CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Nitrogen oxides are abbreviated by the symbol NO\textsubscript{x} and comprise both nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}). Nitric oxide is generated in combustion processes under the influence of high gas temperatures and sufficient local oxygen. Diesel fuel contains only a very small amount of nitrogen, so NO formation occurs almost exclusively through the oxidation of atmospheric nitrogen. A major hurdle in understanding the mechanism of formation and controlling NO\textsubscript{x} emission is that combustion is highly heterogeneous and transient in diesel engines. While NO and NO\textsubscript{2} are lumped together as NO\textsubscript{x}, there are some distinctive differences between these pollutants. NO is a colourless and odourless gas, while NO\textsubscript{2} is a reddish brown gas with pungent odour. Both gases are considered toxic, but NO\textsubscript{2} has a level of toxicity 5 times greater than that of NO. Although NO\textsubscript{2} is largely formed from oxidation of NO, attention has been given on how NO can be controlled before and after combustion (Agrawal et al 2004).

Four different mechanisms lead to the formation of nitric oxide in combustion system.

(i) The thermal NO is formed at high temperatures under slightly lean conditions with the burned products. The involved nitrogen and oxygen stem from the combustion air.
(ii) The prompt NO path, first postulated by Fennimore (1971), describes the reaction of N₂ from combustion air with hydrocarbon radicals in fuel-rich regions.

(iii) The fuel NO which refers to the formation of NO from fuel bound nitrogen as it may be contained in coal and heavy distillates of petroleum. But, there is no fuel bound nitrogen in diesel fuel.

(iv) N₂O intermediate route is activated at lower temperature than the thermal NO in a fuel-lean and high pressure environment. It can become important in gas turbine combustion, but it has only a minor effect in diesel engine combustion.

The NO that was generated through thermal NO accounted for 88% of total NO. Prompt NO (Fennimore) and NO via N₂O accounted for 7% and 1.5% respectively (Jin Kusaka et al 2003). The principal source of NO formation in diesel engines is the oxidation of the nitrogen present in atmospheric air. The nitric oxide formation chain reactions are initiated by atomic oxygen which forms from the dissociation of oxygen molecules at the high temperature reached during the combustion process. The NO formation in diesel combustion is mainly governed by thermal NO described by the extended Zeldovich mechanism. The reaction scheme is given by (Muller et al, 1998)

\[
N_2 + O \leftrightarrow NO + N \quad (2.1)
\]
\[
N + O_2 \leftrightarrow NO + O \quad (2.2)
\]
\[
N + OH \leftrightarrow NO + H \quad (2.3)
\]
NO formation is strong dependent on temperature and oxygen concentration during the combustion phase. Chemical equilibrium consideration indicates that for burnt gases at typical flame temperatures, NO$_2$/NO ratios should be negligibly small. While experimental data shows that this is true for spark ignition engines, in diesels, NO$_2$ can be 10 to 30% of total exhaust emissions of oxides of nitrogen. NO formed in the flame zones can be rapidly converted to NO$_2$ via reactions such as

$$\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$$  \hspace{1cm} (2.4)

Subsequently, conversion of this NO$_2$ to NO occurs via

$$\text{NO}_2 + \text{O} \leftrightarrow \text{NO} + \text{O}_2$$  \hspace{1cm} (2.5)

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 loads in diesels, when cooler regions which could quench the conversion back to NO are widespread (Heywood 1998).

In the diesel engines, the emissions of nitrogen oxides and particulate matter (PM) are of main concern although all the emission regulations also limit the carbon monoxide and unburned hydrocarbons. During 1980s and 1990s considerable advancements in the emission control technology have been made for the diesel engines. The development efforts have been focused on reduction of engine-out emissions, exhaust after treatment and fuel formulation. The reduction of NO$_x$ and PM simultaneously pose the biggest challenge as most of the engine design strategies to reduce either NO$_x$ or PM cause an increase in the other. The diesel engine design mainly focuses on lower fuel consumption, lower pollutant emission and higher thermal efficiency. But, many of the design changes for reduction in NO$_x$ emissions result in higher brake specific fuel consumption. For example,
retarding injection timing would be effective in the reduction of NO\textsubscript{x} formation, but it usually results in an increase in soot emissions and higher BSFC. Similarly, increasing fuel injection pressure can decrease soot emissions, but it can result in higher NO\textsubscript{x} emissions. Combustion chamber design optimization, injection system design, electronic fuel injection to control injection rate and rate-shaping, multiple injection, EGR, variable boost pressure, water injection have been found to provide substantial reduction in both NO\textsubscript{x} and PM from diesel engines.

In the following section the numerical and experimental research efforts of various investigators to reduce the NO\textsubscript{x} and soot emissions and to improve the specific fuel consumption and brake thermal efficiency of diesel engine are presented.

2.2 SIMULATION AND MODELING OF DIESEL ENGINE COMBUSTION AND EMISSION

Sarkar (2009) developed a cycle simulation code for DI diesel engines based on combustion equilibrium model with eleven species and uniform zonal properties concept considering heat release from the injected fuel, heat losses due to exhaust and blowby, heat transfer model and equilibrium state existence at higher temperature. He computed the moles of combustion products CO\textsubscript{2}, H\textsubscript{2}O, CO and NO, formed for operating conditions with equivalence ratio from 0.5 to 1.5. He has also predicted the cylinder pressure for 50% and 100% loads and compared with measured values and showed that the numerical results are closer to the experimental values.

Rosli Abu Bakar et al (1997) numerically investigated the influence of combustion parameters on heat release, cylinder pressure and exhaust emission in a direct injection diesel engine and validated with experimental result. They investigated the effect of combustion parameters on nitric oxide
formation such as injection timing, engine speed, compression ratio and the amount of fuel injection. They concluded that the nitric oxide formation was found to be reduced by decrease of the peak pressure and the temperature in cylinder due to the retarding of fuel injection timing. An increase in the engine speed at a given injection timing decreased the concentration of nitric oxide in the engine exhaust. The increase of fuel injection amount increases the gas pressure and nitric oxide emission. The nitric oxide concentration increases with increase of coolant temperature under the constant operating conditions.

Sundaram et al (2002) simulated four stroke CI engine processes using zero dimensional models to predict the brake thermal efficiency and NOx and validated using experimental results. It was found that the NOx level decreases with increase in engine speed. Similar observation was made by Rosli Abu Baker et al (1997) and they concluded that at lower engine speed, the reactive gas provides a longer time for the nitric oxide to form and this causes in higher nitric oxide concentration in the combustion chamber.

Prasad et al (1997) conducted a comparative study on the prediction of the cylinder pressure and temperature of four stroke diesel engine using single and multizone combustion models and compared the same with the experimental values. They concluded that multizone model predicts values closer to the experimental data in view of the realities of the diesel combustion process included in the model.

Pirouzpanah et al (2000) studied the performance and emission of a diesel engine using a Multi Zone Combustion Model and concluded that thermal NO emission decreases with increase in speed. The same was verified experimentally.
Muller et al (1998) examined the NO and soot formation in diesel engine combustion using a two zone model. In diesel engines due to the diffusion combustion and turbulent mixing process, the fuel oxidation occurs with varying mixture compositions. The combustion process in diesel engines begins with high probability at local air/fuel ratios of $\lambda=0.6$ to 0.8. It was concluded that the local air/fuel ratios of the instantaneously burning mixture and the soot formation areas depend on the engine load, the injection timing and the exhaust gas recirculation rate. They observed that about 30 degree crank angle after the start of combustion nitric oxide formation ceases since the combustion gas temperature drops below a limit of approximately 2200 K. Hence, they concluded that NO formation can be suppressed almost completely by keeping the combustion temperatures below a limit of approximately 2200 K.

Dittrich et al (1998) modeled the effect of injection systems on diesel engine combustion and NO formation using KIVA-II code. Two different injection systems, common rail and cam shaft driven unit pump, were used for the study. It was predicted that there is no measurable NO formation resulting from the premixed burn, NO first appears around the jet periphery, on the downwind side of the swirl induced flow and NO formation continues in the post injection combustion and amount to approximately one-third of all NO produced. They further investigated the effect of number of holes in the injector on NO formation using hydraulically similar 6-hole and 8-hole nozzles. Both the 6 and 8-hole configuration have the same NO formation potential up to approximately 11° ATDC. Beyond this point 8-hole nozzle shows a higher NO formation rate than the 6-hole nozzle because of the delayed homogenization process. The difference can be attributed to the local oxygen concentration at high temperature zone which is slightly lower for 6-hole nozzle than the 8-hole nozzle.
Mather et al (1998) modeled the influence of fuel injection parameters on diesel engine emission. The numerical calculations were performed using a modified version of KIVA-II code with improvement for the turbulence, gas-to-wall heat transfer, ignition, and combustion models. Fuel injection characteristics have a significant effect on the performance and emissions of diesel engine. It was concluded that decreasing the injection duration is to increase NO\textsubscript{x} and to decrease soot.

Chikahisa et al (1994) analyzed the NO formation characteristics using KIVA program and concluded that the NO emission to be inversely proportional to engine speed for engine operated under similar conditions. However, the relationship becomes less dependent on engine speed when the engine speed is low and the excess air ratio is small due to the fact that large part of the combustion zone reaches chemical equilibrium state. The excess air ratio is defined as \((1-\phi)/\phi\) where \(\phi\) is equivalence ratio.

Yuan et al (2007) modeled the NO\textsubscript{x} emission from diesel engine. The NO formation in diesel engine was modeled using the Zeldovich mechanism and the value was multiplied by a calibration factor to predict the NO\textsubscript{x} formed during combustion in the diesel engine which includes both NO and NO\textsubscript{2}. For diesel fuel, the value the calibration factor is 1.533 which is the ratio of molecular weight of NO\textsubscript{2} to NO.

Timoney et al (2005) developed a semi-empirical model for prediction of NO\textsubscript{x} using measured in-cylinder pressure in diesel engine. The simulated fuel burn rate and adiabatic flame temperature are given as input to the model to determine the NO\textsubscript{x} level in the diffusing burning phase of diesel engine.
2.3 EFFECTS OF ENGINE OPERATING PARAMETERS ON NO\textsubscript{x} EMISSION

2.3.1 Introduction

The performance and emission characteristics of diesel engines depend on various factors like fuel quantity injected, fuel injection timing, fuel injection pressure, shape of combustion chamber, position and size of injection nozzle hole, fuel spray pattern, air swirl etc. The fuel injection system in a direct injection diesel engine is to achieve a high degree of atomization for better penetration of fuel in order to utilize the full air charge and to promote the evaporation in a very short time and to achieve higher combustion efficiency.

2.3.2 Effects of air motion and swirl

Monaghan et al (1981) studied the effect of air motion and its effects on diesel engine performance and emission in a single cylinder engine fitted with three different induction systems, namely masked valve, directed port and helical port, using Laser Doppler Velocimeter (LDV) and constant temperature hot wire anemometer (CTA). It was found that the weighted specific fuel consumption and weighted specific NO\textsubscript{x} emission were virtually same for all three ports. It was also found that the weighted specific fuel consumption increases and weighted specific NO\textsubscript{x} decreases when the injection time is retarded in all the three configurations.

Benajes et al (2004) experimentally studied the effect of swirl on combustion and exhaust emission on heavy duty diesel engine. Cylinder pressure measurement was used to investigate the effect of swirl on the combustion process by means of parameters such as heat release rate, combustion duration, ignition delay and burnt gas temperature. This information was completed with an evaluation of the changes of brake
specific fuel consumption (BSFC), NO\textsubscript{x} and soot induced by a modification in swirl. NO\textsubscript{x} emissions in diesel engines are strongly dependent on local temperatures and local equivalence ratios during combustion. Increase in mean swirl rate will cause rapid increase in both in-cylinder pressure and temperature, thus promoting the formation of NO\textsubscript{x}. On the other hand, because swirl enhances mixing and produces a leaning effect, soot production is reduced and soot oxidation is increased, resulting in soot emission reduction. However, very high swirl rate increase in-cylinder heat transfer, resulting in lower mean gas temperature increases soot emission and decrease in NO\textsubscript{x} emissions.

2.3.3 Effects inlet air and cooling water temperature

Torregrosa et al (2006) assessed the potential of coolant and inlet charge temperature management for emissions reduction and performance improvement of DI diesel engines. The cold start experiments were performed with coolant temperatures of 15 °C and 80 °C. HC emissions were 25% lower and the NO\textsubscript{x} emissions 7% higher with higher coolant temperature. The NO\textsubscript{x} emissions were reduced with 20% when the air downstream of the turbocharger was chilled from 50 °C to slightly above 0 °C. Concerning the combustion, only the ignition delay is affected. Heat transfer to the walls, thermal efficiency, pressure and temperature undergo insignificant changes.

2.3.4 Effects of fuel properties

Broering et al (1974) conducted tests with several production diesel engines and one prototype low-emission diesel engine to determine the effect of fuel properties on exhaust emissions and engine performance. NO\textsubscript{x} levels were approximately 6% higher with the more volatile fuel. The volatility of the fuel depends on the boiling point. Both the production engine and low-emission prototype engine with comparable performance showed about 23%
higher NO\textsubscript{x} levels by switching from 47 to 33 cetane fuel. The same trend was observed on the turbocharged and naturally aspirated Vee engine, which averaged 25\% higher NO\textsubscript{x} levels with the low cetane fuel. The low cetane fuel increases the ignition delay. Noise level is seen to increase with decreasing cetane number. This increase in noise level with the lower cetane fuels is thought to occur as a result of the higher rate of cylinder pressure rise caused by longer ignition delay.

Seang-wock Lee et al (2002) studied the effect of fuel characteristics on spray and combustion in a diesel engine using KIVA-3 CFD code and concluded that the liquid penetration distance tends to become somewhat longer with the increased injection pressure at the nozzle due to the enhanced momentum. The mixture formation of the fuel and air was improved and the combustion duration became shorter as the injection pressure became higher.

2.3.5 Effects of fuel injection parameters

Ismet Celikten (2003) has experimentally investigated the effect of injection pressure on engine performance and exhaust emissions on a four cylinder four stroke turbocharged indirect injection diesel engine. Emission and engine performance values such as torque, power, brake mean effective pressure, specific fuel consumption, and fuel flow were measured for both full and part load by changing the injection pressure from 100 to 250 bar and at 50\%, 75\% and 100\% throttle positions of turbocharger. When the fuel injection pressure is low, fuel particle diameters will enlarge and ignition delay period during the combustion will increase. This situation leads to increase in pressure, so, NO\textsubscript{x} and CO emissions also increase since combustion process deteriorates. When injection pressure is increased fuel particle diameters will become small. Since formation of mixing of fuel to air becomes better during the ignition delay period, smoke level and CO
emissions will be less. But, if injection pressure is too high ignition delay become shorter. So, the possibilities of homogeneous mixing decrease and combustion efficiency falls down. Therefore, smoke is formed at the exhaust of the engine.

Yakup Icingur et al (2003) experimentally analyzed the effects of fuel injection pressure and fuel cetane number on direct injection diesel engine emission. Tests were conducted at full engine load on a four stroke four cylinder direct injection diesel engine with fuel cetane numbers of 46, 51, 54.5 and 61.5 at different injection pressures of 100, 200 and 250 bar by varying the engine speed from 1000 rpm to 4500 rpm. NO\textsubscript{x} is found decreasing for increase in engine speed with increase in cetane number. An increase in cetane number ensures a shorter ignition delay and hence better combustion. For an injection pressure of 150 bar, NO\textsubscript{x} emission decreases about 10\% when the fuel cetane number is increased for 46 to 61.

Rosli Abu Bakar et al (2008) conducted experiments on direct injection diesel engine at different fuel injection pressures and concluded that the effect of increasing injection pressure increases the fuel consumption both in fixed load - variable engine speeds and fixed engine speed - variable engine loads.

Aoyama et al (1990) conducted experiments on a single cylinder diesel engine to understand the NO\textsubscript{x} reduction mechanism for two effective methods: injection time retard and pilot injection. These mechanisms were characterized by measuring in-cylinder temperature distributions for the two methods with those of normal injection using high speed photographic technique. The NO\textsubscript{x} reduction by injection timing retard is realized by suppressing the development of high temperature regions, and by lowering the flame temperature throughout the chamber. By the application of pilot injection, both NO\textsubscript{x} and smoke were increased. From the temperature
distribution measurements, it was found that the pilot injection controls the temporal development of high temperature flame regions, while the injection timing change greatly controls their spatial development. Based on the study, they developed a novel method - active secondary injection to control the localized high temperature regions, different from either injection timing retard or pilot injection. Active secondary injection practised the same flame development as normal injection till the commencement of sub-injection, causing the abrupt drop of the temperature of localized high temperature regions around the nozzle hole. Active secondary injection reduces both NO\textsubscript{x} and smoke.

Can Cinar et al (2005) experimentally studied the effect of injection pressure and intake CO\textsubscript{2} concentration on performance and emission parameters in IDI turbocharged diesel engine. They concluded that specific fuel consumption deteriorates with increasing injection pressure and intake CO\textsubscript{2} concentration. NO\textsubscript{x} emission was found to be higher for moderate injection pressure at low CO\textsubscript{2} concentration. They also reported that NO\textsubscript{x} emission decreases drastically as the intake CO\textsubscript{2} concentration increases. Due higher heat capacity of intake CO\textsubscript{2}, it will absorb more combustion enthalpy and consequently reduces maximum in-cylinder temperature and NO\textsubscript{x} formation.

2.4 NO\textsubscript{x} CONTROL BY EXHAUST GAS RECIRCULATION

Exhaust gas recirculation (EGR) is a well known in-cylinder method to reduce NO\textsubscript{x} emissions, particularly on modern direct injection automotive diesel engines, and offers the possibility to decrease temperature during combustion. EGR is one of most effective techniques currently available for reducing NO\textsubscript{x} emissions in internal combustion engines. However, the application of EGR also incurs penalties like worsening specific fuel consumption and particulate emission. The decrease in NO\textsubscript{x} emissions
with the increase in EGR rate is the result of following effects (Maiboom et al 2008)

(i) The thermal effect: Increase of heat capacity due to higher specific heat capacity of recirculated CO\textsubscript{2} and H\textsubscript{2}O compared with O\textsubscript{2} and N\textsubscript{2} resulting in lower gas temperatures during combustion and particularly in lower flame temperature.

(ii) The dilution effect: Decrease of inlet O\textsubscript{2} concentration, whose principle consequence is the deceleration of the mixing between O\textsubscript{2} and fuel resulting in the extension of flame region. Thus, the gas quantity that absorbs the heat release is increasing. As a result, one consequence of the dilution effect is the reduction of local temperature that can be considered as a thermal effect too. Another consequence of the dilution effect is the reduction of the oxygen partial pressure and its effect on kinetics of the elementary NO formation reactions.

(iii) The chemical effect: The recirculated water vapor and CO\textsubscript{2} are dissociated during combustion, modifying the combustion process and the NO\textsubscript{x} formation. In particular endothermic dissociation of H\textsubscript{2}O results in a decrease of the flame temperature.

(iv) The inlet air temperature after mixing with recirculated gases increases with EGR ratio, thus reducing the inlet gas density and in-cylinder trapped mass. This temperature increase tends to increase NO\textsubscript{x} emission, although it is compensated by other effects of EGR listed above.

NO\textsubscript{x} emissions are mainly affected by two factors, the presence of oxygen in the charge and the reaction temperature, which promotes chemical
activity during both the formation and destruction stages. During the formation stage, the reaction temperature is close to the adiabatic flame temperature, which is a consequence of the oxygen concentration in the charge, the initial temperature and pressure and the local fuel-air ratio. EGR reduces the oxygen concentration in the charge and, consequently, the combustion pressure and temperature (Abd-Alla 2002).

Newhall (1967) theoretically studied the control of nitrogen oxides by exhaust recirculation through computer simulation of engine cycle. It was noted that, for low values of recycle fraction, the reduction of nitric oxide is nearly proportional to the amount of exhaust recycled. The influence of recycle temperature on nitric oxide reduction is minimal. It is generally recognized that dilution of the fuel-air mixture with any inert or noncombustible substance reduces flame temperature.

Tsunemoto et al (1980) experimentally studied the role of oxygen in intake and exhaust on NO emission with EGR on various types of engines, namely, direct injection engine, direct injection engine with turbo, indirect injection engine and gasoline engine. It was concluded that the effect of EGR on NO reduction in the diesel engine can be indicated as the result of a reduction of oxygen in the incoming charge regardless of engine types and operating conditions.

Yu and Shahed (1981) experimentally studied the effect of injection timing retard and EGR on emissions from a direct injection diesel engine. EGR and injection timing retard are both effective in reducing nitric oxide emissions at the expense of increasing smoke. The reduction of nitric oxide with EGR and injection timing retard is mainly related to the decreases of local atomic oxygen concentration and local temperature. The local atomic oxygen concentration is a function of local temperature and local molecular oxygen concentration. The local temperature is more important than the local
atomic oxygen concentration in determining the effectiveness of nitric oxide control technique. The formation of nitric oxide is virtually stopped at temperature below 2000 K. The experimental result indicate that for a well optimized direct injection diesel engine, the smoke-nitric oxide trade-off at constant charge-fuel ratio is fairly independent of engine speed, fuel rate, injection timing and exhaust gas recirculation rate. It was suggested that from the smoke-nitric oxide trade-off point of view, there is no difference in nitric oxide control technique between injection timing retardation and EGR.

Pierpont et al (1995) experimentally studied simultaneous reduction of particulates and NO\textsubscript{x} emission using multiple injections combined with EGR in a direct injection diesel engine. Particulates verses NO\textsubscript{x} trade-off at different EGR rates for a single, double and triple injection was presented. Single injection and double injection gave almost similar results, decrease in NO\textsubscript{x} emission and significant increase in particulate level. However, increasing EGR rate using the triple injection allows NO\textsubscript{x} to be reduced to very low levels while particulates are also controlled effectively. For example, 6% EGR and retarding the injection timing produces NO\textsubscript{x} as low as 2.2 g/bhp-hr while particulate is held to 0.07 g/bhp-hr when the EGR is increased to 10% the NO\textsubscript{x} level drops to 1.5 h/bhp-hr. However, the particulate at this point is somewhat above the 0.1 g/bhp-hr target.

Susumu Kohketsu et al (1997) conducted tests on turbocharged and intercooled heavy duty diesel engine using both low pressure route and high pressure route for EGR. The effect of increasing EGR rate on brake specific fuel consumption, NO\textsubscript{x} and smoke emissions on both high pressure route and low pressure are given in the Table 2.1. It was found that the NO\textsubscript{x} decreases, relative smoke increases and BSFC increases with increasing in EGR rate both low pressure and high pressure routes.
Table 2.1  NO\textsubscript{x} and smoke emissions and BSFC at different EGR rates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low Pressure Route (1320 rpm 80% Load)</th>
<th>High Pressure Route (1320 rpm 80% Load)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EGR percentage</td>
<td>EGR percentage</td>
</tr>
<tr>
<td>NO\textsubscript{x} g/h</td>
<td>0           12       22</td>
<td>0           8         12</td>
</tr>
<tr>
<td>Relative smoke BSU</td>
<td>0           0.2        3.5</td>
<td>0           2.5        4.5</td>
</tr>
<tr>
<td>BSFC %</td>
<td>100         103        108</td>
<td>100         110        113</td>
</tr>
</tbody>
</table>

For heavy duty diesel engines, the pressure at intake manifold is higher than the pressure at exhaust manifold. It is difficult to recirculate the exhaust gas to intake manifold by a simple pipe connection. Takayuki Yamada et al (1998) developed a new EGR system for heavy duty engines, which has a recirculation port for exhaust gas to enter between the outlet of impeller and inlet of diffuser of the compressor. This is called as EGR turbo. They conducted test on a six cylinder, 239 kW heavy duty engine fitted with the new EGR turbo and concluded that it is possible to reduce 26% of NO\textsubscript{x} emissions without a severe increase in specific fuel consumption.

Timothy Jacob et al (2003) conducted tests on heavy-duty diesel engine fitted with the variable geometry turbocharger to understand the effect of EGR on performance and emissions at three different conditions, 1200 rpm, 50% load, 1200 rpm, 20% load and 1800 rpm, 50% load. The engine thermal efficiency found to decrease with the amount of EGR at all three cases investigated. Clearly, the deterioration of brake thermal efficiency with increasing EGR is non-negligible, and is more pronounced at 1200 rpm, 50% load conditions that at the other two sets. The two main causes for decreasing brake thermal efficiency are attributed to decreased combustion work and
increased pumping work. As expected, the NO\textsubscript{x} emission decreases with increase in EGR rate in all three types of tests. Based on the advanced in-cylinder visualization techniques, flame temperature images are obtained. The decrease in flame front temperature with increasing EGR rate was explained and concluded that the thermal EGR mechanism plays a dominant role in the observed reduction in flame temperature, and hence NOx emissions.

2.5 \textbf{NO\textsubscript{x} CONTROL BY WATER INJECTION}

2.5.1 \textbf{Introduction}

Water injection into the combustion chamber of diesel engine is one of the methods simultaneously to improve the fuel efficiency and pollutant emissions. The presence of water in the combustion chamber along with reactants influences the physical and chemical kinetics of combustion. During combustion the vaporized water reduces the flame temperature and resulting in higher OH radicals concentration controlling the NO and soot oxidation. The water may be introduced in the combustion chamber of diesel engine by any one of the methods mentioned below:

(i) Water injection into the air intake manifold during the suction stroke along with the air through a separate injector

(ii) Water injection directly into the engine cylinder using a separate injection pump and injection nozzle.

(iii) Water injection directly into the engine cylinder making an emulsion with the fuel and through the fuel injection nozzle.

The benefits of introducing water into the diesel engine combustion chamber are:

(i) Reduction in flame temperature
(ii) Higher concentration of OH radicals

(iii) Secondary atomization through micro-explosion

(iv) Improved combustion efficiency

(v) Reduction in NO\textsubscript{x} and soot emissions

(vi) Reduction in cooling loss owing to lower flame temperature

### 2.5.2 Water injection through intake manifold

Sundaram et al (2003) investigated the performance of a single cylinder diesel engine by injecting the water in the intake manifold using a separate injector and auxiliary pump arrangement. It was reported that the injection of water in the intake manifold reduces the cycle temperature which may be attributed to the reduction of NO\textsubscript{x} emissions. The reduction NO\textsubscript{x} emission found to be proportional to the quantity of water injected. It was also found that there were not much variation in emission of CO, which indicates that the presence of water particles in the air do not affect the combustion as far as incomplete burning is concerned. The heat carried away by cooling water was calculated and it was found that as the water-fuel ratio is increased the heat carried away by the coolant water is decreased which reduces the requirement of cooling water to the engine. The exhaust gas temperature was found to decrease with increase in water-fuel ratio. There is small reduction in brake thermal efficiency with quantity of water injection. Higher quantity of water injection is required compared with other two methods and liquid water present after combustion can contaminate the oil and increase engine wear.

Ryu et al (2004) experimentally studied the effect of water injection on the performance and exhaust emission in an IDI diesel engine. The distilled water is injected in the intake manifold using a two-hole gasoline injector. It was reported that the formation of NO\textsubscript{x} was significantly suppressed by decreasing the gas peak temperature during the initial
combustion process because the water played a role as a heat sink during evaporation in the combustion chamber, but the smoke was slightly increased with increased water amount. However, a simultaneous reduction in smoke and NOx emissions was obtained when the fuel injection is retarded.

2.5.3 Direct water injection in the engine cylinder

Mello et al (1999) studied the prediction of NOx emission from direct injection diesel engines with water/steam dilution with a semi-empirical model called Characteristic Time Model (CTM). The introduction of water/steam into the combustion chamber reduces the rate of NO formation in two ways. First, water/steam can reduce the O-atom concentration through

\[ \text{H}_2\text{O} + \text{O} \rightarrow \text{OH}^+ \]  

(2.6)

where OH radicals does not combine effectively with molecular nitrogen to form NO. Second, the introduction of water reduces the flame temperature, which in turn reduces the rate of NO formation. The later effect is thought to be the important reduction route. It was also concluded that the percentage of reduction of NOx is higher is at higher load conditions.

Bedford et al (2000) numerically studied the effect of direct water injection into the engine cylinder using the same fuel injection nozzle with the help of KIVA-3V CFD program to understand the in-cylinder process and NOx reduction. Experiments for diesel fuel/water injection were performed with a prototype Bosch duel feed injector, where the stratification of the fuel and the water can be controlled. The volumetric flow rate was kept constant in the study. The presence of water in the fuel spray increases both the liquid and vapor penetration. Opposing trends for fuel consumption and soot production are observed experimentally for the 86% and 44% load points as the water/fuel ratio increases. At 44% load conditions, engine out soot, engine
out NO$_x$ and specific fuel consumption decrease with increasing water percentage. At 86% load conditions, engine-out soot and specific fuel consumption increase with increasing water percentages, though engine-out NO$_x$ values decrease with increasing water/fuel ratios. Both load cases showed considerable ignition delay when water was added to the spray. It is also reported that the peak temperatures in the domain are reduced by two localized phenomena. First, vaporization of liquid water decreases the internal energy proportional to the vaporization enthalpy of the liquid water. Secondly, higher concentration of water vapor increases the specific heat of the gas.

Susumu Kohketsu et al (1996) conducted experiments on a six cylinder direct injection diesel engine injecting water directly into the engine cylinder using a stratified fuel-water injection system developed by Mitsubishi Heavy Industries. The water injection system pre-supplies water so that the layers of fuel, water and fuel will be physically placed in that order in the injection nozzle. This occurs within the interval between injections, and water and fuel layers are injected into the cylinder by a single injection. The water injection results in increased penetration and the flame temperature are lowered, which reduces particulate matter, NO$_x$ and other exhaust emissions. The major advantage of the system is that the optimum water and fuel injection quantities can always be maintained according to the engine operating conditions, which makes the system ideally suited for an automobile. From all the experiments varying engine speed, load and fuel injection timing, the magnitude of NO$_x$ reduction is nearly 1:1 by percentage. The maximum water injection quantity was determined as the highest value for which combustion was stable and for which cyclic variation in combustion became severe if any more water was injected.
2.5.4 Water injection in the form of emulsion

Jamil Ghojel et al (2005) developed a heat release model for the combustion of diesel oil emulsion in DI diesel engine using single zone model. They reported that the fuel burning rate during the premixed phase is lower for the diesel oil emulsion because of the reduced amount of diesel fuel being injected during the ignition delay phase. But the burning rate during the diffusion phase is almost the same for both fuels despite the late start of combustion of the diesel oil emulsion.

Jamil Ghojel et al (2006) conducted experiments on four cylinder four stroke cycle diesel engine and concluded that the brake thermal efficiency for diesel oil emulsion is somewhat higher over the test range. NOx emissions are reduced by 29-37% when operating on emulsified fuel. HC emissions exhibited large reduction in the range of 60-90%. They also reported that the pressure is slightly lower during the compression stroke indicating lower compression work and the pressure is slightly higher during the expansion stroke for the diesel oil emulsion. The temperature on the other hand is lower over the combustion and expansion processes under all operating conditions with greater temperature decreases at low loads and high speeds. The heat absorbed by the addition of water attributes the reduction in combustion temperature.

Niko Samec et al (2002) numerically studied the water/oil emulsified fuel combustion in diesel engine using n-heptane as fuel for a better understanding of atomization process influenced by vaporized water droplets. It was reported that the primary spray fuel droplets are further divided as a result of explosive vaporization caused by the rapid heating of water dispersed within the individual fuel droplets. The internal water droplets are converted into steam by absorbing the heat in the combustion chamber. The vaporization produces a rapid expansion of the surrounding oil
droplets, fragmenting the oil into a vast number of smaller fuel droplets representing very intensive micro explosion. The process is called as secondary atomization. Micro explosion of the emulsion fuels seem to enhance the mixing of the fuel with the surrounding air for faster and more efficient combustion also resulting in a higher heat release gradient at the beginning of the combustion process. It has been concluded that the presence of water vapor in reactants influences the physical and chemical kinetics of combustion and has beneficial effects on the rate of heat release history and reduction of pollutants emissions. During combustion vaporized water reduces the flame temperature, changes the chemical composition of the reactants, resulting in higher OH radicals concentration controlling the NO formation rate and soot oxidation. The experimental results revealed that 20% and 18% reduction in NO\textsubscript{x} and 68% and 75% reduction in soot at 10% and 15% water in the emulsion respectively.

Armas et al (2005) conducted test in a Renault F8Q turbocharged intercooler IDI engine with water-emulsified fuel. Better mixing air and fuel was observed when emulsion was used as fuel in diesel engine. It was reported that the improvement in mixing of fuel and air is caused by two phenomena, an additional momentum in jet behaviour and internal droplet micro explosion of water which produce a secondary atomization. The micro explosion is induced by the volatility difference between the water and the fuel. At all load conditions, the NO\textsubscript{x} and particulate emissions decreased with engine load. The reason being the vaporization and sensible heats of water reduce the local adiabatic flame temperature and thus NO\textsubscript{x} formation. The dissociation of water causes increased amount of OH radicals which reduces the formation of soot because high radical concentrations promote carbon oxidation to CO and CO\textsubscript{2}, thereby limiting carbon availability for the formation of soot precursors. Also, when the emulsified fuel was used,
improvement in specific fuel consumption and thermal efficiency were obtained due to the reduction in heat losses.

Abu-Zaid (2004) conducted several diesel engine tests using water/oil emulsion. The total duration of burn, the volume of the oil residue and the burn efficiency decrease with increasing water content of the emulsion in a laboratory scale tests for combustion of water-in-oil emulsion of diesel. It was found that the best performance of the machine with respect to efficiency and NO\textsubscript{x} and soot emissions was when operating at 20% water by volume. It was found that the addition of water to diesel fuel has a great influence on reducing the heat flux, the metal temperature and the thermal loading of combustion chamber components. The water-in-diesel emulsion consisting of diesel fuel and ordinary tap water, were prepared in an electrical blender at a speed of about 1500 rpm. To stabilize the emulsions, a 2% by volume surfactant mixture consisting of Span 80 and Tween 80 was used. It was found that as the percentage of water in the emulsion increases, the torque produced increases. This may be attributed to the additional force on top of the piston provided by the pressure exerted by the steam. As the percentage of water in the emulsion increases, an amount of diesel is displaced by an equal amount of water. This means that less diesel fuel is actually contained within each volume of the emulsion, so BSFC decreases. The water/oil emulsified fuel increases the brake thermal efficiency of internal combustion engine. The maximum increase in brake thermal efficiency occurs when 20% water in the emulsion is used, and this is due to the fact that the BSFC is at its minimum value. It was found that as the percentage of water in the emulsion increases, the exhaust temperature decreases. It may be concluded that the addition of water in the form of emulsion improves the combustion efficiency in the diesel engine, hence the performance of the engine. As the water percentage in the emulsion increases
up to 20% by volume, the engine torque, power, and brake thermal efficiency increase.

Hsu (1986) investigated the combustion of water-in-diesel emulsion in a medium speed diesel engine. The ignition delay found to increase with increase in water amount in the emulsion. The ignition delay changed almost linearly up to about 30% water content. Smoke and NO\textsubscript{x} emissions decrease as the water amount in emulsion is increased (up to 30% water). Due to the overall shortening of combustion duration by introducing water into fuel, fuel saving can be achieved if injection timing is optimized. The pressure rise ignition delay increases almost linearly with water content within the range of investigation. The maximum cylinder pressure did not change significantly at the loads of investigation.

Park et al (2000) experimentally studied the combustion characteristics of emulsified diesel in a rapid compression and expansion machine. They reported that the reduction in the specific fuel consumption with water emulsified diesel is attributed to the following effects:

(i) the formation of finer spray owing to rapid evaporation of water (micro explosion)

(ii) more air entrained in the spray owing to increased momentum and penetrating force

(iii) more fuel burning in premixed combustion owing to a longer ignition delay

(iv) an increase in the local excess air ratio owing to the water content

(v) a decrease in the cooling loss owing to a lower flame temperature
(vi) suppression of thermal dissociation

(vii) more combustion product gas due to water vapour

Although the ignition delay increases with water oil ratio, the overall combustion characteristics are similar to those of the diesel fuel. The emulsion fuels require less pumping work than the diesel fuel owing to a longer ignition delay during the compression stroke. High speed photographs were taken during combustion. Photographic images for ignition and flame propagation of 20 W/O fuel are not much different from those of the diesel fuel. The 20 W/O fuel showed a minor reduction in flame luminosity, while the 40 W/O fuel showed remarkable reduction in flame luminosity with the longest ignition delay. The flames of 40 W/O fuel were dark red, while those of the diesel fuel were bright yellow. This means that the flames of the emulsion fuel were less sooty and at a lower temperature owing to its water content. It is also reported that ignition location of the emulsion fuel are different from those of the diesel fuel. Ignition occurs in the middle of the combustion chamber with the diesel fuel, while it occurs in the bottom region or at multiple points in the middle simultaneously with 40 W/O fuel. The images of 20 W/O fuel showed that strong micro explosions occur in the bottom region of the luminous flames near the spray tip. Micro-explosion of emulsion fuels seems to enhance mixing of the fuel with the surrounding air for faster and more efficient combustion.

Park et al (2001) conducted experiments on six cylinder four stroke cycle diesel engine and concluded that the fuel with a larger emulsion ratio results in a longer ignition delay and a premixed combustion phase. Both the maximum rate of pressure rise and the maximum heat release rate increases as combustion occurs more impulsively with the fuel of a larger emulsion ratio. Higher content of water weakens luminous flames and reduces the peak
temperature during the diffusion-controlled combustion phase. It then leads to a lower peak pressure and a lower level of NO\textsubscript{x} emission.

Kweonha Park et al (2004) studied the effect of water emulsified fuel on a motorway-bus diesel engine. They reported that the water in oil was quickly evaporated by micro-explosion into extremely tiny droplets; this would make the water drops not to reach directly to the combustion chamber wall, so there would be no corrosion on the cylinder surface. The engine parts of an injection system and an intake and exhaust system have no damage and trouble during the 500 hour durability test. It was concluded that the maximum cylinder pressure increases and ignition delay period becomes longer. The specific fuel consumption increases at a low load region, similar at a medium load region and decreases at a full load region. NO\textsubscript{x} and PM were reduced about 12 and 33% respectively in the D-13 test mode.

Chausalkar et al (2008) studied the performance of engine oil using both diesel and bio diesel blend (B5) as fuel. They concluded that the difference in change in viscosity of lubricating oil using diesel and B5 as fuel is negligible and is able to maintain viscosity throughout the test.

The various results suggested that the water injection into the combustion chamber of diesel engine has the potential to reduce the NO\textsubscript{x} and soot simultaneously and to improve the brake specific fuel consumption. Among the various methods of water injection, the water emulsion injection using the same fuel injector seems to be simple method and it does not require any engine modification or retrofitting.

2.6 NO\textsubscript{x} CONTROL BY EXTERNAL METHODS

NO\textsubscript{x} emission may be controlled by modifying the combustion process to prevent the initial formation of NO\textsubscript{x} or by post combustion exhaust
gas treatment to remove the NO after formation. Exhaust gas treatment has the advantage relative to the combustion modification in NO\textsubscript{x} emissions and it can be retrofitted to existing plants. Exhaust gas treatment includes many processes. Two of these processes are Selective Non Catalytic Reduction (SNR) and Selective Catalytic Reduction (SCR).

The SCR process is more complicated and expensive which uses a surface to catalyze for nitric oxide removal. It requires high upstream pressure to force the flow through the catalyst.

The SNR process relies on homogeneous gas phase reaction. The processes are simpler, only injection of the exhaust at a specified temperature. SNR process has shown significant NO removal at fraction of cost of SCR. Currently three processes are utilized for SNR removal of NO, viz., Injection of Ammonia, Injection of Urea and Injection of cyanuric acid. When the ammonia is injected in the exhaust stream the NO is oxidized into N\textsubscript{2}O, the NO removal is increased and the temperature for this removal level is decreased. For further increase in ammonia concentration, the N\textsubscript{2}O concentration in the exhaust stream is increased and in general the overall NO removal is less.

2.7 NO\textsubscript{x} CONTROL BY FUEL ADDITIVES

Fuel additives are added as a mixture with fuel and their chemical stability in the mixture must be ensured for all conditions. The use of fuel additives should not increase the emissions of environmentally harmful substances. Chlopek et al (2005) reported that 0.05% addition of organomagnesium additive causes almost a linear decrease of hydrocarbon emissions and maximum decrease is up to 20% in compression ignition engine. On the other hand, Nibin et al (2005) reported that 5% addition of diethyl carbonate (DMC) with diesel decreases the smoke level, particulate
matter and NO\textsubscript{x} emission and a marginal increase in brake thermal efficiency in a diesel engine.

NanoXXL fuel additive is used in this research which is hundred percent organic fuel catalyst enabled with nano-biotechnology. The ash content is 0.02\%, Total organic matter and moisture is 99.98\%, and flash point is greater than 200 °C. The additive is non toxic and non hazardous.

The summary of various technique used to control NO\textsubscript{x} is given in Table 2.2.
### Table 2.2 Summary of NOx control techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>System Modification</th>
<th>% Reduction of NOx</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection Retardation</td>
<td>Engine adjust</td>
<td>&lt; 30%</td>
<td>Relatively simple to implement, increase SFC</td>
</tr>
<tr>
<td>Increased injection pressure</td>
<td>New fuel pump, injector and fuel line required</td>
<td>&lt;10 %</td>
<td>Increase the cost of fuel injection equipment, increase SFC</td>
</tr>
<tr>
<td>Direct Water injection</td>
<td>New cylinder head, injectors, cam shafts and fuel and water system</td>
<td>&lt;40%</td>
<td>Increase the cost of the injection equipment</td>
</tr>
<tr>
<td>Water emulsion injection</td>
<td>N/A</td>
<td>&lt;40%</td>
<td>Stability of emulsion</td>
</tr>
<tr>
<td>Exhaust Gas Recirculation</td>
<td>Valve and pipe arrangements</td>
<td>&lt;30%</td>
<td>Increased cost of the engine</td>
</tr>
<tr>
<td>Selective Catalytic Reduction</td>
<td>External modification to engine</td>
<td>&lt;95%</td>
<td>Urea storage required onboard, Ammonia slippage problems, additional cost to procure and operate</td>
</tr>
<tr>
<td>Fuel additive</td>
<td>No modification in the engine</td>
<td>20%</td>
<td>Easy to apply</td>
</tr>
</tbody>
</table>