant for the reaction;

a, b, c are experimentally determined powers.

Since the two rates are equal at dynamic equilibrium, there is

$\frac{[C]^c}{[A]^a[B]^b} = \frac{k_f}{k_r} = K'$, which is the concentration equilibrium constant for the reversible reaction.

It follows from Avogadro's principle that

$K = \frac{p_C^c}{p_A^a p_B^b}$, which is known as partial pressure equilibrium constant for the reversible reaction.

Furthermore, $\frac{p_X}{p} = \frac{\text{mol}X}{\text{total} - \text{mol}}$, where p is the total pressure.

Thus in each case, p_X can be expressed as follows:

$$p_X = p \left(\frac{n_X}{n_t} \right)$$

Where n_X is the mole of X;

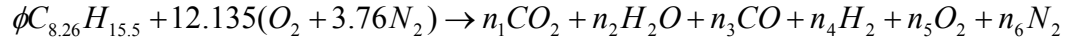
n_t is the total moles of product present.

(Goodger, E., 2000)

5.2 Equilibrium model of combustion

Studies show that the major species present in combustion products of gasoline at relatively high temperatures are mainly 13, which include CO_2 , H_2O , CO , H_2 ,

O_2 , N_2 , OH , NO , O , H , N_2O , NO_2 , and N . These species may vary significantly with temperature, pressure, type of fuel and equivalence ratio. In this report, only 6 species combustion products are considered, which are CO_2 , H_2O , CO , H_2 , O_2 , N_2 . Therefore the combustion reaction can be written as:



According to atom balance, there are:

$$C: 8.26\phi = n_1 + n_3; \quad (1)$$

$$H: 15.5\phi = 2n_2 + 2n_4; \quad (2)$$

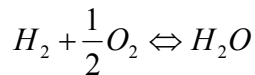
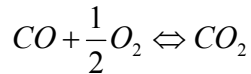
$$O: 24.27 = n_3 + 2n_5; \quad (3)$$

$$N: 45.6276 \times 2 = 2n_6 \Rightarrow n_6 = 45.6275. \quad (4)$$

To solve 6 unknown values, 2 more equations are needed. Then the partial equilibrium constants of CO_2 and H_2O are suggested.

Partial pressure equilibrium constants of CO_2 and H_2O

At high temperature, CO_2 and H_2O experience dissociation, which are:



Hence the partial pressure equilibrium constants are achieved by:

$$K_{CO_2} = \frac{p(CO_2)}{p(CO)p(O_2)^{0.5}} = \frac{nCO_2}{nCO(p \cdot \frac{n_{O_2}}{n_t})^{0.5}} \quad (5)$$

$$K_{H_2O} = \frac{p(H_2O)}{p(H_2)p(O_2)^{0.5}} = \frac{nH_2O}{nH_2(p \cdot \frac{n_{O_2}}{n_t})^{0.5}} \quad (6)$$

There are 6 equations for 6 unknowns, then the method of solving the mass molar of combustion product is given as follows:

- Calculating partial pressure equilibrium constants K_{CO_2} and K_{H_2O} based on Gibbs function

- b. Assume value for n_5/n_t , and evaluate $(p \cdot \frac{n_5}{n_t})^{0.5}$
- c. Evaluate $n_1/3$ and n_2/n_4 from K_{CO_2} and K_{H_2O} expression respectively, using step b.
- d. Evaluate n_1 and n_3 from carbon balance, and n_2 and n_4 from hydrogen balance using step c values.
- e. Evaluate n_5 from oxygen balance
- f. Evaluate n_6 from nitrogen balance
- g. Evaluate $n_t = n_5 / (\text{assumed} - n_5 / n_t)$, and compare with $\sum n_j$, with $j=1$ to 6.
- h. Using “Goal seek” to make the $n_t - \sum n_j = 0$, then the produced oxygen n_5 and nitrogen n_6 are achieved (Goodger, E., 2000).

5.3 Combustion product calculation

5.3.1 K_{CO_2} and K_{H_2O}

From the Gibbs function, the equilibrium constant at constant pressure is defined as:

$$K_p = \exp(-\Delta G^\circ / RT)$$

For reactions $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$ and $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$, according to JANAF table, the gibbs free energy of CO , O_2 , H_2 , CO_2 , H_2O is given in Table 4.1.

Table 5.1 Gibbs free energy of CO , O_2 , H_2 , CO_2 , H_2O

T/K	O_2 <i>kJ / mol</i>	H_2 <i>kJ / mol</i>	H_2O <i>kJ / mol</i>	CO <i>kJ / mol</i>	CO_2 <i>kJ / mol</i>
2000	0	0	-135.528	-286.034	-396.33
2100	0	0	-129.721	-294.372	-396.304
2200	0	0	-123.905	-302.672	-396.262
2300	0	0	-118.082	-310.936	-396.209
2400	0	0	-112.252	-319.164	-396.142
2500	0	0	-106.416	-327.356	-396.062
2600	0	0	-100.575	-335.514	-395.969

2700	0	0	-94.729	-343.638	-395.862
2800	0	0	-88.878	-351.729	-395.742
2900	0	0	-83.023	-359.789	-395.609
3000	0	0	-77.163	-367.816	-395.461

(Glassman, I., 2014).

Then, the total gibbs free energy of these two reactions are calculated.

$$\Delta G_{CO+0.5O_2 \rightarrow CO_2} = g(CO_2) - g(CO) - 0.5g(O_2)$$

$$\Delta G_{H_2+0.5O_2 \rightarrow H_2O} = g(H_2O) - g(H_2) - 0.5g(O_2)$$

Therefore the partial pressure equilibrium constants for CO_2 and H_2O are obtained by:

$$K_{pCO_2} = \exp(-\Delta G_{total}^o / RT)$$

$$K_{pH_2O} = \exp(-\Delta G_{total}^o / RT)$$

The results of total gibbs free energy and partial pressure constants are generated in Table 5.2.

Table 5.2 The partial pressure equilibrium constants for CO_2 and H_2O

T/K	$H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$		$CO + \frac{1}{2}O_2 \Leftrightarrow CO_2$	
	$\Delta G_{H_2+0.5O_2 \rightarrow H_2O}$ <i>kJ / mol</i>	K_{pH_2O} / <i>atm^{-0.5}</i>	$\Delta G_{CO+0.5O_2 \rightarrow CO_2}$ <i>kJ / mol</i>	K_{pCO_2} / <i>atm^{-0.5}</i>
2000	-135.528	3465.42087	-110.296	759.8711698
2100	-129.721	1685.581455	-101.932	343.1715297
2200	-123.905	874.9533943	-93.59	166.7974197
2300	-118.082	480.643722	-85.273	86.43319726
2400	-112.252	277.4529895	-76.978	47.36342055
2500	-106.416	167.3096091	-68.706	27.26372031
2600	-100.575	104.8695693	-60.455	16.39078289
2700	-94.729	68.03131431	-52.224	10.24166356
2800	-88.878	45.50920918	-44.013	6.623724033
2900	-83.023	31.29390107	-35.82	4.417852035
3000	-77.163	22.05848594	-27.645	3.029420726

5.3.2 Molars of combustion products

To solve the n_5 , assume a value for n_5/n_t , and evaluate $(p \cdot \frac{n_5}{n_t})^{0.5}$. Then based on achieved K_{CO_2} and K_{H_2O} , then n_1/n_3 and n_2/n_4 are calculated. Process is shown as follows:

$$p \cdot \frac{n_5}{n_t} \Rightarrow K_{CO_2} = \frac{n_1}{n_3 (p \cdot \frac{n_5}{n_t})^{0.5}} \Rightarrow \frac{n_1}{n_3}$$

$$p \cdot \frac{n_5}{n_t} \Rightarrow K_{H_2O} = \frac{n_2}{n_4 (p \cdot \frac{n_5}{n_t})^{0.5}} \Rightarrow \frac{n_2}{n_4}$$

For atom balance equations:

C: $8.26\phi = n_1 + n_3 = n_3 (\frac{n_1}{n_3} + 1)$, given the n_1/n_3 , then the n_3 is evaluated.

Similarly, for H: $15.5\phi = 2n_2 + 2n_4 = 2n_4 (\frac{n_2}{n_4} + 1)$, given the n_2/n_4 , then the n_4 is evaluated as well.

For O balance, $24.27 = n_3 + 2n_5 \Rightarrow n_5 = 0.5(24.27 - n_3)$, and for N balance $n_6 = 45.6275$.

The total mole of product are equal to

$$n_t = n_1 + n_2 + n_3 + n_4 + n_5 + n_6$$

And the assumed n_t' is calculated by $n_t' = n_5 / (n_5 / n_t)$, where n_5 / n_t is a guessed value. Then the error between guessed the value and real value is

$$error = n_t - n_t'$$

Using the function of “Goal seek” in excel to make the error be zero, then the correct n_5 is achieved.

5.3.3 Polynomial method for calculating n_5

During combustion, the burned temperature is calculated, which is from 2000K to 3000K and varies per degree. Using goal seek to calculate n_5 per degree for all rpm

range is quite difficult and complicated, then the polynomial method is applied for calculating n_5 for combustion duration.

Step 1: For a certain equivalence ratio, using the Goal seek to calculate the n_5 at 10bar for temperature from 2000 to 3000K.

Guess n5/nT	P	p=n5/nt	(p*n5/nt)^1/Kco2	Kh2o	n1/n3	n2/n4	1/lambda	n3	n4	n1	n2	n6	n5	nt	n5/nt	error/guess		
0.00795	2000	10	0.079497	0.281952	7.60E+02	3.47E+03	2.14E+02	9.77E+02	0.961538	0.036899	7.62E-03	7.905409	7.444304	45.6276	0.488989	61.51082	0.00795	5.19E-08
0.008353	2100	10	0.083531	0.289017	3.43E+02	1.69E+03	99.18245	487.1619	0.961538	0.079278	0.015265	7.863029	7.436658	45.6276	0.514003	61.53583	0.008353	1.91E-07
0.009067	2200	10	0.090674	0.30112	1.67E+02	9.75E+02	50.22612	263.4664	0.961538	0.155044	0.029177	7.787264	7.423746	45.6276	0.558341	61.58017	0.009067	4.52E-07
0.010212	2300	10	0.102124	0.319569	8.64E+01	4.81E+02	27.62135	153.5987	0.961538	0.277496	0.048202	7.664812	7.403721	45.6276	0.62958	61.65141	0.010212	4.94E-07
0.011892	2400	10	0.118918	0.344845	4.74E+01	2.77E+02	16.33305	95.67936	0.961538	0.458217	0.07708	7.48409	7.374844	45.6276	0.734379	61.75621	0.011892	2.42E-07
0.014176	2500	10	0.141762	0.376514	2.73E+01	1.67E+02	10.26516	62.99433	0.961538	0.705033	0.116447	7.237275	7.335476	45.6276	0.877471	61.8993	0.014176	4.69E-07
0.017096	2600	10	0.170962	0.413475	1.64E+01	1.05E+02	6.777186	43.36099	0.961538	1.021232	0.167984	6.921076	7.283939	45.6276	1.061338	62.08217	0.017096	7.62E-07
0.020641	2700	10	0.206411	0.454325	1.02E+01	6.80E+01	4.653039	30.9083	0.961538	1.404962	0.233542	6.537345	7.218381	45.6276	1.285983	62.30781	0.020641	1.89E-06
0.024754	2800	10	0.247538	0.497532	6.623724	45.50921	3.295517	22.6423	0.961538	1.848976	0.315194	6.093332	7.136729	45.6276	1.548816	62.57065	0.024753	7.61E-07
0.029343	2900	10	0.293425	0.541687	4.417852	31.2939	2.393095	16.95151	0.961538	2.34027	0.415114	5.601581	7.036809	45.6276	1.844651	62.86648	0.029342	1.59E-07
0.034289	3000	10	0.342885	0.585564	3.029421	22.05849	1.77392	12.91666	0.961538	2.863207	0.535468	5.079101	6.916455	45.6276	2.166068	63.1879	0.03428	8.75E-06

Step 1.1: Repeat this process and get the n_5 for a range of pressure from 10 bar to 90 bar.

Step 2: change the equivalence ratio and repeat the process of step 1.

Step 3: Pot the graphs of n_5 VS temperature for pressure from 10bar to 90bar, and show the polynomial equations

Step 4: At a certain equivalence ratio, for pressure p and temperature T , the n_5 is obtained by:

$$n_5(p,T) = \frac{Eq_n_5(a+10,T) - Eq_n_5(a,T)}{10 \times 10^5} + (p - a \times 10^5) \times Eq_n_5(a,T)$$

where a presents the pressure in bar, the value of a may be 10, 20, 30, 40, 50, 60, 70, 80, which depends on p because p is in range of $[a, a+10]$.

Chapter 6 NOx prediction

6.1 NOx model literature review

Nitric oxide (NO) and nitrogen dioxide (NO_2) are generally grouped as nitrogen oxides (NO_x) emissions. In a spark ignition engine, most of NOx comes out as NO.

Over the years extensive research has been undertaken for developing models that better both the understanding of NOx formation and prediction of NOx level in engines.

In 1946, Zeldovich was the first to suggest the importance of reactions of NO formation which is known as Zeldovich or thermal mechanism.



In 1970, Lavoie, Heywood and Keck added the reaction



Which also makes contribution to NO production, especially in near stoichiometric and rich fuel-air mixture burning. Eq (5.1) to (5.3) is called Extended-Zeldovich mechanism (EZM), which takes main responsibility of forming NO in the post flame gas zone. The results of two-zone thermodynamic model and EZM in a S.I. Engine obtained by Heywood (1970) show that the EZM, a rate controlled model, delivers better results compared to equilibrium concentration during the combustion process.

Raine, Stone and Gould(1995) applied multi-zone thermodynamic model and EZM to predict NO. The results showed that a multi-zone thermodynamic model was likely to help accurately to predict the NOx emission and 5 or 10 burned zones are efficient for most purposes(Raine, R.R., Stone, C.R. &Gould, J., 1995)

Miller et al.(1998) at Ford Motor company made a new reaction scheme for NOx production which was incorporated into a steady state quasi-dimensional engine combustion simulation. The reaction kinetics includes 67 reactions and 13 chemical species, and assumed equilibrium concentration for all other chemical species. The General Engine SIMulation (GESIM) was used to model the engine cycle. The new reaction scheme was called a super-extended Zeldovich mechanism (SEZM). Super-Extended Zeldovich Mechanism is shown to be able to predict the NOx formation within 10% of experimental engine test data for both fuel-rich and fuel-lean conditions and for EGR (Exhaust Gas Recirculation) dilution, while the extended-Zeldovich mechanism approximately gives an error of 50% or more under similar conditions(Chindaprasert, N., 2007).

6.2 Kinetics of NO formation

Nitric oxide is the predominant oxide of nitrogen produced during combustion, which can be formed in three different ways - thermal NO, prompt NO and fuel NO. In this report, thermal NO, which is formed among the combustion products at high temperatures according to extended-Zeldovich mechanism is mainly discussed and applied for NOx prediction.

6.2.1 Thermal NO

The mechanism of NO formation from atmospheric nitrogen has been studied extensively. It is generally accepted that in combustion of near stoichiometric fuel-air

mixtures the principal reactions governing the formation of NO from molecular nitrogen (and its destruction) are (Heywood J.B., 1988)



Where k_i is the speed constants, which can be experimentally determined.

r and l represent forward and reverse reactions.

Then the NO formation rate is obtained with reaction equations (6.1) to (6.3):

$$\begin{aligned} \frac{d[NO]}{dt} = & k_{1,r}[O][N_2] + k_{2,r}[N][O_2] + k_{3,r}[N][OH] \\ & - k_{1,l}[NO][N] - k_{2,l}[NO][O] - k_{3,l}[NO][H] \end{aligned} \quad (6.4)$$

And for the temporal change of [N] concentrations follows

$$\begin{aligned} \frac{d[N]}{dt} = & k_{1,r}[O][N_2] - k_{2,r}[N][O_2] - k_{3,r}[N][OH] \\ & - k_{1,l}[NO][N] + k_{2,l}[NO][O] + k_{3,l}[NO][H] \end{aligned} \quad (6.5)$$

The first reaction possesses a high activation energy because of the stable N_2 triple bond and thus proceeds sufficiently fast only at high temperature; hence the designation “thermal”. It is therefore the rate-limiting step.

Considering the reaction speed of equation (6.1) is much slow than that of equation (6.2) and (6.3), the [N] formed in the first reaction step is immediately further converted to NO in the second and third steps. Thus the [N] can be considered to be constant after a short initial phase. As the [N] is assumed to quasi-steady, then there is:

$$\frac{d[N]}{dt} \approx 0 \quad (6.6)$$

Adding the Eq(4.4) and (4.5):

$$\begin{aligned} \frac{d[NO]}{dt} \approx & \frac{d[NO]}{dt} + \frac{d[N]}{dt} = k_{1,r}[O][N_2] + k_{2,r}[N][O_2] + k_{3,r}[N][OH] - k_{1,l}[NO][N] \\ & - k_{2,l}[NO][O] - k_{3,l}[NO][H] + k_{1,r}[O][N_2] - k_{2,r}[N][O_2] - k_{3,r}[N][OH] - k_{1,l}[NO][N] \\ & + k_{2,l}[NO][O] + k_{3,l}[NO][H] = 2k_{1,r}[O][N_2] - 2k_{1,l}[NO][N] \end{aligned}$$

$$\text{Therefore } \frac{d[NO]}{dt} \approx \frac{d[NO]}{dt} + \frac{d[N]}{dt} = 2k_{1,r}[O][N_2] - 2k_{1,l}[NO][N] \quad (6.7)$$

For the unknown concentration of nitrogen atoms [N], it can be obtained via the transformation of equation (4.5) under observance of equation (4.6)

$$[N] = \frac{k_{1,r}[O][N_2] + k_{2,l}[NO][O] + k_{3,l}[NO][H]}{k_{1,l}[NO] + k_{2,r}[O_2] + k_{3,r}[OH]} \quad (6.8)$$

From the Equation(6.8), besides the concentration of NO, only the easily determined concentration of N_2 and the concentrations O, O_2 , OH, and H of the OHC system. The OHC system can be described by the following equation system.

$$H_2 = 2H \quad (6.9)$$

$$O_2 = 2O \quad (6.10)$$

$$H_2O = \frac{1}{2}H_2 + OH \quad (6.11)$$

$$H_2O = \frac{1}{2}O_2 + H_2 \quad (6.12)$$

$$CO_2 = CO + \frac{1}{2}O_2 \quad (6.13)$$

The five reactions (6.9) to (6.13) proceed very fast compared with the reactions of the Zeldovich mechanism (6.1) to (6.3) at burned temperatures during the combustion.

Thus, for a simplified estimation of nitrogen oxide formation, the reverse reactions can be neglected at first and OHC system is ignored. Equation (6.7) is then simplified to

$$\frac{d[NO]}{dt} = 2k_{1,r}[O][N_2] \quad (6.14)$$

Then the main problem is determining the O atom concentration(Merker, G., 2005).

6.2.2 Determining O radical concentration

For reaction $O_2 \rightleftharpoons O + O$

The partial pressure equilibrium is expressed as

$$K_p = \frac{\left(\frac{n_O}{n_t} \cdot p\right)^2}{\frac{n_{O_2}}{n_t} \cdot p} \quad (6.15)$$

The unit of K_p is pressure.

And the equilibrium constant K_c is expressed as

$$K_c = \frac{[O][O]}{[O_2]} = \frac{\left(\frac{n_o}{V}\right) \cdot \left(\frac{n_o}{V}\right)}{\left(\frac{O_2}{V}\right)} \quad (6.16)$$

Based on ideal gas law $pV = nRT$

$$\text{Then } p = \frac{nRT}{V} \quad (6.17)$$

Applying Eq(5.15) into Eq(5.17), then the equation of K_p in relation to K_c is obtained:

$$K_p = \frac{\left(\frac{n_o}{n_t} \cdot p\right)^2}{\frac{n_{O_2}}{n_t} \cdot p} = \frac{\left(\frac{n_o}{n_t} \cdot \frac{n_t RT}{V}\right)^2}{\frac{n_{O_2}}{n_t} \cdot \frac{n_t RT}{V}} = \frac{\left(\frac{n_o}{V}\right)^2 \cdot RT}{\frac{n_{O_2}}{V}} = K_c \cdot RT \quad (6.18)$$

Meanwhile K_p is calculated by Gibbs function, which is

$$K_p = \exp\left(-\frac{\Delta G}{RT}\right) \quad (6.19)$$

Where $\Delta G = 2\Delta G_O^\circ - \Delta G_{O_2}^\circ$ is in kJ/mol ;

$$R = 8314 J / kmol \cdot K$$

T is in kelvin.

$$\text{Therefore } K_c = \frac{K_p}{RT} = \frac{\exp\left(-\frac{\Delta G \times 10^6}{RT}\right)}{RT} \quad (6.20)$$

From the eq(6.15), the unit of K_p is atm, and from eq(6.16) the unit of K_c is $kmol/m^3$.

From ideal gas law $pV = nRT$,

$$R = \frac{P(pa)V(m^3)}{n(kmol)T(K)} = 8314 J / kmol \cdot K$$

$$K_c = \frac{K_p}{RT} = \frac{\exp\left(-\frac{\Delta G \times 10^6}{RT}\right)(atm)}{R(J / kmol \cdot K) \times T(K)} = K_c \left(\frac{kmol}{m^3}\right) \quad (6.21)$$

From Eq(6.16), the concentration of O radical is then determined by

$$[O]^2 = [O_2] \cdot K_c \Rightarrow [O] = [O_2]^{\frac{1}{2}} \times K_c^{\frac{1}{2}}$$

For calculating O atom concentration for a range of temperature, there are 3 methods of determining $K_c^{\frac{1}{2}}$ (only depending on temperature) discussed in this part.

Method 1: polynomial equation

For example at 2000K, the free energy of O and O_2 are 121.709 kJ/mol and 0 J/kmol respectively, then the total free energy is

$$\Delta G = 2\Delta G_O^\circ - \Delta G_{O_2}^\circ = 2 \times 121.709 - 0 = 243.418 \text{ kJ/mol}$$

Then the partial equilibrium constant is calculated by

$$K_p = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{243.418 \times 10^6}{8314 \times 2000}\right) = 4.38879E-07 \text{ atm}$$

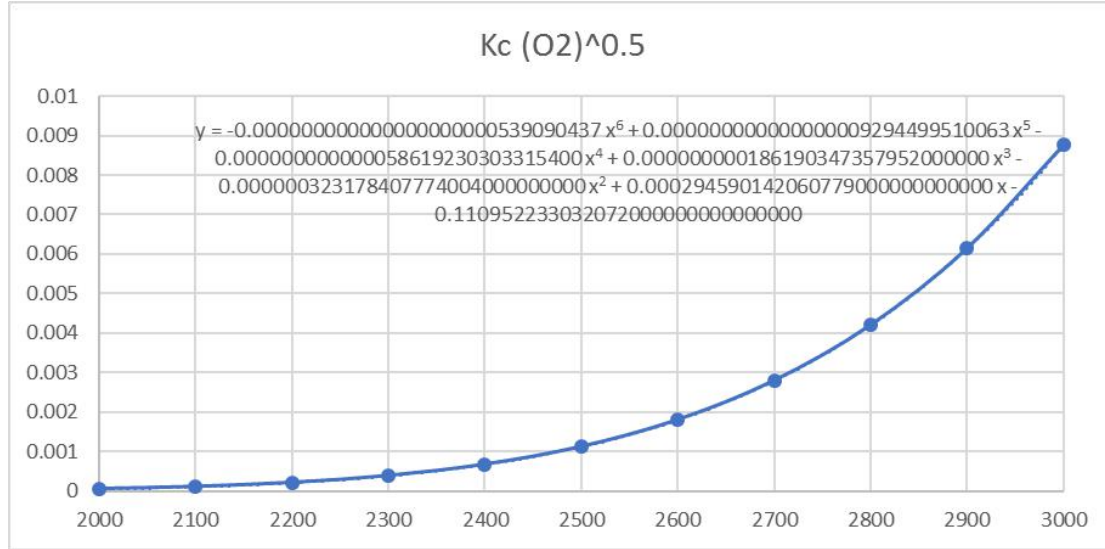
Therefore $K_c = \frac{K_p}{RT} = \frac{(4.38879E-07) \times 101325 \text{ pa}}{8314 \text{ J/kmol} \cdot K \times 2000 \text{ K}} = 2.67442E-09$

Then the equilibrium constants are calculated from 2000K to 3000K, which are presented in Table 1.

Table 6.1 Equilibrium constants from 2000K to 3000K

Kp=Kc*RT						
	Gibbs free energy		G total			
T	O	O2	O2=O+O	Kp(O2)	Kc (O2)	Kc (O2) ^0.5
2000	121.709	0	243.418	4.38879E-07	2.67442E-09	5.17E-05
2100	115.023	0	230.046	1.89545E-06	1.15504E-08	0.000107
2200	108.329	0	216.658	7.17298E-06	4.37103E-08	0.000209
2300	101.627	0	203.254	2.41986E-05	1.4746E-07	0.000384
2400	94.918	0	189.836	7.38206E-05	4.49845E-07	0.000671
2500	88.203	0	176.406	0.000206094	1.25589E-06	0.001121
2600	81.483	0	162.966	0.00053193	3.24145E-06	0.0018
2700	74.757	0	149.514	0.001280482	7.80293E-06	0.002793
2800	68.027	0	136.054	0.002895942	1.76471E-05	0.004201
2900	61.292	0	122.584	0.006193612	3.77423E-05	0.006143
3000	54.554	0	109.108	0.012594831	7.67498E-05	0.008761

Plot the graph of $K_c(O_2)^{0.5}$ VS T.



From the graph, the polynomial equation of $K_c(O_2)^{0.5}$ in relation to the temperature is shown as

$$K_c(O_2)^{0.5} = -0.0000000000000000053909043 \cdot T^6 + 0.00000000000000009294499510063 \cdot T^5 - 0.000000000000058619230303315400 \cdot T^4 + 0.000000000186190347357952000000 \cdot T^3 - 0.000000323178407774004000000000 \cdot T^2 + 0.000294590142060779000000000000 \cdot T - 0.110952233032072000000000000000$$

Therefore the equation of O atom concentration is expressed as:

$$[O] = [O_2]^{\frac{1}{2}} \times K_c^{\frac{1}{2}} = -0.0000000000000000053909043 \cdot T^6 + 0.00000000000000009294499510063 \cdot T^5 - 0.000000000000058619230303315400 \cdot T^4 + 0.000000000186190347357952000000 \cdot T^3 - 0.000000323178407774004000000000 \cdot T^2 + 0.000294590142060779000000000000 \cdot T - 0.110952233032072000000000000000 \cdot [O_2]^{\frac{1}{2}}$$

Method 2: Bockhorn equation: $[O] = 130[O_2]^{1/2} \exp\left\{-\frac{29468}{T}\right\}$

At 2000K, the partial pressure equilibrium constant is calculated by

$$K_p = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{243.418 \times 10^6}{8314 \times 2000}\right) = \exp\left(\frac{29278.09}{2000}\right)(atm)$$

From eq(7), there is

$$K_c = \frac{K_p}{RT} = \frac{\exp\left(-\frac{\Delta G \times 10^3}{RT}\right) \times 101325 \text{ pa}}{8314 \text{ J/kmol} \cdot K \times T(K)}$$

Then

$$K_c = \frac{K_p}{RT} = \frac{\exp(-\frac{29278.09}{2000}) \times 101325 \text{ pa}}{8314 \text{ J/kmol} \cdot \text{K} \times 2000 \text{ K}} = \frac{12.1875}{2000} \times \exp(-\frac{29278.09}{2000})$$

Therefore a general equation of K_c in relation to temperature T is described :

$$K_c = \frac{12.1875}{T} \times \exp(-\frac{\Delta G \times 10^6 / 8314}{T}) \quad (6.22)$$

And

$$\begin{aligned} K_c^{1/2} &= [\frac{12.1875}{T} \times \exp(-\frac{\Delta G \times 10^6 / 8314}{T})]^{1/2} = 3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 500000 / 8314}{T}) \\ &= 3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14}{T}) \end{aligned} \quad (6.23)$$

To make up a “ $\exp(-\frac{29468}{T})$ ” in equation (6.23)

$$\begin{aligned} K_c^{1/2} &= 3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14}{T}) \times \frac{\exp(-\frac{29468}{T})}{\exp(-\frac{29468}{T})} \\ &= 3.491 \times T^{-1/2} \times \frac{\exp(-\frac{\Delta G \times 60.14}{T})}{\exp(-\frac{29468}{T})} \times \exp(-\frac{29468}{T}) \\ &= 3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14}{T} + \frac{29468}{T}) \times \exp(-\frac{29468}{T}) \\ &= 3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14 + 29468}{T}) \times \exp(-\frac{29468}{T}) \end{aligned} \quad (6.24)$$

The part of $3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14 + 29468}{T})$ is calculated from 2000K to 3000K, and results are generated in Table 2.

Table 6.2 $3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14 + 29468}{T})$

T	$3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14 + 29468}{T})$
2000	129.571506
2100	130.2835174
2200	130.8497328
2300	131.2939862

2400	131.6294334
2500	131.8669271
2600	132.0154718
2700	132.0943488
2800	132.1029273
2900	132.0569562
3000	131.9540713

From table 6.2, the part of $3.491 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14 + 29468}{T})$ can be roughly approximated as 130, then we obtain the equation of O atom concentration according to Bockhorn (1997):

$$[O] = 130[O_2]^{1/2} \exp\{-\frac{29468}{T}\}$$

(Merker, G., 2005)

Method 3: Westenberg equation: $[O] = 3.97 \times 10^5 [O_2]^{1/2} \exp\{-\frac{31090}{T}\}$

From eq(6.21), $K_c (kmol / m^3)$ is expressed as:

$$K_c (\frac{kmol}{m^3}) = \frac{\exp(-\frac{\Delta G \times 10^6}{RT}) atm}{R \times T(K)}$$

Then $K_c (mol / m^3)$ is written as

$$K_c (\frac{mol}{m^3}) = K_c (\frac{kmol}{m^3}) \times 10^3 = \frac{\exp(-\frac{\Delta G \times 10^6}{RT}) \times 101325 pa}{8314 J / kmol \cdot K \times T(K)} \times 1000 \quad (6.25)$$

And $K_c (mol / m^3)^{1/2}$ is changed based on eq(6.25)

$$\begin{aligned} K_c^{1/2} &= [1000 \times \frac{12.1875}{T} \times \exp(-\frac{\Delta G \times 10^6 / 8314}{T})]^{1/2} = 110.395 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 500000 / 8314}{T}) \\ &= 110.395 \times T^{-1/2} \times \exp(-\frac{\Delta G \times 60.14}{T}) \end{aligned}$$

To make up a “ $\exp(-\frac{31090}{T})$ ” in above equation

$$\begin{aligned}
K_c (mol/m^3)^{1/2} &= 110.395 \times T^{-1/2} \times \exp\left(-\frac{\Delta G \times 60.14}{T}\right) \times \frac{\exp\left(-\frac{31090}{T}\right)}{\exp\left(-\frac{31090}{T}\right)} \\
&= 110.395 \times T^{-1/2} \times \exp\left(\frac{-\Delta G \times 60.14}{T} + \frac{31090}{T}\right) \times \exp\left(-\frac{31090}{T}\right) \\
&= 110.395 \times T^{-1/2} \times \exp\left(\frac{-\Delta G \times 60.14 + 31090}{T}\right) \times \exp\left(-\frac{31090}{T}\right)
\end{aligned}
\tag{6.26}$$

The part of $110.395 \times \exp\left(-\frac{\Delta G \times 60.14 + 31090}{T}\right)$ is calculated from 2000K to 3000K, and results are generated in Table 6.3.

Table 6.3 $110.395 \times \exp\left(-\frac{\Delta G \times 60.14 + 31090}{T}\right)$

T(K)	$110.395 \times \exp\left(-\frac{\Delta G \times 60.14 + 31090}{T}\right)$
2000	412322.78
2100	408733.1931
2200	405674.4516
2300	403070.277
2400	400838.4
2500	398911.1267
2600	397232.2024
2700	395789.7192
2800	394522.7451
2900	393428.3744
3000	392456.9023

From table 6.3, the part of $110.395 \times \exp\left(-\frac{\Delta G \times 60.14 + 31090}{T}\right)$ can be averaged as 397000, then the equation of O atom concentration according to Westenberg is achieved:

$$[O] = 3.97 \times 10^5 \times T^{-1/2} [O_2]^{1/2} \exp\left\{-\frac{31090}{T}\right\} \text{ gmol} / m^3.$$

6.2.3 NO formation rates

The rate constants for the Extended-Zeldovich mechanism have been measured in plenty of experimental studies. Table 6.4 presents three published speed coefficients for the first forward reactions of extended-Zeldovich mechanism. .

Table 6.4 Speed coefficients for the forward reactions of the extended-Zeldovich mechanism

Reaction i	$k_{i,r} [cm^3 / mol \cdot s]$	Author
1	$1.8 \times 10^{14} \exp[-\frac{38370}{T}]$	Baulch et al. (1991)
	$0.544 \times 10^{14} T^{0.1} \exp[-\frac{38020}{T}]$	GRI-MECH 3.0 (2000)
	$0.76 \times 10^{14} \exp[-\frac{38000}{T}]$	Heywood (1998)
2	$6.4 \times 10^9 T \exp[-\frac{3150}{T}]$	Baulch et al. (1991)
	$9.0 \times 10^9 T \exp[-\frac{3280}{T}]$	GRI-MECH 3.0 (2000)
	$1.48 \times 10^8 T^{1.5} \exp[-\frac{2860}{T}]$	Heywood (1998)
3	3.0×10^{13}	Baulch et al. (1991)
	$3.36 \times 10^{13} \exp[-\frac{195}{T}]$	GRI-MECH 3.0 (2000)
	4.1×10^{13}	Heywood (1998)

(Merker, G., 2005)

In this report, the NO model uses the speed coefficient of the first forward reaction from Baulch et al.(1991)

$$k_r = 1.8 \times 10^{14} \exp[-\frac{38370}{T}] cm^3 / mol \cdot s$$

Change the unit into $m^3 / kmol \cdot s$, thus $k_r = 1.8 \times 10^{11} \exp[-\frac{38370}{T}] m^3 kmol \cdot s$

6.3 NOx calculation

A simplified estimation of nitrogen oxide formation is calculated by

$$\frac{d[NO]}{dt} = 2k_{1,r}[O][N_2]$$

$$\text{Where } k_r = 1.8 \times 10^{11} \exp[-\frac{38370}{T}] m^3 kmol \cdot s$$

And in this report, Bockhorn equation is used to determine [O]:

$$[O] = 130[O_2]^{1/2} \exp\{-\frac{29468}{T}\}$$

Therefore the NO formation rate is equal to

$$\frac{d[NO]}{dt} = 4.7 \times 10^{13} \cdot [N_2][O_2]^{0.5} \cdot \exp\left(-\frac{67837}{T}\right)$$

From this equation, the NOx formation rate shows a strong dependency on the burned temperature, and it is also reliant on the concentration of O_2 and N_2 .

For one cylinder sucking, the real combustion equation is multiplied both sides by α , which is expressed as:

$$\alpha[\phi C_{8.26}H_{15.5} + 12.5(O_2 + 3.76N_2)] = \alpha[n_1CO_2 + n_2H_2O + n_3CO + n_4H_2 + n_5O_2 + n_6N_2]$$

Then the fuel mass in cylinder can be calculated by:

$$m_{fuel} = a \cdot \phi C_{8.26}H_{15.5} = a \cdot \phi(8.26 \times 12 + 15.5) \quad (6.27)$$

Since fuel mass provided for each rpm is given by measured engine data, then the fuel mass for each cylinder and one cycle is equal to:

$$m_{fuel-1} = \frac{m_{fuel}}{RPM \times 60 \times 1.5} \quad (6.28)$$

Combining the eq(6.27) and eq(6.28), therefore the a is obtained by:

$$a = \frac{m_{fuel}}{RPM \times 60 \times 1.5} \div [\phi \times (8.26 \times 12 + 15.5)]$$

Then $[N_2]$ and $[O_2]$ concentration are calculated by:

$$[N_2] = \frac{a \cdot MFB \cdot N_2}{V_b} \text{ kmol} / m^3$$

$$[O_2] = \frac{a \cdot MFB \cdot O_2}{V_b} \text{ kmol} / m^3$$

Applying $[N_2]$ and $[O_2]$ to the extended-Zeldovich model to predict the NOx concentration levels.

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

$$\text{Time for } 1^\circ \text{ is } \frac{1}{360} \times \frac{60}{rpm} = \frac{1}{6rpm} \text{ sec}$$

$$\frac{d[NO]}{dQ} = \frac{d[NO]}{dt} \times \frac{1}{6 \times rpm} = \frac{d[NO]}{dt} \times \frac{1}{6 \times RPM}$$

And the kmols of NOx for each degree is

$$NO = \frac{d[NO]}{dQ} \times V_b \text{ m}^3$$

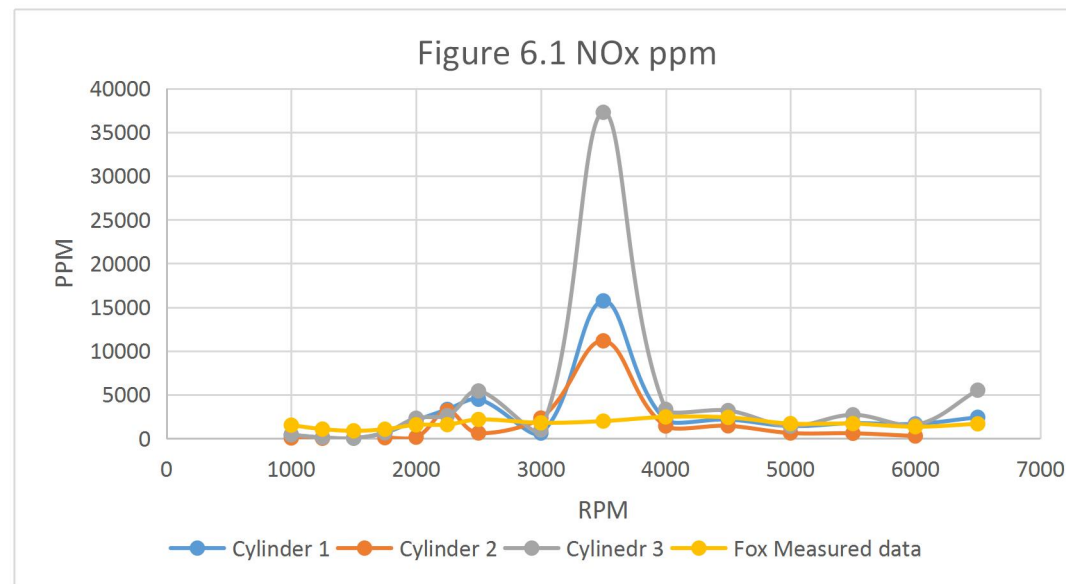
The sum of NO for each degree from SOC to EOC then is equal to $\sum_{SOC-EOC} NO$.

Therefore the total NOx produced in parts per million (PPM) is

$$PPM = \frac{\sum_{SOC \rightarrow EOC} V_{d[NO]} \frac{dQ}{dQ}}{\alpha \times n_t} \times 10^6$$

6.4 NOx prediction results

The figure 6.1 shows the predicted NOx level of three cylinders and the measured Fox data.



From the graph, generally, comparing three cylinders, cylinder 3 and cylinder 2 predict the highest and lowest NOx level respectively, and the predicted NOx level of cylinder 2 is relatively closer to the measured data. Comparing the predicted NOx level with measured NOx data, when running slightly lean at low rpm this model is under predicting while when running rich at high rpm, the model is over predicting. Besides there is an abnormal rise at 3500 rpm for all cylinders. For investigating the reason for a high NOx level at 3500rpm and adjusting predicted NOx level to be closer to the measured data, the NO model sensitivity analysis is implemented.

6.5 NO model sensitivity analysis

Based on the NO predicted equation $\frac{d[NO]}{dt} = 2k_{1,r}[O][N_2]$, then the NO model sensitivity analysis is based on the five parts:

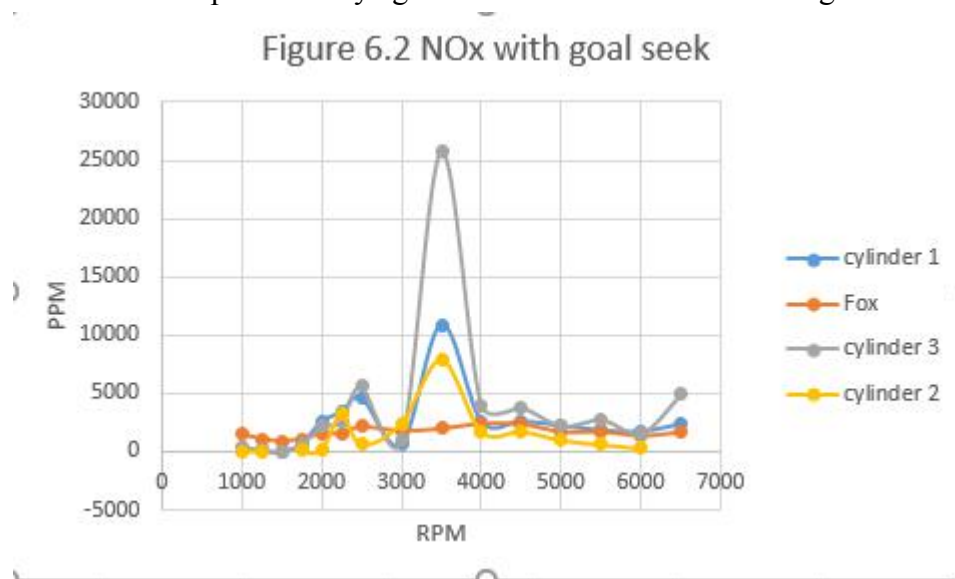
- $n_5(O_2)$ calculation method
- different $[O]$ concentration method
- different first forward speed
- different lambda

- burned temperature, which includes polytropic index and MFB sensitivity analysis.

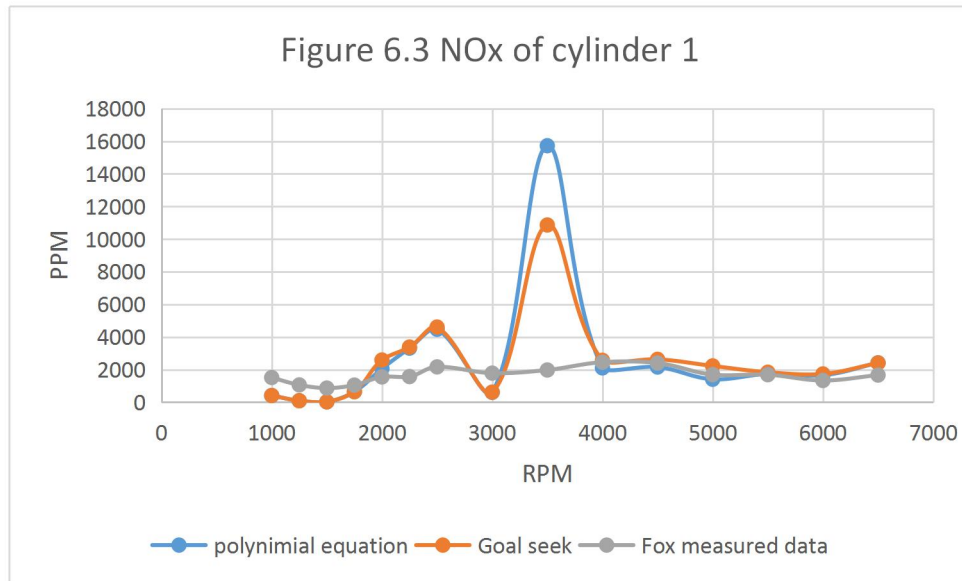
6.5.1 $n_5(O_2)$ calculation method

In chapter 5, the O_2 produced during combustion is calculated based on the polynomial equations. But considering the O_2 produced per degree is a quite small value, the polynomial equation may not accurate enough, and the error caused by this method probably influence the NOx prediction results. Therefore the method of using goal seek to calculate $n_5(O_2)$ per degree during combustion is implemented.

The NOx level predicted by “goal seek” method is shown in Figure 6.2.



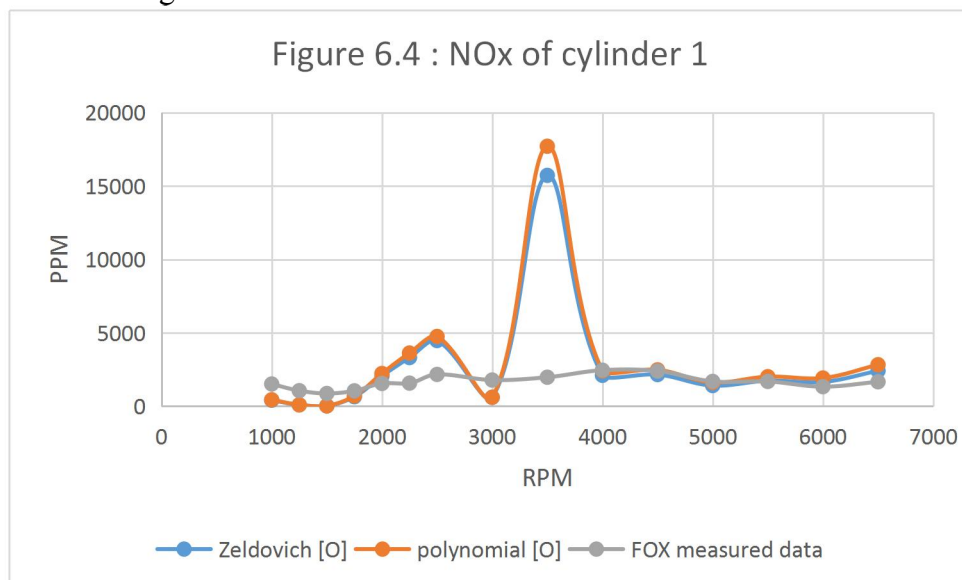
Similarly from the figure, the NOx emission level of cylinder 1 is the closest to the measured data, then Figure 6.3 shows the NOx prediction results of cylinder 1 using polynomial equation method and goal seek method respectively.



From the graph, the NOx level predicted from polynomial equation and goal seek are quite similar for most RPM, but at 3500rpm, the goal seek method predicts a lower NOx emission. Therefore using goal seek method can help reduce the NOx level at 3500rpm.

6.5.2 Different [O] concentration method

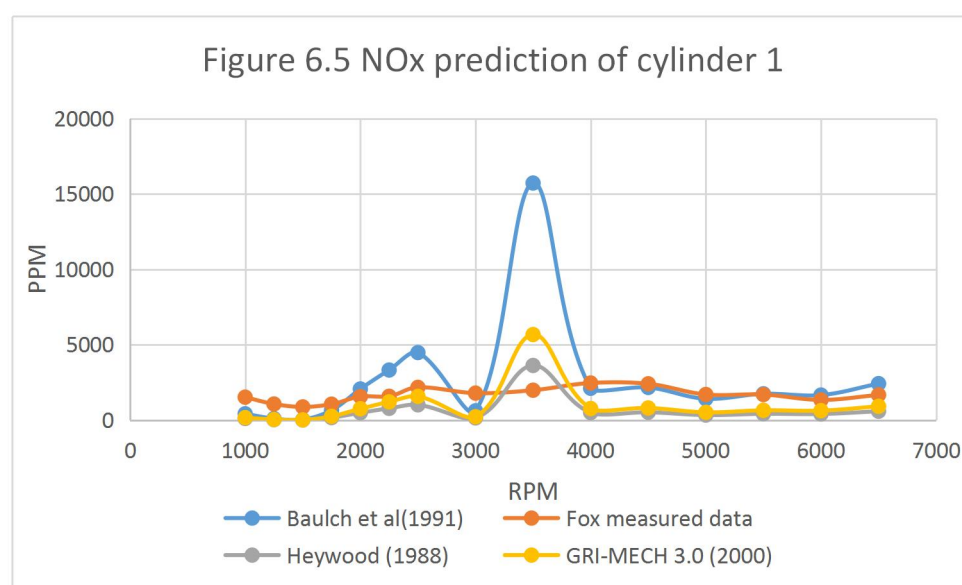
The polynomial method of [O] is applied for NOx prediction, and the results are shown in Figure 6.4.



The results of NOx predicted using polynomial equation of [O] is very close to the predicted NOx level using Bockhorn equation, but at 3500rpm it predicts a higher NOx emission at 3500rpm, Therefore for the Fox engine NOx prediction, the [O] according to Bockhorn is better than the polynomial equation of [O].

6.5.3 Different first forward speed

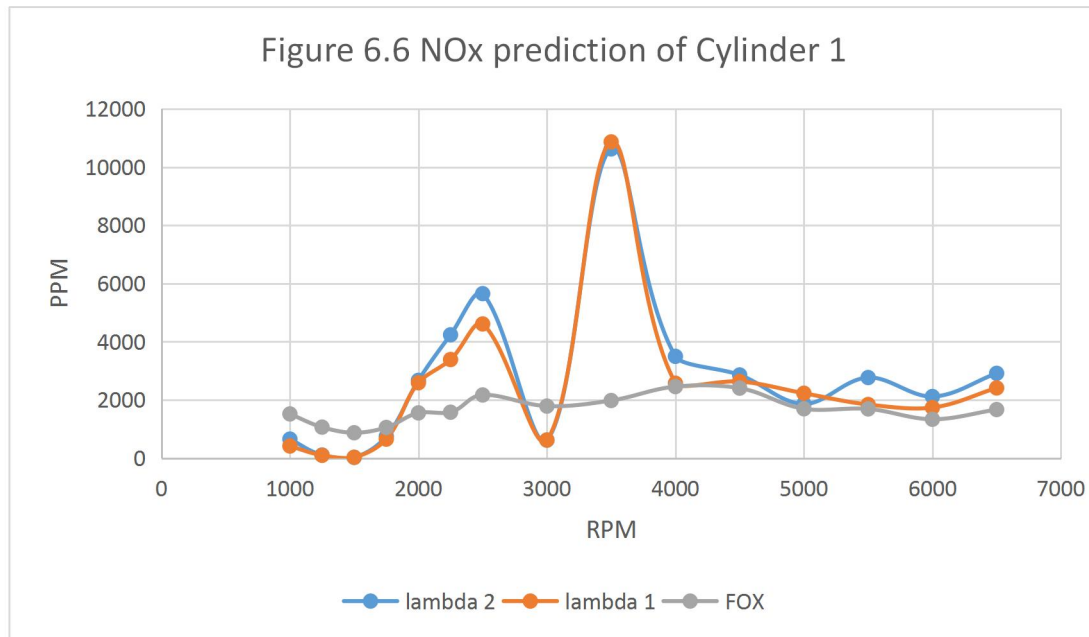
There are different published speed coefficients for the forward reaction of extended Zeldovich mechanisms. This current NO model uses rate coefficients from Baulch (1991). For comparison of NO prediction with another speed coefficient, 2 different speed coefficients collected in table 6.4 are used to predict NOx. NOx emissions with different rate are shown in the Figure 6.5.



From the figure, it is obvious that the speed coefficient used from Baulch predicts the highest NOx, and the rate coefficient of Heywood has the lowest NOx level. Comparing three predicted NOx levels with Fox measured data, the current model with the speed coefficient from Baulch shows a better performance on NOx prediction. The Heywood forward speed coefficient can be used at 3500rpm to lower the predicted NOx level.

6.5.5 Different lambda data

The Ford company provides two measured lambda data, the current NO model uses the lambda 1. The figure 6.6 shows the NOx prediction of cylinder 1 with different lambda data.



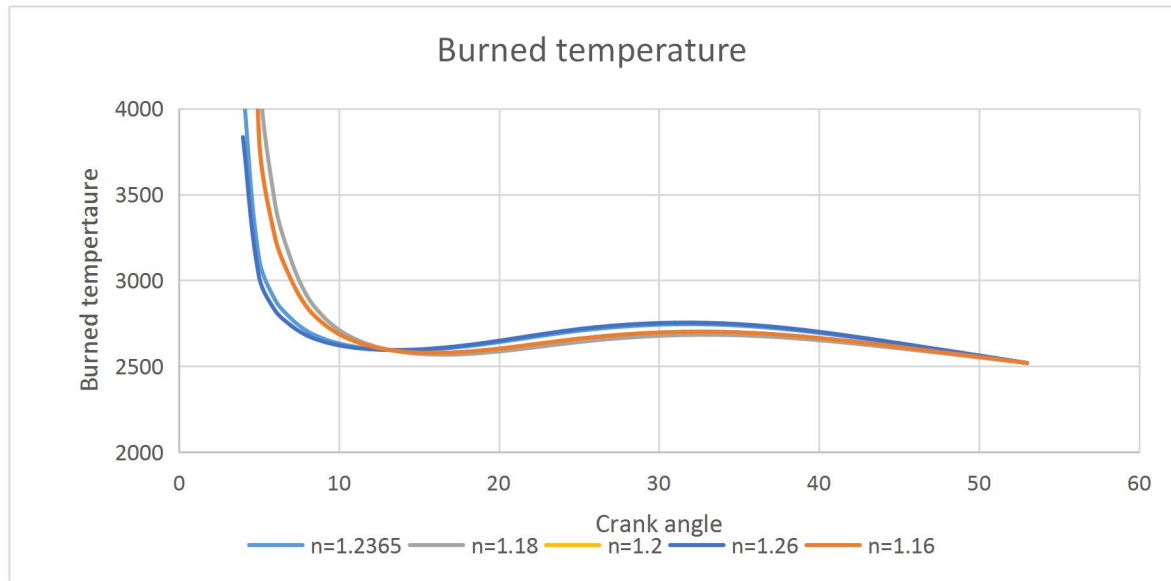
From the graph, since the two lambda data provided are close, then the results of NO_x prediction are close as well, and 3500rpm, there still is a peak.

6.5.5 Burned temperature sensitivity analysis

At 3500rpm, the current NO predicts a extremely high NO_x emission value, which is probably due to the high burned temperatures during combustion. The burned temperature sensitivity analysis is discussed by adjusting polytropic index and trying different MFB method.

6.5.5.1 Polytropic index sensitivity analysis

For 3500rpm, the expansion polytropic index used is 1.2365, the polytropic index at SOC is 1.15, then the polytropic index 1.16, 1.18, 1.2, 1.26 are used for the sensitivity analysis. The burned temperature calculated from different polytropic index is shown in the Figure 6.9.



From the graph, the burned temperature decreases with the a smaller polytropic index. The NO_x prediction results with different polytropic index are generated in table 6.5.

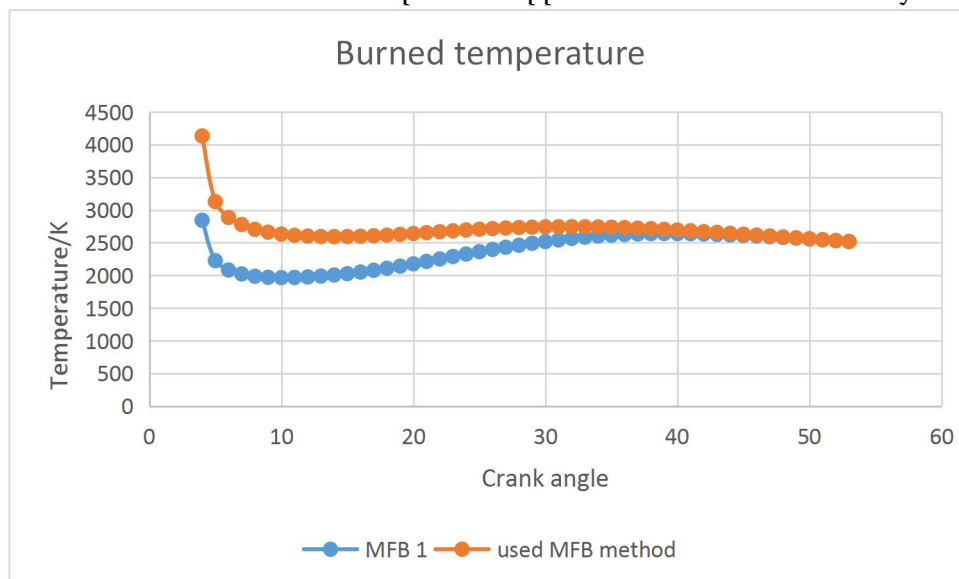
Table 6.5 NO_x results with different polytropic index

Current model: $n=1.2365$, NO _x = 15724.88ppm			
$n=1.16$	7485.312ppm	$n=1.18$	8898.33ppm
$n=1.2$	10536.94ppm	$n=1.26$	17080ppm

From the table, the NO_x level is higher with a big polytropic index, thus modifying the polytropic index can help lower the NO_x level at 3500rpm.

6.5.4.2 MFB sensitivity analysis

The method 1 discussed in chapter 4 is applied for the MFB sensitivity analysis.



From the graph, it is obvious that the burned temperature calculated from MFB

method 1 is much lower than that from method2. The NO_x prediction with method 1 is 4932ppm, which is near twice of the measured data (1979ppm). The method 1 is not applied for the burned temperature calculation because it predicts a much lower burned temperature, which is even lower than 2000K during combustion.

6.6 NO model limitations

The current NO model predicts NO using cylinder pressure data based on 2-zone combustion model and extended-Zeldovich mechanism. Then the limitations of NO is based on the 3 parts: cylinder pressure data analysis; 2-zone combustion model; extended-Zeldovich mechanism.

6.6.1 1-zone combustion model limitation

2-zone combustion model assumes there is only one burned zone. In reality, there are more than one burned zone in cylinder because of the temperature gradient which is established in the burned mixture due to the consecutive nature of combustion. Generally temperature difference of about 100-200K is reported between the first and last burned regions, the first burned attaining the highest temperature(Chindaprasert, N., 2007).

6.6.2 Cylinder pressure data analysis limitations

A. Pressure data problem

- For 3 cylinders, especially for cylinder 2, the polytropic varies each degree, which is difficult to determine the compression and expansion polytropic index.
- The minimal provided pressure data is one degree, which cannot accurately determine the SOC and EOC.

B. MFB

3 methods based on Rassweiler and Withrow model needs the polytropic index, thus the polytropic index problem will influence the MFB and then have an effect on the burned temperature and NO_x prediction.

The Wiebe function doesn't require the polytropic index, but it needs the CAD (or other computation technologies) to model the graph of MFB m and a for each cycle, which is too complicated.

C. Burned temperature

The burned temperature will be influence by the MFB, burned volume. Since at the beginning of combustion, the MFB is near zero which will cause a big burned temperature. Unreasonable burned temperatures are not used for the NO_x calculation, which may be the reason for under predicting at low RPM.

6.6.3 Extended-Zeldovich mechanism limitation

A. Ignoring the reverse reaction

This mechanism considers the first forward reaction of NO formation, while in fact, no matter how minimal the reverse reactions of (6.1) to (6.3) are, they slow down the actual NO production and can even lead to a minor reduction of NO concentrations towards the end of the working cycle(Merker, G., 2005).

B. First forward reaction speed

For different engine speed and operating conditions, the first forward reaction speed uses the same equation, which only depends on the temperature. However studies have shown that pressure effect on the reaction speed is important(Drake, M. C., & Blint, R. J, 1991). An empirical parametric variation of R1 is introduced which incorporates the influence of pressure.

The modification of the rate limiting reaction R1 presents as follows:

$$K_f = C_p \cdot 1.8 \times 10^{14} \exp(-38370/T)$$

Where P is the in-cylinder pressure, C_p varies from 0.2 to 1, which depends on cylinder pressure.

$$C_P = \begin{cases} 1.00 & P < 15 \\ 0.70 & 15 < P < 20 \\ 0.48 & 20 < P < 25 \\ 0.31 & 25 < P < 30 \\ 0.25 & 30 < P < 35 \\ 0.20 & P > 35 \end{cases}$$

(Miller, R., 1998)

7. Conclusion

This report mainly includes 3 parts. Two-zone thermodynamic model, cylinder pressure data analysis and extended-Zeldovich mechanism.

For the two zone-combustion model, the thermodynamic states and properties of unburned and burned zones are discussed and calculated from the first law of thermodynamics. The cylinder pressure data analysis based on two-zone combustion model focuses on the SOC, MFB, and burned temperatures. The SOC is determined

by a combined method considering the polytropic index varies during compression and expansion processes and the extra pressure problem at SOC is investigated. Different MFB methods are introduced and discussed, and the method 2 is applied for the following calculations. The burned temperature has an important influence on NO formation, which is also a vital part of NO sensitivity analysis.

For the NO prediction, the extended-Zeldovich mechanism is introduced and applied. The predicted NO_x level is close to the measured data. Generally at low rpm when running lean this model is a little under predicting and when running rich at high rpm, it is kind of over predicting. But at 3500 rpm, it predicts a much higher NO_x emission. Then NO model sensitivity is implemented and methods of lowering the NO_x level at 3500rpm are concluded as follows:

- using goal seek method to calculate n_5 ;
- using the first forward reaction speed from Heywood;
- employing a smaller polytropic index;
- only using the extra pressure to calculate MFB.

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Appendix A Chemical equilibrium

ants A_a , A_b , etc, which form the products A_c , A_d , etc. can be described as follows

A chemical reaction between the react



Where v_i designate the so-called stoichiometric coefficients of the reaction. As each chemical reaction can run both forwards and backwards in principle, the reaction arrow in (1) can be replaced with an equal sign. Then the general form of the reaction equation is obtained by:

$$\sum_i v_i A_i = 0,$$

Where v_i are conventionally negative for all educts and positive for all products.

Every chemical reaction strives towards reaching its state of equilibrium when sufficient time is available. This state of equilibrium can be interpreted as a situation, in which both the forward and reverse reactions progresses with identical speed. The microscopically visible reaction rate is thus reduced to zero, and the material composition no longer changes. This material composition in the state of equilibrium can be determined from both laws of thermodynamics.

For a closed, compressible system with constant temperature and constant pressure, the first and second laws of thermodynamics read as follows

$$dU = dQ + dW = dQ - pdV \quad (2)$$

$$dS = \frac{dQ}{T} + dS_{irr} \quad (3)$$

dS_{irr} designates the increase of entropy due to irreversibilities, which is always greater than or equal to zero. Combining (2) and (3), there is:

$$TdS - dU - pdV \geq 0 \quad (4)$$

The Gibbs free energy G is expressed as

$$G = H - TS = U + pV - TS \quad (5)$$

After differentiation and corresponding conversion

$$dG - Vdp + SdT \leq 0 \quad (6)$$

For a closed system with constant temperature and constant pressure, the dissipation of Gibbs free energy is always less or equal to zero, which means that every alteration of the composition through chemical reactions reduces the value of G and that the condition

$$dG|_{r,p} = 0 \quad (7)$$

is satisfied in chemical equilibrium.

For a combustible mixture, the Gibbs free energy is a function of temperature, pressure and compositions,

$$G = G(T, p, n_1, n_2, n_3, \dots) \quad (8)$$

Where n_i represents the number of moles of the various species i .

μ_i is the chemical potential, which is defined as the partial derivative of the Gibbs free energy with respect to the number of moles of i ,

$$\mu_i = \left. \frac{\partial G}{\partial n_i} \right|_{T,p,n_j, j \neq i} \quad (9)$$

From the equation, it can be shown that for an ideal gas - and this is an acceptable assumption for most combustible gases - the chemical potential is identical to the molar Gibbs function (Moran and Shapiro, 1992).

$$\mu_i = \tilde{g}_i(T, p_i) = \tilde{g}_i^o + \tilde{R}T \ln \frac{p_i}{p^o} \quad (10)$$

The index “ ^{o} ” represents the condition under a reference pressure of 1 atm. The first term on the right side of the equation (10) stands for

$$\tilde{g}_i^o = \tilde{h}_i(T) - T\tilde{s}_i^o(T) \quad (11)$$

$$\text{Where } \tilde{h}_i(T) = \tilde{h}_{f,i}^o + \Delta \tilde{h}_i(T) \quad (12)$$

If the chemical potential introduced in (9) is inserted into the condition of equilibrium (6), then form of dG is obtained by:

$$dG|_{T,p} = \sum_i \mu_i dn_i = 0 \quad (13)$$

However, for a general chemical reaction corresponding to (2), changes in the material quantities dn_i are proportional to the corresponding stoichiometric

coefficients, so that the equation

$$dn_i = v_i d\varepsilon \quad (14)$$

With the proportionality factor $d\varepsilon$ is satisfied for all components i . The equation (14) can thus be simplified to the form

$$\sum_i \mu_i v_i = 0 \quad (15)$$

It then contains all the necessary information regarding the equilibrium composition. However, the solution of (15) according to the various species concentrations is only iteratively possible and thus very costly. In order to avoid this problem, the concept of equilibrium constant is introduced. Through the insertion of (11) into (15), we obtain the relation

$$\sum_i v_i \tilde{g}_i^o + RT \ln \prod_i \left(\frac{p_i}{p^o} \right)^{v_i} = 0 \quad (16)$$

Where the logarithmic term corresponds to the equilibrium constant

$$K_p = \prod_i \left(\frac{p_i}{p^o} \right)^{v_i} = 0 \quad (17)$$

The equilibrium constant K_p now contains the information about the equilibrium material composition in terms of the partial pressure p_i of the various species i . As the first term of (16) is exclusively dependent on the temperature, it is evident that the equilibrium constant K_p is also only a function of T . With (17), it follows from

$$\ln K_p = \frac{-\sum_i v_i \tilde{g}_i^o}{\tilde{R}T} = \frac{-\Delta_R \tilde{g}^o}{\tilde{R}T} \quad (18)$$

Where the numerator in (18) is customarily designated as free molar reaction enthalpy (Merker, G., 2005).

Appendix B Heat release model

From the first law of thermodynamics:

$$dQ = m \cdot C_v \cdot dT + p dV \quad (1)$$

Based on ideal gas law. There is

$$pV = mRT \Rightarrow p dV + dpV = mR dT \Rightarrow dT = \frac{p dV + dpV}{mR}; \quad (2)$$

$$\text{Then } dQ = \frac{p dV + dpV}{mR} \cdot mC_v + p dV = \frac{C_v}{R} (p dV + dpV) + p dV \quad (3)$$

According to $C_p = C_v + R \Rightarrow \frac{C_p}{C_v} = \frac{C_v}{C_v} + \frac{R}{C_v} \Rightarrow \gamma = 1 + \frac{R}{C_v} \Rightarrow \frac{C_v}{R} = \frac{1}{\gamma - 1}$ (4)

Applying eq(5) into eq(4):

$$dQ = \frac{pdV + dpV}{\gamma - 1} + pdV = \frac{\gamma pdV + dpV}{\gamma - 1} \quad (5)$$

For compression and expansion processes, the polytropic index model is applied, which is

$$pV^n = C$$

Then we can get:

$$d(pV^n = C) \Rightarrow p \cdot nV^{n-1}dV + V^n dp = 0 \Rightarrow npdV + Vdp = 0 \Rightarrow Vdp = -npdV \quad (6)$$

Substituting eq(6) into eq(5):

$$dQ = \frac{\gamma pdV + dpV}{\gamma - 1} = \frac{\gamma pdV - npdV}{\gamma - 1} = \frac{\gamma - n}{\gamma - 1} pdV$$

Before TDC, the piston moves down, $dV < 0$, for heat loss there is $\gamma < n$;

After TDC, the piston moves up, $dV < 0$, for heat loss there is $\gamma > n$;

Appendix C $PV^\gamma = C$

From the first law of thermodynamics:

$$dQ = dU + PdV \quad (1)$$

For an adiabatic process, $dQ = 0$, then

$$dQ = 0 = dU + PdV \quad (2)$$

Based on ideal gas law, there is $PV = mRT$, then

$$\begin{aligned} dPV + PdV &= mRdT \\ dT &= \frac{dP \cdot V + P \cdot dV}{mR} \end{aligned} \quad (3)$$

Applying eq(3) into the internal energy equation, then we get:

$$dU = m \cdot C_v \cdot dT = m \cdot C_v \cdot \frac{dPV + VdP}{mR} = C_v \cdot \frac{dPV + VdP}{R} \quad (4)$$

$$\text{Therefore: } dQ = 0 = dU + PdV = C_v \cdot \frac{dPV + VdP}{R} + PdV \quad (5)$$

As known that:

$$\gamma = 1 + \frac{R}{C_v} \Rightarrow \gamma - 1 = \frac{R}{C_v} \Rightarrow \frac{1}{\gamma - 1} = \frac{C_v}{R} \quad (6)$$

Applying eq(6) into eq(5), then we have

$$0 = \frac{C_v}{R} \cdot (dPV + PdV) + PdV = \frac{dPV + PdV}{\gamma - 1} + PdV$$

Multiplying $\gamma - 1$ for both sides, then

$$0 = dPV + PdV + PdV(\gamma - 1) = dPV + \gamma PdV$$

Dividing PV for both sides again:

$$\frac{0}{PV} = \frac{dPV}{PV} + \frac{\gamma PdV}{PV} = \frac{dP}{P} + \frac{\gamma dV}{V} = 0$$

$$\int 0 = \int \frac{dP}{P} + \int \gamma \frac{dV}{V}$$

$$C = \ln P + \gamma \ln V \Rightarrow C = \ln P + \ln V^\gamma = \ln PV^\gamma$$

Therefore we get

$$PV^\gamma = \text{constant}$$

Appendix D Unburned temperature during combustion

Assuming the isentropic process for unburned mixture during combustion, then there is: $pV^\gamma = C$ (D.1)

According to the ideal gas law, $pV = mRT \Rightarrow V = \frac{mRT}{p}$ (D.2)

Assuming there is no heat transfer and heat loss to cylinder wall, then there is

$$p_1 V_1^\gamma = p_2 V_2^\gamma \Rightarrow \frac{p_2}{p_1} = \left(\frac{V_1}{V_2} \right)^\gamma \quad (D.3)$$

Applying eq(D.2) into eq(D.3)

$$\frac{p_2}{p_1} = \left(\frac{\frac{mRT_1}{p_1}}{\frac{mRT_2}{p_2}} \right)^\gamma = \left(\frac{p_1}{p_2} \right)^\gamma \left(\frac{T_1}{T_2} \right)^\gamma \Rightarrow \left(\frac{p_2}{p_1} \right)^{1-\gamma} = \left(\frac{T_1}{T_2} \right)^\gamma \quad (D.4)$$

Therefore for T_2 , there is

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} \Rightarrow T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} \quad (D.5)$$

Appendix E Dissociation constants

Table E Standard-based total thermochemical enthalpy levels for gases, kJ/mol.
(derived from JANAF table)

restricted dissociation (Fig. AC4.3).

Temperature, K	$H_f^\circ T = (HT + \Delta H_f^\circ)$ for compounds			$H_f^\circ T = HT$ for elements		
	CO ₂	H ₂ O	CO	H ₂	O ₂	N ₂
298.15	-393.52	-241.83	-110.53	0	0	0
300	-393.46	-241.76	-110.47	0.054	0.054	0.054
500	-385.21	-234.91	-104.60	5.883	6.088	5.912
1000	-360.12	-215.85	-88.843	20.686	22.707	21.460
1500	-331.81	-193.73	-71.680	36.267	40.610	38.405
2000	-302.07	-169.14	-53.790	52.932	59.199	56.141
2100	-296.02	-164.00	-50.154	56.379	62.986	59.748
2200	-289.95	-158.79	-46.509	59.860	66.802	63.371
2300	-283.85	-153.53	-42.853	63.371	70.634	67.007
2400	-277.73	-148.22	-39.183	66.915	74.492	70.651
2500	-271.60	-142.86	-35.505	70.492	78.375	74.312
2700	-259.27	-132.01	-28.121	77.718	86.199	81.659
3000	-240.66	-115.47	-16.987	88.743	98.098	92.738

(Goodger, 2000)

Appendix F Unburned and burned gamma

Appendix F.1 Unburned gamma

The unburned mixture during combustion is assumed to be the reactants, which are fuel ($\phi C_{8.26}H_{15.5}$) and air $12.135(O_2 + 3.76N_2)$. Then the specific heat of unburned mixture is calculated by:

$$C_{p_{unburned}} = \frac{\phi C_p(C_{8.26}H_{15.5}) + 12.135(C_p(O_2) + 3.76C_p(N_2))}{\phi + 12.135(1 + 3.76)}$$

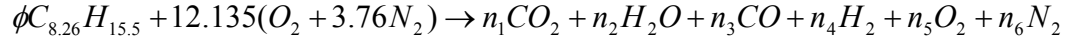
Where for each species i in its standard state at temperature (K), the specific heat

$\tilde{C}_{p,i}$ is approximated by

$$\frac{\tilde{C}_{p,i}}{R} = a_{i1} + a_{i2}T + a_{i3}T^2 + a_{i4}T^3 + a_{i5}T^4$$

Appendix F.2 Burned gamma

For the burned zone, the combustion equation can be expressed as:



The burned mixture during combustion is assumed to be products, which are $n_1CO_2, n_2H_2O, n_3CO, n_4H_2, n_5O_2, n_6N_2$. Then the specific heat of burned mixture is calculated by:

$$C_{p_{burned}} = \frac{n_1C_p(CO_2) + n_2C_p(H_2O) + n_3C_p(CO) + n_4C_p(H_2) + n_5C_p(O_2)}{n_1 + n_2 + n_3 + n_4 + n_5}$$

Where n_1, n_2, n_3, n_4, n_5 are calculated based on burned temperature.

Appendix G MFB - heat release method application

The heat release method calculates MFB by:

$$MFB = \frac{\sum_{soc-\theta} \frac{V\Delta p_c}{\gamma_{av} - 1}}{\sum_{soc-eoc} \frac{V\Delta p_c}{\gamma_{av} - 1}}$$

Where γ_{av} is the average γ_{av} during combustion, $\gamma_{av} = (1 - MFB)\gamma_u + MFB\gamma_b$

The process of using method 3 to calculate MFB is shown as follows:

Step 1: for the first degree of MFB calculation

Considering at the first degree of combustion, the MFB is quite small, then the average gamma can be approximated as the burned gamma

$$\gamma_{av} = (1 - MFB)\gamma_u + MFB\gamma_b \approx \gamma_u \quad \text{for the first degree}$$

$$\text{Therefore } dQ_{1st} = \frac{V_1 \Delta p}{\gamma_u - 1}$$

The $\sum_{soc-eoc} dQ$ is the heat release from fuel burning, then using calorific value of fuel (LHV) to calculate the energy from the fuel.

$$Q_{total} = LHV_{fuel} \cdot M_{fuel}$$

In this case, $LHV_{fuel} \approx 44.3 MJ/kg$

Therefore the first degree of MFB is calculated by

$$MFB = \frac{dQ_{1st}}{Q_{total}}$$

Based on the MFB of the first degree, then the burned volume, burned temperature are calculated, then n_1, n_2, n_3, n_4, n_5 are calculated based on the burned temperature. Therefore burned gamma of the first degree can be calculated.

Step 2: The second degree MFB calculation

Assuming a value of MFB(1), using the burned gamma of the first degree and unburned gamma of the second degree calculate the average gamma, then the MFB(2) is calculated. Using the goal seek to make that MFB(1) is MFB (2), then the correct the MFB can be achieved. Then calculating the burned temperature and n_1, n_2, n_3, n_4, n_5 .

Step 3: repeat the step 2 calculating MFB for all combustion degrees. Adding then together and adjusting 1 to be 1.

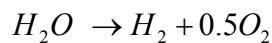
The difficulty of employing this method is the calculated burned temperature at first degree is usually a big value, which is not correct. Then based on the burned temperature, n_1, n_2, n_3, n_4, n_5 are got, and the burned gamma is calculated and applied into the MFB of second degree calculation. The first step cannot get the correct answer then the following steps will be influence.

Appendix H Dissociated specific heat

The investigate the effect of dissociation and specific heat, the dissociation of the burned mixture during combustion can be divided in to parts: dissociation and heating the products.

Firstly consider the enthalpy neede for dissociation:

At 2000K, $CO_2 \rightarrow CO + O_2$



The enthalpy for the dissociation reactions are:

$$H_{CO_2} = 396.808MJ - 118.902 - 0.5 * 0 = 227,906MJ$$

$$H_{H_2O} = 396.808MJ - 118.902 - 0.5 * 0 = 227,906MJ$$

Then the total enthalpy required for dissociation from 2000K to 2100K is equal to

$$H_{2000-2100} = (n_1(2000) - n_1(2100))H_{CO_2} + (n_2(2000) - n_2(2100))H_{H_2O}$$

The heat required at constant pressure to heat the products per kmol by 1 K is:

$$\Delta C_p = \frac{(n_1(2000) - n_1(2100))H_{CO_2} + (n_2(2000) - n_2(2100))H_{H_2O}}{(T_{2100} - T_{2000})n_t}$$

The average specific heat is calculated by

$$C_{p_{av}} = \frac{n_1 C_p(CO_2) + n_2 C_p(H_2O) + n_3 C_p(CO) + n_4 C_p(H_2) + n_5 C_p(O_2) + n_6 C_p(N_2)}{n_t}$$

Then the total specific heat including dissociation and heating products is

$$C_{p-total} = \Delta C_p + C_{p_{average}}$$

Therefore the dissociated gamma is

$$\gamma = \frac{C_{p-total}}{C_v}$$

Step 1: For $\phi = 1, p = 10 \text{ bar}$, using goal seek to get n_1, n_2, n_3, n_4, n_5 .

T/K	n1	n2	n3	n4	n5	n6
1500	8.257554529	7.749111084	0.002445471	0.000888916	0.001667193	45.6276
1600	8.253687252	7.748022561	0.006312748	0.001977439	0.004145093	45.6276
1700	8.236994176	7.746639949	0.023005824	0.003360051	0.013182938	45.6276
1800	8.229610997	7.742487028	0.030389003	0.007512972	0.018950988	45.6276
1900	8.20137134	7.736801929	0.05862866	0.013198071	0.035913366	45.6276
2000	8.154434535	7.728062727	0.105565465	0.021937273	0.063751369	45.6276
2100	8.081030803	7.715212683	0.178969197	0.034787317	0.106878257	45.6276
2200	7.972166935	7.6970225	0.287833065	0.0529775	0.170405283	45.6276
2300	7.818443257	7.672082182	0.441556743	0.077917818	0.25973728	45.6276
2400	7.610954741	7.638797515	0.649045259	0.111202485	0.380123872	45.6276
2500	7.342719837	7.595382402	0.917280163	0.154617598	0.53594888	45.6276
2600	7.01000077	7.539861673	1.24999923	0.210138327	0.730068779	45.6276
2700	6.613673604	7.470063753	1.646326396	0.279936247	0.963131321	45.6276
2800	6.160081687	7.383655001	2.099918313	0.366344999	1.233131656	45.6276
2900	5.661364231	7.278361348	2.598635769	0.471638652	1.53513721	45.6276

Step 2: Dissociation required enthalpy

The dissociation enthalpy is presented in table 2.

T/K	CO2/ MJ	H2O/MJ	CO/MJ	H2/MJ	O2/MJ	N2/MJ	CO2-CO+0.5O2 MJ	H2O-H2+0.5O2 MJ
1500	-395691	-250267	-115225	0	0	0	280466	250267
1600	-395897	-250597	-115925	0	0	0	279972	250597

1700	-396110	-250890	-116644	0	0	0	279466	250890
1800	-396332	-251151	-117380	0	0	0	278952	251151
1900	-396564	-251384	-118132	0	0	0	278432	251384
2000	-396808	-251594	-118902	0	0	0	277906	251594
2100	-397065	-251783	-119687	0	0	0	277378	251783
2200	-397338	-251955	-120488	0	0	0	276850	251955
2300	-397626	-252113	-121305	0	0	0	276321	252113
2400	-397931	-252261	-122137	0	0	0	275794	252261
2500	-398253	-252399	-122984	0	0	0	275269	252399
2600	-398594	-252532	-123847	0	0	0	274747	252532
2700	-398952	-252659	-124724	0	0	0	274228	252659
2800	-399329	-252785	-125616	0	0	0	273713	252785
2900	-399725	-252909	-126523	0	0	0	273202	252909

Step 3: Average specific heat and gamma

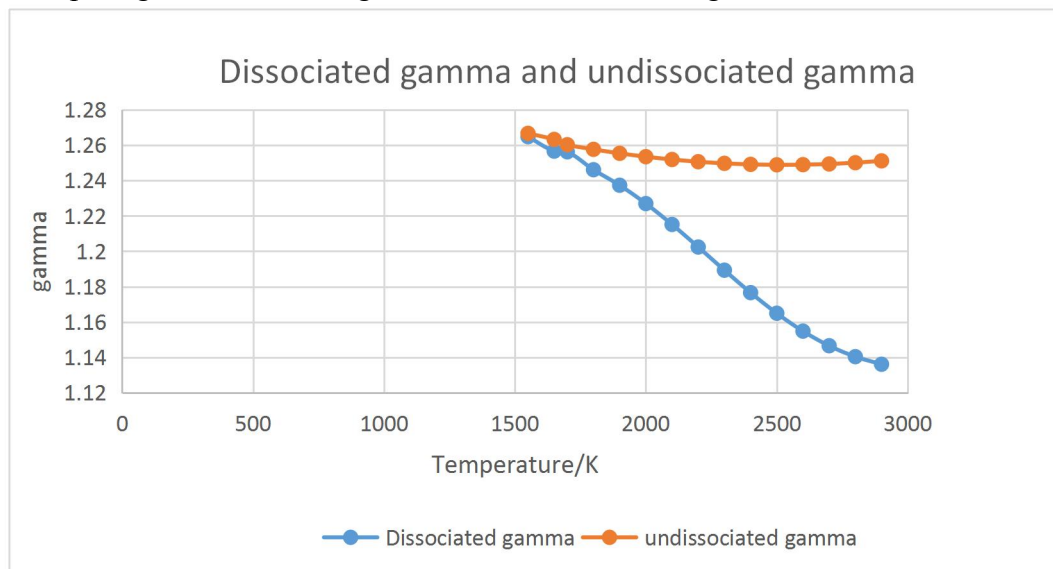
T/K	CO2 KJ/kmol K	H2O KJ/kmol K	CO KJ/kmol K	H2 KJ/kmol K	O2 KJ/kmol K	N2 KJ/kmol K	Cp average KJ/kmol K	Gamma
1500	58.292	47.103	35.178	32.356	36.49	34.805	39.49754923	1.266614937
1600	58.836	48.035	35.451	36.768	36.768	35.099	39.90351412	1.2631886
1700	59.316	48.901	35.694	37.036	37.036	35.361	40.26348552	1.260223283
1800	59.738	49.705	35.91	37.296	37.296	35.595	40.59022878	1.257588954
1900	60.108	50.451	36.101	37.546	37.546	35.803	40.87431928	1.255341476
2000	60.433	51.143	36.271	37.788	37.788	35.988	41.11978481	1.253430913
2100	60.717	51.784	36.421	38.023	38.023	36.152	41.32538448	1.251852509
2200	60.966	52.378	36.553	38.25	38.25	36.298	41.49044999	1.250599446
2300	61.185	52.927	36.67	38.47	38.47	36.428	41.61302485	1.249676981
2400	61.378	53.435	36.774	38.684	38.684	36.543	41.69079434	1.249095222
2500	61.548	53.905	36.867	38.891	38.891	36.645	41.72282983	1.248856367
2600	61.701	54.34	36.95	39.093	39.093	36.737	41.71078254	1.248946137
2700	61.839	54.7742	37.025	39.289	39.289	36.82	41.66008961	1.249324586
2800	61.965	55.115	37.093	39.48	39.48	36.895	41.56352962	1.25004865
2900	62.083	55.459	37.155	39.665	39.665	36.946	41.42662831	1.251082455

Step 4 Dissociated specific heat and gamma

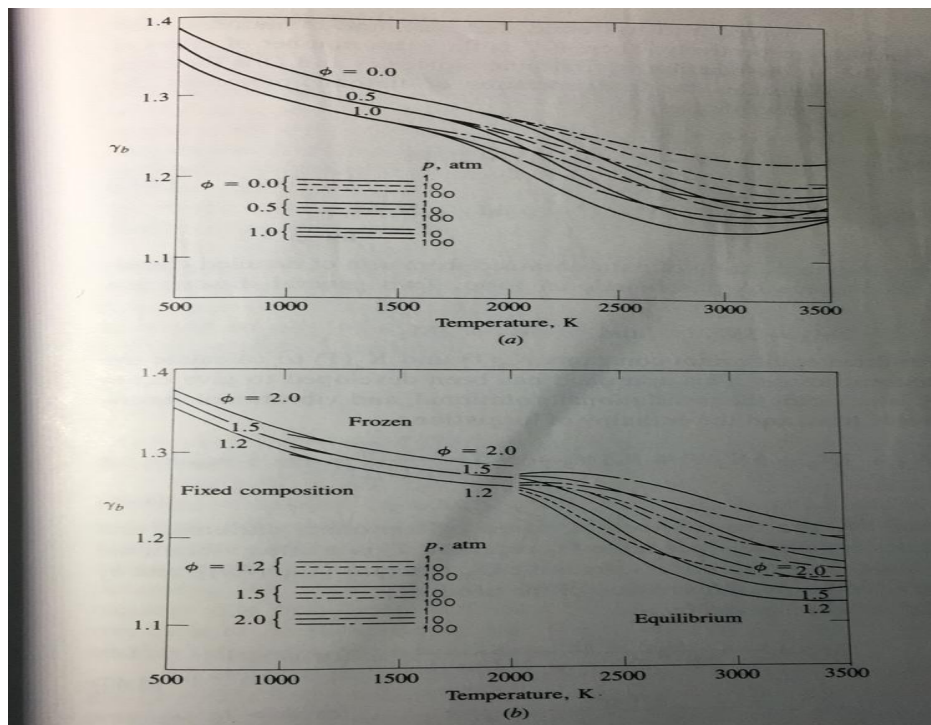
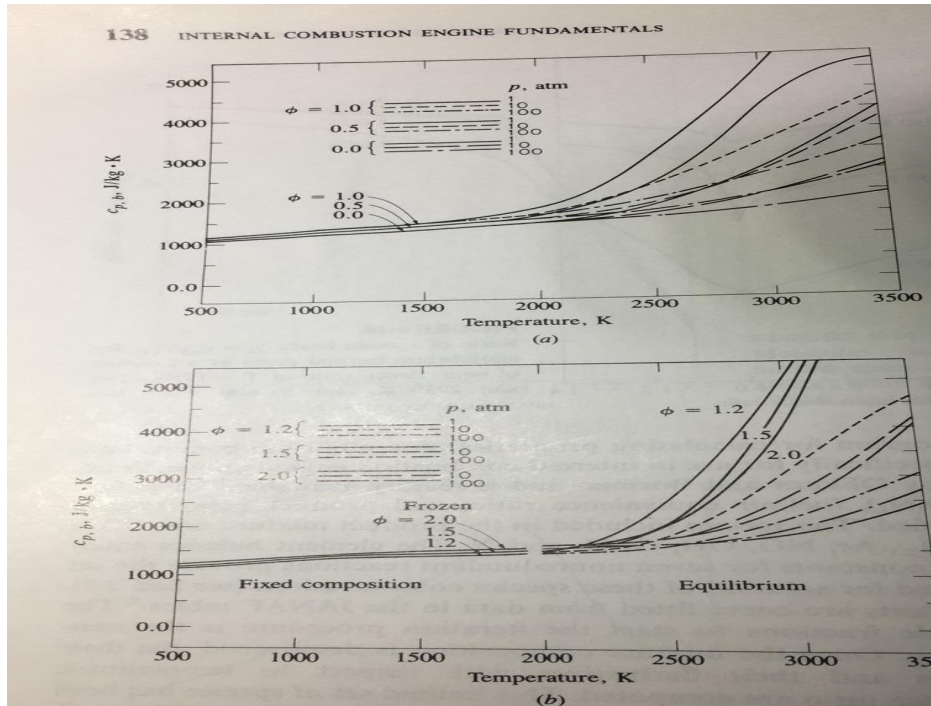
T	Cp average	Gamma	ΔC_p	Dissociated Cp	Dissociated gamma
1500	39.49754923	1.266614937	0.220161774	39.717711	1.264745781
1600	39.90351412	1.2631886	0.814394955	40.71790908	1.256573982

1700	40.26348552	1.260223283	0.503687655	40.76717318	1.256184502
1800	40.59022878	1.257588954	1.50921953	42.09944831	1.246082276
1900	40.87431928	1.255341476	2.475228499	43.34954778	1.237301841
2000	41.11978481	1.253430913	3.830115716	44.94990052	1.226935871
2100	41.32538448	1.251852509	5.632312729	46.95769721	1.215145046
2200	41.49044999	1.250599446	7.902251107	49.3927011	1.202391989
2300	41.61302485	1.249676981	10.61837785	52.2314027	1.18930992
2400	41.69079434	1.249095222	13.69439437	55.38518871	1.17662609
2500	41.72282983	1.248856367	16.98481484	58.70764466	1.164981121
2600	41.71078254	1.248946137	20.28549574	61.99627828	1.154874202
2700	41.66008961	1.249324586	23.35748323	65.01757284	1.146622154
2800	41.56352962	1.25004865	25.94563523	67.50916485	1.14045066
2900	41.42662831	1.251082455	27.94737064	69.37399895	1.136161155

Comparing the dissociated gamma with undissociated gamma.



Appendix I Specific heat and Gamma graph



(Heywood, 1989)

