CHAPTER 5
THEORITICAL MODELLING FOR EMISSION PREDICTION

5.1 THEORETICAL EMISSION CALCULATIONS

In these modern days the use of vehicles has become inseparable from men for the day to day life transportation. As a result of increase in vehicles the environment gets polluted due to the toxic emissions.

The exhaust emission of diesel engine consists of the following hazardous species.

1. Un-burnt hydro carbons (HC)
2. Oxides of carbon (CO & CO₂)
3. Oxides of nitrogen (NO & NO₂)
4. Oxides of sulphur (SO₂ & SO₃)
5. Particulates
6. Soot smoke

5.2 REASON FOR FORMATION OF EXHAUST

Table 5.1 Reason for formation of Exhaust

<table>
<thead>
<tr>
<th>Name of the gas</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC, CO</td>
<td>Incomplete burning of fuel</td>
</tr>
<tr>
<td>NOₓ</td>
<td>High temperature during combustion</td>
</tr>
</tbody>
</table>
In the above exhaust, HC and CO are formed due to incomplete burning of fuels. NO\textsubscript{x} is formed due to high temperature during operation. CO which is one of the exhausts has a great impact on the atmosphere and as a result ozone layer is depleted. The depletion of ozone (O\textsubscript{3}) layer increases the earth temperature leading to global warming and green house effect.

5.2.1 Ozone Depletion Reaction

CO combines with ozone (O\textsubscript{3}) forming oxygen and carbon dioxide. Oxygen formed as the result of the reaction being heavier, comes down which thinners the ozone layer.

\[
\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 \quad (5.1)
\]

NO\textsubscript{x} another exhaust, if continuously inhaled for 10 minutes leads to respiratory problems in human beings. So, there arises a need to control the emission of these gases which are hazardous to the environment and human beings.

5.2.2 Stoichiometric Proportion of Air-Fuel Mixture

For a complete combustion of the fuel, the stoichiometric proportion of air-fuel mixture should be 9:1. The proportion varies between 8:1 to 10:1 and never exceeds or comes below this level. In case of 8:1, it is called as rich mixture (rich in fuel content) and in case of 10:1, it is called as lean mixture (lean in fuel content). The mean of these two proportions is known as stoichiometric proportions.
5.3 MECHANISM OF FORMATION OF POLLUTANTS

5.3.1 Kinetics of NO Formation

While nitric oxide (NO) and nitrogen dioxide (NO$_2$) are usually grouped together as NO$_x$ emissions, nitric oxide is the predominant oxide of nitrogen produced inside the engine cylinder. The principal source of NO is the oxidation of atmospheric (molecular) nitrogen. However, if the fuel contains significant nitrogen, the oxidation of the fuel nitrogen-containing compounds is an additional source of NO. Gasoline contains negligible amounts of nitrogen; although diesel fuels contain more nitrogen, current levels are not significant.

The mechanism of NO formation from atmospheric nitrogen has been studied extensively. It is generally accepted that in combustion of near stoichiometric fuel-mixtures the principal reactions governing the formation of NO from molecular nitrogen (and its destruction) are

\[ \text{O} + \text{N}_2 \rightarrow \text{NO} + \text{N} \quad (5.16) \]

\[ \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} \quad (5.17) \]

\[ \text{N} + \text{OH} \rightarrow \text{NO} + \text{H} \quad (5.18) \]

This is often called as the extended Zeldovich mechanism. Zeldovich was the first to suggest the importance of reactions a and b. Lavoie et al added reaction c to the mechanism.
Table 5.2 Kinetics of NO Formation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant ( \text{(cm}^3/\text{mol*s}) )</th>
<th>Temperature range(K)</th>
<th>Uncertainty, factor of or %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O+N}_2 \rightarrow \text{NO+N} ) ( -1 )</td>
<td>( 7.6 \times 10^{13} \exp(-38000/T) ) ( 1.6 \times 10^{13} )</td>
<td>( 2000-5000 ) ( 300-5000 )</td>
<td>( 2 \pm 20% \text{ at } 300K ) ( 2 \text{ at } 2000-5000K )</td>
</tr>
<tr>
<td>( \text{N+O}_2 \rightarrow \text{NO+O} ) ( -2 )</td>
<td>( 6.4 \times 10^9 T \exp(-3150/T) ) ( 1.5 \times 10^9 T \exp(-19,500/T) )</td>
<td>( 300-3000 ) ( 1000-3000 )</td>
<td>( \pm 30% 300-1500K ) ( 2 \text{ at } 3000 K ) ( \pm 30%\text{at } 1000 K ) ( 2 \text{ at } 3000 K )</td>
</tr>
<tr>
<td>( \text{N+OH} \rightarrow \text{NO+H} ) ( -3 )</td>
<td>( 4.1 \times 10^{13} ) ( 2.0 \times 10^{14} \exp(-23,650/T) )</td>
<td>( 300-2500 ) ( 2200-4500 )</td>
<td>( \pm 80% ) ( 2 \text{ at } 3000 K )</td>
</tr>
</tbody>
</table>

5.3.2 Rate Constants for NO Formation Mechanism

NO forms in both the flame front and the post flame gases. In engines, however, combustion occurs at high pressure so the flame reaction zone is extremely thin (~0.1 mm) and residence time within zone is short. Also the cylinder pressure reaches the maximum, immediately after the combustion. Thus, the NO formation in the post flame gases almost always dominates any flame-front-produced by NO. It is therefore, appropriate to assume that the concentrations of O, O\(_2\), OH, H and N\(_2\) by their equilibrium values at the local pressure and equilibrium temperature.

High temperatures and high oxygen concentrations result in high NO formation rates. For adiabatic constant- pressure combustion (an appropriate model for each element of fuel that burns in an engine), this initial NO formation rate peaks at the stoichiometric composition and decreases rapidly as the mixture becomes leaner or richer.
Evidence that this formation model is valid under conditions typical of those found in engines is provided by high-pressure combustion bomb studies. Newhall and Shamed have measured the NO production, using the q-band absorption technique, behind hydrogen-air and planar flames propagating axially in a cylindrical bomb. Some results are compared with predictions made with this kinetic scheme coupled with an “unmixed” combustion calculation to determine local pressure and temperature. Note that the NO concentration rises smoothly from close to zero, indicating that at these high pressures there is negligible NO production within the flame front itself.

Fuel nitrogen is also a source of NO via a different and yet to be fully explained mechanism. During distillation, the fuels, the nitrogen can exist as amines and ring compounds are likely to undergo some thermal decomposition prior to entering the combustion zone. The precursor to NO formation from these compounds is limited. Oxidation to NO is usually rapid, occurring on a time scale comparable to that of the combustion reactions. The NO yield (amount of fuel nitrogen converted to NO) is sensitive to the fuel/air equivalence ratio. Relatively high NO yields (approaching 100 percent) are obtained for lean and stoichiometric mixtures; relatively low yields are found for rich mixtures. NO yields are only weakly dependent on temperature, in contrast to the strong temperature dependence of NO formed from atmospheric nitrogen.

5.3.3 Formation of NO$_2$

Chemical equilibrium considerations indicate that for burned gases at typical flame temperatures, NO$_2$/NO ratios should be negligibly small. While experimental data show this is true for spark-ignition engines, in diesels NO$_2$ can be 10 to 30 percent of the total exhaust oxides of nitrogen.
emissions. A plausible mechanism for the persistence of NO\(_2\) is the following. NO formed in the flame zone can be rapidly converted to the NO\(_2\) via reactions such as

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \tag{5.19}
\]

Subsequently, conversion of this NO\(_2\) to NO occurs via

\[
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \tag{5.20}
\]

Unless the NO\(_2\) formed in the flame is quenched by mixing with cooler fluid. This explanation is consistent with the highest NO\(_2\)/NO ratio occurring at light load in diesels, when cooler regions which could quench the conversion back to NO is widespread.

NO and NO\(_2\) emissions data from a spark ignition and a diesel. The maximum value for the (NO\(_2\)/NO) for the SI engine is 2 percent, at an equivalence ratio for about 0.85 for the diesel this ratio is higher and is highest at light load and depends on the engine speed.

It is customary to measure total oxides of nitrogen emissions, NO plus NO\(_2\), with a chemiluminescence’s analyzer and call the combination NO\(_x\). It is always in terms of mass of NO or mass of NO\(_2\), which have molecular weights of 30 and 46, respectively.

\subsection{5.3.4 NO\(_x\) Formation in Compression Ignition Engines}

The fuel-air mixing and combustion processes are extremely complex. During the premixed or uncontrolled diesel combustion phase immediately after the ignition delay has over. The fuel-air mixture inside the cylinder is a heterogeneous mixture, in which the mixture about stoichiometric, burns due to spontaneous ignition and flame propagation.
During the mixing controlled combustion phase, the burning mixture is likely to be closer to stoichiometric (the flame structure is that of a turbulent, though unsteady, diffusion flame). However, throughout the combustion process mixing between already burned gases, air, and lean and rich unburned fuel vapor-air mixture occurs, changing the composition of any gas elements that burned at a particular equivalence ratio. In addition to these composition (and hence temperature) changes due to mixing, temperature changes due to compression and expansion occur as the cylinder pressure rises and falls.

The critical time period is when burned gas temperatures are at a maximum: i.e., between the start of combustion and shortly after the occurrence of peak cylinder pressure. Mixture which burns early in the combustion process is especially important since it is compressed to a higher temperature, increasing the NO formation rate, as combustion proceeds and cylinder pressure increases. After the time of peak pressure, burned gas temperatures decrease as the cylinder gases expand. The decreasing temperature due to expansion and due to mixing of high temperature gas with air or cooler burned gas freezes the NO chemistry. This second effect (which occurs only in the diesel) means that freezing occurs more rapidly in the diesel than in the spark-ignition engine, and much less decomposition of the NO occurs.

Local NO concentrations rise from the residual gas value following the start of combustion, to a peak at the point where the local burned gas equivalence ratio changes from rich to lean (where the CO₂ concentration has its maximum value). As the local burned gas equivalence ratio becomes leaner due to mixing with excess air, NO concentrations decrease since formation becomes much slower as dilution occurs. At the time of peak NO concentrations within the bowl (15° aTDC), most of the bowl region was filled with flame. The total amount of NO within the cylinder of this type of
direct-injection diesel during the NO formation process has also been measured. At a predetermined time in one cycle, once steady-state warmed-up engine operation had been achieved, the contents of the cylinder were dumped into an evacuated tank by rapidly cutting open a diaphragm which had previously sealed off the tank system. NO concentrations reach a maximum shortly after the time of peak pressure. There is a modest amount of NO decomposition. Variations in engine speed have little effect on the shape of this curve. The 20 crank angle degrees after the start of combustion is the critical time period.

Results from similar cylinder-dumping experiments where injection timing and load (defined by the overall equivalence ratio) were varied also showed that almost all of the NO forms within the 20° following the start of combustion. As injection timing is retarded, the combustion process is also retarded. The NO formation occurs later, and concentrations are lower since peak temperatures are lower. At high load, with higher peak pressures and hence temperatures, and larger regions of close-to-stoichiometric burned gas, NO levels increase. Both NO and NOx concentrations were measured, NO2 is 10 to 20 percent of total NOx. Though NO levels decrease with a decreasing overall equivalence ratio, they do so much less rapidly than do spark-ignition engine NO emissions due to the non-uniform fuel distribution in the diesel. Though the amount of fuel injected decreases proportionally as the overall equivalence ratio is decreased, much of the fuel still burns close to stoichiometric. Thus NO emissions should be roughly proportional to the mass of the fuel injected (provided burned gas pressures and temperatures do not change greatly).

Similar gas-sampling studies have been done with indirect-injection diesel engines. Modeling studies suggest that most of the NO forms within the pre-chamber and is then transported into the main chamber where the
reactions freeze as rapid mixing with air occurs. However, the pre-chamber, except at light load, operates rich overall so some additional NO can form as the rich combustion products are diluted through the stoichiometric composition. The gas mixture rapidly becomes the stoichiometric or fuel-rich. Composition non-uniformities across the pre-chamber are substantial. Peak NO concentrations, as expected correspond approximately to locally stoichiometric regions. Because the mixture remains fuel-rich in the pre-chamber as the burned gases expand (after the time of peak pressure which occurs between 6° and 10° aTDC), substantial NO decomposition within the pre-chamber can occur. However, by this time much of the gas (and NO) in the pre-chamber has been transferred to the main chamber where freezing of the NO chemistry will occur.

Cylinder-gas dumping experiments, where both main chamber and pre-chamber gases were dumped and quenched, confirm this description. Cylinder average NO, determined by rapidly opening a diaphragm which separated the engine cylinder from an evacuated tank at predetermined points in the cycle of an otherwise normally operated IDI engine, rise rapidly once combustion starts until the NO chemistry is effectively frozen at about 15° aTDC. Little net NO decomposition occurs. Heat release-rate diagrams obtained from pressure data analysis for the same IDI engine indicate that combustion is only about one-half complete at the time the NO formation process ceases.

Diluents added to the intake air (such as recycled exhaust) are effective at reducing the NO formation rate, and therefore NOx exhaust emissions. As with spark-ignition engines, the effect is primarily one of reducing the burned gas temperature for a given mass of fuel and oxygen burned. The heat capacity of CO₂ (per mole) at the temperatures relevant to diesel combustion is about twice that of N₂. That of exhaust gas is slightly
higher than that of $N_2$. Therefore these data show that the effect is primarily one of reduced burned gas temperatures. Note that the composition of the exhaust gas of a diesel varies with load. At idle, there is little $CO_2$ and $H_2O$ are substantially higher. Similar studies in an indirect-injection engine show comparable trends. Addition of diluents (exhaust gas and nitrogen) reduces peak flame temperatures and $NO_x$ emissions; also, addition of oxygen (which corresponds to a reduction in diluents fraction) increases flame temperatures and therefore increases $NO_x$ emissions.

5.3.5 Carbon Monoxide

Carbon monoxide (CO) emissions from internal combustion engines are controlled primarily by the fuel/air equivalence ratio. CO emissions are significant and must be controlled. Diesels, however, always operate well on the lean side of stoichiometric; CO emissions from diesels are low enough to be unimportant, therefore, and will not be discussed further.

The levels of CO observed in spark-ignition engine exhaust gases are lower than the maximum values measured within the combustion chamber but are significantly higher than equilibrium values for the exhaust conditions. Thus the processes which govern CO exhaust levels are kinetically controlled. In premixed hydrocarbon-air flames, the CO concentration increases rapidly in the flame zone to a maximum value, which is larger than the equilibrium value for adiabatic combustion of the fuel-air mixture. CO formation is one of the principal reaction steps in the hydrocarbon combustion mechanism, which may be summarized by

$$RH \rightarrow R \rightarrow RO_2 \rightarrow RCHO \rightarrow RCO \rightarrow CO$$ (5.21)
Where, R stands for the hydrocarbon radical. The CO formed in the combustion process via this path is then oxidized to CO$_2$ at a slower rate. The principal CO oxidation reaction in hydrocarbon-air flames is

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (5.22)$$

It is generally assumed that in the post flame combustion products in a spark-ignition engine, at conditions close to peak cycle temperatures (2800 K) and pressures (15 to 40 atm), the carbon-oxygen-hydrogen system is equilibrated. Thus CO concentrations in the immediate post flame burned gases are close to equilibrium. However, as the burned gases cool during the expansion and exhaust strokes, depending on the temperature and cooling rate, the CO oxidation process may not remain locally equilibrated.

Newhall carried out a series of kinetic calculations for an engine expansion stroke assuming the burned gas at the time of peak cylinder pressure was uniform and in equilibrium. Of the reactions important to CO chemistry, only three-body radical-recombination reactions such as

$$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M} \quad (5.23)$$

$$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \quad (5.24)$$

$$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad (5.25)$$

Were found to be rate controlling. The bimolecular exchange reactions and the CO oxidation reaction were sufficiently fast to be continuously equilibrated. Only during the later stages of the expansion stroke was the CO concentration predicted to depart from equilibrium. Using this technique to predict average CO levels at the end of expansion over a range of equivalence ratios (rich to lean), Newhall obtained a good match to
experimental data. The kinetically controlled aspects of the CO emissions mechanism have thus been confirmed.

These calculations showed that a partial equilibrium amongst the bimolecular exchange reactions occurred a posteriori. Analyses based explicitly on this partial equilibrium assumption (which are considerably simpler) have been carried out. The blow down of cylinder pressure to the exhaust manifold level during the exhaust process and the decrease in gas temperature that accompanies it occupies a substantial portion of the cycle—about 60 crank angle degrees. Thus, the temperature and pressure-time profiles of parts of the charge at different locations throughout the cylinder differ, depending on when these parts of the charge burn and when they exit the cylinder through the exhaust valve and enter the exhaust manifold.

The partial equilibrium calculations show the burned gases are close to equilibrium until about 60 crank angle degrees after to dead center. During the exhaust blow-down process after the exhaust valve opens, gas which leaves the cylinder early cools more rapidly than gas which leaves late. In these calculations, mixing between gas elements which burn at different times was neglected. It can be seen that a CO gradient exists across the burned gases and that the CO concentrations in the exhaust gases is unlikely to be uniform. Experiments with single-cylinder engines support these calculations that CO is in equilibrium during the combustion process but deviates from equilibrium late in the expansion stroke.

Conclusions from these detailed studies are as follows. The measured average exhaust CO concentrations for fuel-rich mixtures are close to equilibrium concentrations in the burned gases during the expansion process. For close-to-stoichiometric mixtures, the partial equilibrium CO predications are in agreement with measurements and are orders of magnitude
above CO equilibrium concentrations corresponding to exhaust conditions. For fuel-lean mixtures, measured CO emissions are substantially higher than predictions from any of the models based on kinetically controlled bulk gas phenomena. One possible explanation of this lean-mixture discrepancy is that only partial oxidation to CO may occur of some of the unburned hydrocarbons emerging during expansion and exhaust from crevices in the combustion chamber and from any oil layers or deposits on the chamber walls.

While many questions about details of the CO oxidation mechanisms remain, as a practical matter exhaust emissions are determined by the fuel-air equivalence ratio. The degree of control achieved within the engine to date has come from improving mixture uniformity and leaning-out the intake mixture. In multi cylinder engines, because CO increases rapidly as the inlet mixture becomes richer than stoichiometric, cylinder-to-cylinder variations in equivalence ratio about the mean value are important; non-uniform distribution can significantly increase average emissions. Thus improved cylinder-to-cylinder fuel-air ratio distribution has become essential. Also, because it is necessary to enrich the fuel-air mixture when the engine is cold, CO emissions during engine warm-up are much higher than emissions in the fully warmed-up state. Further, in transient engine operation during acceleration and deceleration, control of fuel metering has had to be improved. Additional reductions in CO beyond what can be achieved in the engine are possible with exhaust treatment devices.

5.4 EQUIVALENCE RATIO

Equivalence ratio is defined as the ratio of normal fuel-air ratio to the stoichiometric fuel-air ratio.

Equivalence ratio ($\phi$) = actual fuel-air ratio/stoichiometric fuel-air ratio
5.5 BASIC EQUATIONS

The various emissions formed during stoichiometric combustion is given in the Equation 5.2.

\[ C_\alpha H_\beta O_\gamma N_\delta + \text{as/} \varphi (O_2 + 3.76N_2) \rightarrow n_1 CO_2 + n_2 H_2O + n_3 N_2 + n_4 O_2 + n_5 CO + n_6 H_2 + n_7 H + n_8 O + n_9 OH + n_{10} NO \]

(5.2)

The Equation 5.3 shows the modified basic equation

\[(1-x)C_\alpha H_\beta O_\gamma N_\delta + x H_2O + \text{as/} \varphi (O_2 + 3.76N_2) \rightarrow n_1 CO_2 + n_2 H_2O + n_3 N_2 + n_4 O_2 + n_5 CO + n_6 H_2 + n_7 H + n_8 O + n_9 OH + n_{10} NO \]

(5.3)

where

\[ X – \text{Fraction of water in the fuel} \]

C: \[ \alpha = (y_1+y_5) N \]  \hspace{1cm} (5.4)

H: \[ \beta = (2y_2+2y_6+y_7+y_9) N \]  \hspace{1cm} (5.5)

O: \[ \gamma + 2 \text{ as/} \varphi = (2y_1+y_2+2y_4+y_8+y_9+y_{10}) N \]  \hspace{1cm} (5.6)

N: \[ \delta + (2 \times 3.76) \text{ as/} \varphi = (2y_3+y_{10}) N \] \hspace{1cm} (5.7)

\[ \sum_{i=1}^{10} y_i - 1 = 0 \] \hspace{1cm} (5.8)

\[ \frac{1}{2} H_2 \leftrightarrow H \hspace{2cm} K_1 = \frac{y_7 P^{1/2}}{y_6^{1/2}} \] \hspace{1cm} (5.9)

\[ \frac{1}{2} O_2 \leftrightarrow O \hspace{2cm} K_2 = \frac{y_8 P^{1/2}}{y_4^{1/2}} \] \hspace{1cm} (5.10)

\[ \frac{1}{2} H_2 + \frac{1}{2} O_2 \leftrightarrow OH \hspace{2cm} K_3 = \frac{y_9}{y_4^{1/2} y_6^{1/2}} \] \hspace{1cm} (5.11)

\[ \frac{1}{2} O_2 + \frac{1}{2} N_2O \leftrightarrow NO \hspace{2cm} K_4 = \frac{y_{10}}{y_4^{1/2} y_3^{1/2}} \] \hspace{1cm} (5.12)
\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{H}_2\text{O} \quad K_s = \frac{y_2}{y_4^{1/2} y_6 P^{1/2}} \quad (5.13) \]

\[ \text{CO} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{CO}_2 \quad K_6 = \frac{y_1}{y_4^{1/2} y_3 P^{1/2}} \quad (5.14) \]

\[ \log K_i(T) = A_i \ln \left( \frac{T}{100} \right) + \frac{B_i}{T} + C_i + D_i T + E_i T^2 \quad (5.15) \]

The set of eleven equations are non-linear and are solved by Gauss–Jordan Iteration method. The solution of the above equation gives the theoretical values of mole fraction of the components in the emission. In this theoretical calculation, the inputs like peak temperature, peak pressure, fuel used and the equivalence ratio are to be required.

The peak cycle pressure is noted from the pressure-crank angle diagram. The peak cycle temperature is calculated by the following calculations.

### 5.6 SIMULATION OF ETHANOL IN COMPRESSION IGNITION ENGINE

For simulating of ethanol in compression ignition engines, following assumptions are made.

**Input data:**

- **Bore**: 78 mm
- **S=Stroke**: 68 mm
- **L=Connecting rod length**: 210 mm
- **Compression ratio**: 18.1
- **Reference air-fuel ratio**: 1.5
Initial pressure : 1 bar
Initial temperature : 300 K

The crank angle at which the fuel is injected : 167 degrees of crank angle (for zero dimensional combustion model)

EVO : 340
EVC : 554
IVO : 527
IVC : 750
Combustion duration : 50 (combustion of duration in degrees crank angle)

Nx : 0
urp : 1503760 kJ/kmol
hrp : 1498800 kJ/kmol

5.6.1 Pre-calculations

bru = 0.001*B
stu = 0.001*S
s_area = 3.14*bru*stu*rcr*4/4
v_dis = (3.14*B*B*S*.000001)/4
v_bdc = rcr*v_dis
v_tdc = v_bdc-v_dis

Volume at all degree crank angles is found in cc by using the following formula,
\[ V(\theta) = V_{dis} \times \left[ \frac{r}{r-1} - \frac{1 - \cos \theta}{2} + \frac{L}{S} - \frac{1}{2} \sqrt{\left( \frac{2L}{S} \right)^2 - \sin^2 \theta} \right] \quad (5.16) \]

and

\[ V'(\theta) = \frac{V_{dis}}{2} \times \left[ \frac{1}{2} \sin \theta \sin 2 \theta - \sin \theta \right] \quad (5.17) \]

\[ y_{cc} = n_{mc} + (.25 \times n_{mh}) - (.5 \times n_{mo}) \]
\[ y_{min} = y_{cc} - (.5 \times n_{mc}) \]
\[ y = y_{cc} \times raf \]

\( y_{cc} \) denotes the chemically correct amount of oxygen per mole of fuel for combustion.

\( y_{min} \) denotes the minimum amount of oxygen required in the reactants per mole of fuel.

\( n_{mc} = \) no. of moles of carbon atom in fuel=2
\( n_{mh} = \) no. of moles of hydrogen atom in fuel=6
\( n_{mo} = \) no. of moles of oxygen atom in fuel=1

For the two conditions of \( y \) calculation for finding out \( n_1, n_2, n_3, n_4, n_5 \):

(i) \( y > y_{cc} \)

\[ n_1 = 0 \]
\[ n_2 = n_{mc} \]
\[ n_3 = 0.5 \times n_{mh} \]
\( n_4 = 3.76 \times y \)
\( n_5 = y - y_{cc} \)
\( \text{afr} = 4.76 \times y \)
\( N_{po} = n_1 + n_2 + n_3 + n_4 + n_5 \)
\( N_{mo} = 1 + (4.76 \times y) \)

(ii) \( y_{\min} \leq y \leq y_{cc} \)
\( n_1 = 2 \times (y_{cc} - y) \)
\( n_2 = 2 \times (y - y_{\min}) \)
\( n_3 = 0.5 \times n_{mh} \)
\( n_4 = 3.76 \times y \)
\( n_5 = 0 \)

\( N_{po} = n_1 + n_2 + n_3 + n_4 + n_5 \) (Kilo moles of products formed from the combustion of \( n_{mo} \))

\( N_{mo} = 1 + (4.76 \times y) \) (Kilo moles of air plus fuel vapor in a mixture containing 1 kilo mole of fuel)

\[
\begin{align*}
\text{cpr}_{rr} &= \text{acpa} + (\text{bcpa} \times T_1) \\
\text{cpr} &= \frac{((\text{cpr}_{rr} \times N_a) + (N_x \times \text{cp}))/(N_a + N_x)}{\text{kr}} = \frac{\text{cpr}}{\text{kr}} \\
\end{align*}
\]

(5.18) \hspace{5cm} (5.19) \hspace{5cm} (5.20)

\[ 5.6.2 \quad \text{For Compression Stroke} \]

1. Pressure values from 0 degree to 180 degree calculated by the following formula.
\[ P[i+1] = P[i] \times \left( \frac{\text{VOL} \ (i)}{\text{VOL} \ (i+1)} \right)^{\text{kr}} \]
2. Temperature values from 0 degree to 180 degree calculated by the following formula.

\[ T_{[i+1]} = T[i] \times \left( \frac{\text{VOL}(i)}{\text{VOL}(i+1)} \right)^{(k_r-1)} \]  \hspace{1cm} (5.22)

**P, V, T AT POINT 2**

- \( P_2 = P_1 \times \frac{V_1}{V_2} \) \(^{K_r}\)
- \( V_2 = \nu_{dc} \)
- \( T_2 = T_1 \times \frac{V_1}{V_2} \) \(^{(K_r-1)}\)
- \( Q_v = - \left( \text{urp} + (n_1 \times 281400) \right) \times (\text{Na}/\text{Nm}) \)  \hspace{1cm} (5.23)
- \( W_{comp} = (\text{Na} + \text{N_x}) \times c_{vr} \times (T_{ibc} - T_1) \)  \hspace{1cm} (5.24)

### 5.6.3 Adiabatic Flame Temperature

\( T = 3000 \text{ K} \) (assumed temperature)

\[ T_{\text{new}} = T - \left( \text{cm} \times (\text{up}(T_2) - \text{up}(T)) - Q_v \right) / \text{cv}(T) \]  \hspace{1cm} (5.25)

\( T_3 = T_{\text{new}} \)

\( P_3' = P_2 \times \frac{T_3}{T_2} \times \frac{(\text{N}_p/\text{N}_a)}{(\text{N}_a+\text{N}_d)} \)  \hspace{1cm} (5.26)

\( P_3 = P_2 \)

\( T = T_2 \)

\( \text{cpp} = \text{CP} \times (T_2) \)

\( k_p = \text{cpp} / (\text{cpp} - \text{R}) \)

\( \text{Gasmas} = \left( \frac{P_1 \times \text{vbdc} \times \text{fpm} \times \text{fvm}}{\text{rmix} \times 1000 \times T_1} \right) \)  \hspace{1cm} (5.27)

### 5.6.4 For Combustion Part

The two zone combustion model was used, the delay period was also taken into account. The Ignition delay period was determined by Wolfer’s relation.
$$\int_{t_0}^{t_{\text{ign}}} \frac{\text{d}t}{t(p,T)} = \frac{1}{C} \int_{t_0}^{t_{\text{ign}}} \frac{\text{d}t}{[p(t)]^q \exp \left[ \frac{E}{RT(t)} \right]} = 1$$ (5.28)

\[ t = \text{time in seconds or in °CA} \]
\[ C = 2272 \]
\[ Q = -1.19 \]
\[ E/R = 4650 \]
\[ I_c = \text{ibc} + \text{id} (\text{icb= end of combustion}) \]
\[ P[i\theta+1] = p[i\theta] \cdot (\text{VOL}(i\theta)/\text{VOL}(i\theta+1))^K \]
\[ T[i\theta] = T1 \cdot (\text{VOL}(i\theta)/\text{VOL}(i\theta))^{(K-1)} \]
\[ P_{\text{del}} = p[i+1] - p[i] \]
\[ V_{\text{del}} = \text{vol}[i+1] - \text{vol}[i] \]
\[ W_{\text{comb}} = (\text{prs} + (p_{\text{del}}/2)) \cdot v_{\text{del}} \cdot f_{\text{pm}} \cdot f_{\text{vm}} \]

5.6.5 For Expansion Stroke

\[ T_{\text{eac}} = \text{The temperature at the crank angle when combustion ends} \]
\[ T_{\text{eac}} = p[\text{ice}] \cdot \text{VOL}(\text{ice})/(R_{\text{lit}} \cdot N_{p}) \]
\[ K_p = \frac{C_P(T_{\text{eac}})}{(C_P(T_{\text{eac}}) - R)} \]
\[ T_{4} = T_{\text{eac}} \cdot (\text{VOL}(\text{iec})/\text{VOL}(\text{evo}))^{(K_p-1)} \]
\[ \text{Upt}_{\text{eac}} = (c_{m} \cdot h_{p}(T_{\text{eac}})) - (R \cdot N_{p} \cdot T_{\text{eac}}) \]
\[ \text{Upt}_{4} = (c_{m} \cdot h_{p}(T_{4})) - (R \cdot N_{p} \cdot T_{4}) \]
\[ W_{\text{exp}} = \text{pteac} - \text{Upt}_{4} \]
\[ W_{\text{net}} = w_{\text{exp}} + w_{\text{comb}} - w_{\text{comp}} \]
\[ P[i\theta+1] = (i\theta) \cdot (\text{VOL}(i\theta)/\text{VOL}(i\theta+1))^K_p \]
\[ T[i\theta] = T_{\text{eac}} \cdot (\text{VOL}(\text{iec})/\text{VOL}(i\theta))^{(K_p-1)} \]
The practical values of mole fraction of the component are recorded using the field analysis. The emissions from a normal diesel engine are recorded. This is referred to as Base readings.

5.7 SOLVING BASIC EQUATIONS

The mole fraction of the emission of the emission gases are calculated theoretically by solving the eleven nonlinear equations had been analyzed and the Gauss-Jordan method has been selected for solving the basic equation.

To solve the equation a C program has been developed. After solving the equation the experimental values of the mole fraction is calculated by measuring techniques.

5.8 SOLUTION OF NON-LINEAR SYSTEM OF EQUATIONS

The methods which are used for non-linear system of equations are as follows. They are,

1. Graphical method (2*2)
2. Gauss-Seidel method
3. Gauss-Jordan method
4. Newton-Raphson method
5. Alpha Constant technique
6. Riks-Wempner method
7. Method of steepest descent
8. Modified Newton-Raphson method
5.8.1 Working on the Basic Equations

The equilibrium constant curve-fit coefficients are given in the table. For Ethanol (C\(_2\)H\(_5\)OH), at a temperature of 3000K and pressure of 3000kpa, the equilibrium constant values are,

\[
\begin{align*}
K_1 &= 0.157309313 \\
K_2 &= 0.112398739 \\
K_3 &= 1.162124775 \\
K_4 &= 0.122019800 \\
K_5 &= 22.03772183 \\
K_6 &= 3.056943025
\end{align*}
\]

For Ethanol, the values of
\[
\begin{align*}
\alpha &= 2 \text{ (no. of carbon atoms),} \\
\beta &= 6 \text{ (no. of hydrogen atoms),} \\
\gamma &= 1 \text{ (no. of oxygen atoms),} \\
\delta &= 0 \text{ (no. of nitrogen atoms).}
\end{align*}
\]

By substituting the equilibrium constant values and no. of atoms, we get the following 11 equations which can be solved by the Gauss-Jordan method.

\[
\begin{align*}
n_1 + n_5 &= 2 & (5.29) \\
2n_1 + 2n_6 + n_7 + n_9 &= 6 & (5.30) \\
2n_1 + n_2 + 2n_4 + n_5 + n_8 + n_9 + n_{10} &= 13 & (5.31) \\
2n_3 + n_{10} &= 45.12 & (5.32) \\
n_{10} - 0.1220198\sqrt{(n_3 \cdot n_4)} &= 0 & (5.33) \\
n_9 - 1.162124615\sqrt{(n_4 \cdot n_6)} &= 0 & (5.34) \\
n_8 - 0.020521106\sqrt{n_4} &= 0 & (5.35)
\end{align*}
\]
\[ n_7 - 0.028722045\sqrt{n_6} = 0 \]  \hspace{1cm} (5.36)
\[ n_2 - 120.766\sqrt{n_4} = 0 \]  \hspace{1cm} (5.37)
\[ n_1 - 16.74356635\sqrt{n_4} = 0 \]  \hspace{1cm} (5.38)
\[ n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8 + n_9 + n_{10} = N \]  \hspace{1cm} (5.39)

### 5.8.2 Algorithm for Gauss-Jordan Method

**STEP 01**: Start

**STEP 02**: Get the input equations

**STEP 03**: Input value for the initial assumption

**STEP 04**: Get the input for number of iterations

**STEP 05**: Substitute the initial assumptions and find out the initial values for the unknowns.

**STEP 06**: The first iterated results are again substituted in the equations and the corresponding values are found out.

**STEP 07**: The second iterated results are again substituted in the equations and the equations are iterated for the given number of iterations.

**STEP 08**: The last iteration values are compared with the last but one value. If they are found to be same, then the final iteration values are said to be converged.

**STEP 09**: If the values have not been converged, then the steps one to seven are repeated with the number of iterations increased.

**STEP 10**: Print the converged values

**STEP 11**: Stop

By solving these basic equations we get the theoretical mole fractions of various exhausts.
5.8.3 Calculation of Exhaust Species Liberation Rate

Let

- $y_1$ - mole fraction of CO$_2$
- $y_2$ - mole fraction of H$_2$O
- $y_3$ - mole fraction of N$_2$
- $y_4$ - mole fraction of O$_2$
- $y_5$ - mole fraction of CO
- $y_6$ - mole fraction of H$_2$
- $y_7$ - mole fraction of H
- $y_8$ - mole fraction of O
- $y_9$ - mole fraction of OH
- $y_{10}$ - mole fraction of NO

- $m_1$ - molecular weight of CO$_2$ = 44 kg/mol
- $m_2$ - molecular weight of H$_2$O = 18 kg/mol
- $m_3$ - molecular weight of N$_2$ = 28 kg/mol
- $m_4$ - molecular weight of O$_2$ = 32 kg/mol
- $m_5$ - molecular weight of CO = 28 kg/mol
- $m_6$ - molecular weight of H$_2$ = 2 kg/mol
- $m_7$ - molecular weight of H = 1 kg/mol
- $m_8$ - molecular weight of O = 16 kg/mol
- $m_9$ - molecular weight of OH = 17 kg/mol
- $m_{10}$ - molecular weight of NO = 30 kg/mol

Mass of individual species in a mole of exhaust gas $M_i = y_i \cdot m_i$

Total mass per mole of exhaust gas $M = \sum_{i=0}^{10} y_i \cdot m_i$

Mass fraction of individual species $x_i = M_i \cdot y_i / M$

Theoretical, Mass of individual species of exhaust emitted per hour producing unit power
\[ E_i = x_i \cdot (m_a + m_f) / P \text{ kg/kW-h} \]

where,

- \( m_a \) – mass flow rate of air, kg/h
- \( m_f \) – mass flow rate of fuel, kg/h
- \( P \) – Brake Power, kW

Experimental, Mass of individual species of exhaust emitted per hour producing unit power

\[ E_i = [(m_a + m_f) \cdot \text{PPM} \cdot 10^{-6} \cdot m_i] / (29 \cdot P) \text{ kg/kW-h} \]

5.9 COMPARISON OF THEORETICAL AND EXPERIMENTAL NO\textsubscript{x} VALUES

From the above results, Figure 5.1 shows the theoretical and experimental values of the nitric oxide emission with respect to the equivalence ratio. It is observed that, The NO\textsubscript{x} emission decreases with increasing the equivalence ratio for the diesel fuel. The NO\textsubscript{x} emission trend of all the fuels decreases with increasing the equivalence ratio.

Figure 5.2, Figure 5.3, Figure 5.4, Figure 5.5, Figure 5.6, Figure 5.7, Figure 5.8, Figure 5.9 and Figure 5.10 shows the variation of nitric oxide emission with respect to the equivalence ratio for ethanol, W3, W6, W10, W15, W20, W25 fuels respectively. The variation of nitric oxide emission for the coated engine was higher than the non-coated engine for all operating conditions. But the theoretically predicted nitric oxide emission values are slightly higher than the experimental values. The variation of nitric oxide emission, comparing with theoretical and experimental was upto 3.5%.
Figure 5.1  Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a Diesel fuelled engine

Figure 5.2  Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in an Ethanol fuelled, Spark Ignited engine
Figure 5.3  Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a W3% fuelled, Spark Ignited engine

Figure 5.4  Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a W6% fuelled, Spark Ignited engine
Figure 5.5 Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a W10% fuelled, Spark Ignited engine

Figure 5.6 Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a diesel fuelled, Surface Ignited engine
Figure 5.7  Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a W10 fuelled, Surface Ignited engine

Figure 5.8  Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a W15 fuelled, Surface Ignited engine
Figure 5.9 Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a W20 fuelled, Surface Ignited engine

Figure 5.10 Comparison of Theoretical and Experimental emission of Nitric oxide with respect to Equivalence ratio in a W25 fuelled, Surface Ignited engine