2. CHAPTER 2: LITERATURE REVIEW

This chapter is describes literature review especially related to diesel combustion, emission formation, diesel exhaust after-treatment technologies and role of additives used along with diesel fuel. Alcohol as a fuel and new combustion technologies like early direct injection, PREDIC and premixed techniques are discussed in great details.

2.1 INTRODUCTION

The purpose of internal combustion engine is to transform chemical energy in fuel into thermal energy by combustion or oxidation inside the engine. The working fluid is air-fuel mixture before combustion and combustible gases after combustion. Since the combustible gases only undergo an expansion of work generation, therefore, it is named as an internal combustion engine. Nevertheless, combustion product and fluid undergoes expansion during energy transformation is different in case of external combustion engine, i.e., closed-cycle gas turbine and steam sterling engine.

J. J. E Lenoir developed first engine in 1860 which uses coal-gas air mixture without any compression mechanism. Induction of charge and air takes place in the first and then charge was ignited by the spark, subsequently expansion produces work output. This was the first commercial engine; nearly 5000 engines were sold during 1860 to 1865.

Nicolaus A. Otto and Eugen Langen invented an atmospheric engine operated up to 11% efficiency in 1867, which is considered as a more successful attempt than previous one. Later on, to overcome the low efficiency and excessive weight shortcomings, four stroke prototype engines was built in 1876 by Otto, this is considered as one of the great breakthroughs in the engine invention, almost 50,000 units were sold till the end of 1890.

Rudolf Diesel a German Engineer had come out with a totally different concept of initiating combustion, injecting liquid fuel into the hot air environment results into the start of combustion, no spark-plug is required.
The advantage was demonstrated in terms of efficiency, it was double than other engine. Later on it was named as a diesel engine and becomes inevitable as an engine for all sphere of applications.

2.1.1 Combustion in Diesel Engine

The liquid fuel is injected at very high velocities into the combustion chamber through one or more orifices or nozzles in the injector tip. The fuel injection mechanism transforms the large pressure energy of the fuel into higher kinetic energy and the liquid fuel is atomized into small drops. The next stage of combustion begins with entertainment of fuel particles with air, the vaporization of the atomized fine fuel particles started. The latent heat of vaporization is given off by compressed air in the cylinder which has already attained high pressure and temperature due to compression. However, the cylinder pressure and temperature are above the fuel’s auto-ignition point. The three stages of combustion, atomization, and vaporization, fuel air mixing and burning are repeated till the last portion of fuel injected into the cylinder. High speed photography studies was carried out under normal operating conditions and is shown in Fig. 2.1 (Heywood 1988).

![Image](image_url)

**Figure 2.1**: Combustion of four sprays in DI diesel with swirl (Heywood 1988)

From the above discussions it is clear that the fuel enters the cylinder as a liquid and ignition does not start until a portion of it has vaporized and mixed with air. As a
consequence, the flame develops under extremely non-uniform conditions of fuel in the air. Even though the overall fuel-air ratio is always lean in a diesel engine, there are large variations in the equivalence ratio across the combustion chamber at both a large and small scale (Stone 1999). This heterogeneous distribution of fuel within the cylinder and the corresponding heterogeneous burning process are the hallmark of diesel combustion. They are also the main reasons why diesel engines have a tendency to emit high levels of their most prominent pollutants, namely PM and NOx.

2.1.1.1 Stages of DI Diesel Engine Combustion

Fig 2.2 shows a typical heat-release diagram which depicts four different stages of DI diesel combustion.

![Figure 2.2: Typical DI engine heat-release-rate diagram (Heywood 1988)](image)

**Ignition delay (ab):** The liquid fuel is injected into the cylinder at the end of compression. Injection is done at high pressures which lead to form a fuel jet and it breaks liquid fuel into small droplets and starts vaporizing in the hot-air environment. The period between the start of fuel injection into the cylinder and the start of combustion is known as an ignition delay. However, combustion does not start until a visible flame or a measured in-cylinder pressure rise can be detected (Taylor 1985). Ignition delay depends on several parameters like injection pressure, injection timing, and cetane number of fuel. Further, fuels with poor auto-ignition properties exhibit longer delay periods.
Rapid combustion (pre mixed combustion (bc)): The mixture after completion of the delay period, mixing of fuel vapor and air, and subsequent chemical reactions within the charge lead to ignite spontaneously. It results in a rapid rise in the in-cylinder pressure and temperature due to combustion. Therefore, the rate of burning and duration of the premixed phase are closely related to the extent of the delay period. The cloud of charge, which ignites spontaneously, results in a very sharp increase in the cylinder pressure and may lead to knocking sound. This depends on the other parameters in diesel engines.

Thus, the premixed phase is characterized by high rates of pressure increase and heat release. It is in the high temperature, fuel-rich regions inside this premixed flame, thus soot precursors are originated before the soot itself is nucleated and grown in the richer regions of the subsequent diffusion flame.

Mixing-controlled combustion (cd): After completion of the premixed combustion phase, the remaining unburned portions of the fuel get compressed and preparation time (ignition delay) gets shortened. Therefore, in the mixing controlled phase, the combustion reactions are controlled by the rate at which fuel-air mixture is formed, or diffusion of fuel into air or vice-versa takes place. This phase is also known as the diffusion combustion phase. The diffusion flames are also responsible for the formation and growth of soot particles.

Late combustion phase (de): As described by Heywood (Heywood 1988), due to a fall in the temperature of the in-cylinder gases, the reaction rates are slow down during this phase. As the last stage of expansion there is a possibility that a small fraction of energy yet to be released from fraction of fuel energy associated with the soot particles and fuel-rich gases. Therefore a small fraction of fuel is burnt, and oxidation of soot and fuel-rich combustion products can also take place. This is also known as the late combustion phase.

2.1.2 Diesel Engine Exhausts Emissions

In spite of the advantages of using compression ignition engines (high thermal efficiency and durability) there are drawbacks in the case of emissions. As mentioned
previously, NOx emissions still a one of the major problem from diesel engines. Generally, NOx consists mainly of nitrogen monoxide or nitric oxide (NO) and nitrogen dioxide (NO2). Compared to spark ignition engines, diesel engines produce more nitrogen oxides (NOx) and Particulate Matter (PM). However, diesel engines emit relatively lower carbon monoxide (CO) and unburned hydrocarbons (UHC). Due to the hazardous effects on the environment and on human health of these pollutants, legislation norms have been proposed for all passenger cars in countries like Japan, USA (EPA 2012) and EU for these pollutants.

2.2 NO FORMATION IN CI ENGINES

In diesel engines combustion starts after completion of the ignition delay. Fuel and air that are mixed together form flammable mixtures around stoichiometric compositions. In the premixed combustion phase the net heat release becomes positive and the first peak is observed, in the mixing-controlled combustion phase, also combustion occurs in the region where the local equivalence ratio is close to stoichiometric. NO formation rates depend on the local equivalence ratio and temperature.

Chemical pathway for no formation

NO is formed during combustion. The mechanism of its formation is explained below (Mellor and Mello 1998):

- Thermal
- Prompt
- Nitrous oxide

2.2.1 Thermal Mechanism

NOx formation occurs in the hot combustion gases at sufficiently high temperatures (>=1800 K). It describes the NO formed as atomic oxygen reacts with nitrogen in the presence of free radicals (O, N, H, and OH). The Zeldovich mechanism (1946) clearly explains this by the following reactions (Heywood 1988; Stone 1999)

\[
\begin{align*}
O + N_2 & \rightarrow NO + N \quad \text{Eqn. (1.1)} \\
N + O_2 & \rightarrow NO + O \quad \text{Eqn. (1.2)} \\
N + OH & \rightarrow NO + H \quad \text{Eqn. (1.3)}
\end{align*}
\]
Lavoie et al. (Lavoie and Heywood 1970) had introduced the third reaction (Eqn. 1.3) whereas the first two were suggested by Zeldovich.

The formation of NO mainly occurs in the high temperature zone, in excess oxygen regions through reaction (Eqn. 1.1), leaving one free atom of nitrogen. It can be later combined with oxygen (Eqn. 1.2) or with the OH radical (Eqn. 1.3), already present in the combustion process, to form nitrogen monoxides.

The already formed NO during combustion can be further converted to NO₂ by reaction (Eqn. 1.4) as given below. Afterwards, it can be also be converted back to NO by reaction Eqn. 1.5 (Heywood 1988)

\[
\begin{align*}
\text{NO} + \text{HO}_2 & \rightleftharpoons \text{NO}_2 + \text{OH} \quad \text{Eqn. (1.4)} \\
\text{NO}_2 + \text{O} & \rightleftharpoons \text{NO} + \text{O}_2 \quad \text{Eqn. (1.5)}
\end{align*}
\]

From the environmental and health point of view, NOₓ are harmful. They can destroy the ozone in the atmosphere. Moreover, favorable conditions (presence of ammonia or moisture) lead to the formation of nitric acid vapour which is affecting human health, mainly because of respiratory and heart diseases (EPA 2013).

2.2.2 Prompt Mechanism

NO is formed in the flame as CH, CH₂ etc. The CH, CH₂ radicals react with N₂ to give intermediate species, HCN and CN, by the reactions (Mellor and Mello 1998):

\[
\begin{align*}
\text{CH} + \text{N}_2 & \rightleftharpoons \text{HCN} + \text{N} \quad \text{Eqn. (1.6)} \\
\text{CH}_2 + \text{N}_2 & \rightleftharpoons \text{HCN} + \text{NH} \quad \text{Eqn. (1.7)}
\end{align*}
\]

The thermal NO formation in the burnt gas behind the flame front is much higher as compared to any NO in the flame front. Therefore, prompt NO formation is small in the case of CI engines. However, prompt NO may be significant (Hochgreb 1998) in diesel engines with EGR.

Nitrous oxide mechanism: In diesel engines, high pressure combustion involves decomposition and formation reactions. Therefore, the Zeldovich mechanism alone does not predict exact NO formation. N₂O formation and decomposition may also lead to significantly amounts of NO generation. This could be generated in both premixed and diffusion-controlled combustion (Mellor and Mello 1998) phase.
\[ \text{N}_2\text{O} + \text{O} \rightleftharpoons 2\text{NO} \] \hspace{1cm} \text{Eqn. (1.8)}
\[ \text{N}_2 + \text{O} + \text{M} \rightleftharpoons \text{N}_2\text{O} + \text{M} \] \hspace{1cm} \text{Eqn. (1.9)}

By adding the reaction:
\[ \text{O}_2 + \text{M} \rightleftharpoons 2\text{O} + \text{M} \] \hspace{1cm} \text{Eqn. (1.10)}

All the above reactions can be balanced so that the overall reaction is:
\[ 2\text{O}_2 + 2\text{N}_2 \rightleftharpoons 4\text{NO} \] \hspace{1cm} \text{Eqn. (1.11)}

### 2.2.3 NO\textsubscript{2} Formation

NO\textsubscript{2} emissions from SI engines are almost negligible. Since, NO is of the order of several thousand of ppm while NO\textsubscript{2} is approximately 60 to 70 ppm. However, in case of CI engines the fraction of NO\textsubscript{2} emissions typically varies from 10 to 30% of the total NO\textsubscript{x} emissions. Hilliard et al. (Hilliard and Wheeler 1979) and Merryman et al. (Merryman and Levy 1975) presented the following mechanism for the formation of NO\textsubscript{2} in diesel engines, in which NO is converted to NO\textsubscript{2} by the reaction of NO with HOO\textsuperscript{-} radicals. The reactions are as follows

\[ \text{NO} + \text{HO}_2 \rightleftharpoons \text{NO}_2 + \text{OH} \] \hspace{1cm} \text{Eqn. (1.12)}

In the post-flame region, NO\textsubscript{2} reacts with atomic oxygen and is converted into NO and O\textsubscript{2} (produces NO again):

\[ \text{NO}_2 + \text{O} \rightleftharpoons \text{NO} + \text{O}_2 \] \hspace{1cm} \text{Eqn. (1.13)}

If the high turbulence prevails in the engine, mixing of the burnt gases with colder air or air-fuel mixture may quench the decomposition reactions, so it leads to suppression of the conversion of NO\textsubscript{2} into NO. In diesel engines at low loads, the ratio of NO\textsubscript{2}/NO becomes high due to the freezing of the decomposition reactions (Hilliard and Wheeler 1979).

The fuel and air first react in the fuel-rich mixture, leading to soot formation, and then this rich mixture burns out in a high-temperature diffusion flame at the jet periphery, leading to NO\textsubscript{x} formation. The combustion model proposed by Dec (Dec 1997) suggested premixed combustion occurs in the rich mixture (\(\phi = 2\) to 4). Thus, neither thermal NO nor prompt NO is likely to be formed in significant concentrations during
premixed combustion. Most of the NO is formed during mixing controlled combustion phase. The NO formation region is around the periphery of the spray.

2.3 Particulate Matter

PM is defined as any solid or liquid (excluding water) that can be collected on a filter when filtering the diluted exhaust. Also, the temperature of the filtering is not higher than 52 °C. Particulate matter besides NO$_x$ emissions are a major pollutant from combustion in compression ignition engines. Particulate matter results from incomplete combustion of fuel hydrocarbon. Also some of it is contributed by the lubricating oil (Heywood 1988). Diesel particulates consist principally of combustion generated carbonaceous materials (soot) on which some organic compounds have been absorbed. They are basically a complex mixture of elemental carbon, hydrocarbons, sulfur compound and ash. And they may vary greatly in size, composition, solubility and in toxicity (Burtscher 2005). The model of soot formation in diesel spray has been proposed by Dec (Dec 1997) and is illustrated in Figure 2.3.

![Figure 2.3: Dec combustion model for DI diesel engine. (Dec 1997)](image)

Generally, the particles from diesel combustion can be divided as carbonaceous (soot particles), and volatile fraction (SOF/VOF).
The solid fraction consists of:
- carbonaceous agglomerates (soot)
- inorganic ash, while

The volatile fraction consists of:
- organic compounds (hydrocarbons)
- inorganic compounds (sulfuric acid and sulfates)

In the later part of combustion, sulfur usually reacts with water vapor to form sulphuric acid, and together with SOF/VOF may start to condense on the solid carbon particles at lower temperatures. In Figure 2.4 a detailed diagram of particulate matter composition is presented accordingly to the work done by Kittelson (Kittelson 1998).

![Figure 2.4: Soot particles composition (Kittelson 1998).](image)

The solid fraction is responsible for most of the total particle mass, and its constituents (soot and ash) are formed directly by the combustion process. Soot has been the foremost and also the most characteristic pollutant emitted by diesel engines. Soot formation process starts when the fuel and air first react in the fuel-rich mixture of the premixed flame. Rich mixture regions have large hydrocarbon molecules from the fuel undergoing thermal decomposition (cracking) due to the high temperatures and the relative absence of oxygen. This process is analogous to a pyrolysis process and produces compounds that are precursors to soot formation. During combustion,
the formation process starts with a fuel molecule (12 to 22 carbon atoms and an H/C ratio of about 2) and ends up with particles of about hundred nanometers in diameter, composed of spherules 20 to 30 nm in diameter each containing some $10^5$ carbon atoms and having an H/C ratio of about 0.1 (Heywood 1988). Soot precursors include unsaturated hydrocarbons, such as ethylene, acetylene and polycyclic aromatic hydrocarbons (PAHs). Typical conditions are characterized by temperatures between about 1000 and 2800 K, and pressures of 50 to 100 atm. (Heywood 1988). As on the periphery of the spray, soot particles start to oxidize and it depends on the diffusion of reactants to and products from the surface as well the kinetics of the reaction. Estimates have suggested that over 90% of the soot eventually oxidizes. A higher rate of oxidation decreases tail pipe soot emissions.

The measurement of particulate matter can be done in the exhaust tail pipe by

- Smoke meter for smoke opacity measuring or the filtration method, smoke number (SN) - Bosch Scale
- Transmission electron microscopy (TEM)-particle size, aggregate size and morphology of soot particles

However, increasing concern due to the hazardous effect of PM emission on human health (causes asthma, lung cancer, cardiovascular issues, and in extreme cases, premature death) various means are adopted to cut it down.

- Common rail and unit injection system - high pressure, electrically controlled fuel injection system capable to precise control of the fuel and air mixing process in the cylinder which, in turn, reduces PM (smoke in particular) from the tail pipe
- Oxidation catalysts and particulate traps - effective only at high temperature (500-600°C)
- Fuel oxygenates:
  - fuel-borne oxygen shifts the products of thermal cracking by displacing the long carbon chains that exist in regular diesel fuel
- during the premixed combustion phase, oxygenates can dramatically increase the concentration of free radicals such as O, OH, and HCO. These radicals help oxidize carbon to CO and CO$_2$. As a result, the availability of carbon to form soot precursors is decreased.

- high concentrations of those free radicals (OH in particular) can also oxidize soot precursors in the diffusion flame, limiting the formation and growth of PAHs and inhibiting the inception of soot particles.

Benvenutti et al. (Benvenutti and Marques 2005) reported that the methyl radical (CH$_3$) is also an important precursor for the formation of soot-oxidizing radicals, such as OH.

### 2.4 Unburned Hydrocarbons and Carbon Monoxide

The unburnt hydrocarbon emissions from compression ignition engines are comparatively much smaller than the spark-ignition engines. As the boiling points of hydrocarbon compounds associated with diesel fuel are higher, they have higher molecular weights than gasoline. This results in complex unburned hydrocarbon products. Diesel engine fuel spray shows wide variation in the equivalence ratio which occurs from the spray cone to the outer boundary. The fuel close to the spray boundary has low equivalence ratio ($\phi=0.3$) which is leaner than the lean limit of combustion. Therefore, it will not auto-ignite or sustain a fast reaction front. The magnitude of UHC depends on the quantity of fuel injected during ignition delay, mixing rate with air, and in cylinder conditions are favorable to auto-ignition. Therefore, over mixing (over leaning) is one of the important cause of UHC formation during normal operation and it becomes more predominant at light-load operation when the ignition delay is longer (Greeves and Khan 1977; Yu and Shahed 1981).

However, undermixing which is resulting in over-rich mixtures also considered as a one of the major causes of UHC emission. The fuel that leaves the injector at low velocity relatively in the later part of combustion process is another important source of UHC (Heywood 1988). This mechanism occurs more frequently especially when injection of fuel is being done after the ignition delay period and during over-fueling conditions, such as while accelerating at high loads. Advancing fuel injection timing
tends to cause higher combustion temperatures and pressures, thus promoting the oxidation of hydrocarbons.

Carbon monoxide is a product of incomplete combustion, usually when the engine is operating at very rich air-fuel mixture condition. Accordingly, the CO emissions from IC engines are controlled by the fuel-air equivalence ratio. As the spark-ignition engines operate close to stoichiometric fuel-air equivalence ratio at part load, but fuel rich at full load. Since CO concentrations in the exhaust increases with increasing fuel-air equivalence ratio, as the excess fuel increases (Harrington and Shishu 1973). Thus, it needs to be controlled at high engine loads. To control CO emission in case of spark-ignition engines, exhaust gas treatment is required, such as oxidation catalysts. In contrast, diesel engines operate with excess air. Thus, overall lean combustion ensures very low levels of CO emissions. In the case of well-designed diesel engine, CO emission is low enough and can be considered not relevant.

2.5 NO\textsubscript{X}-REDUCING TECHNIQUES
Some commonly-used techniques for decreasing the emissions of NO\textsubscript{X} in diesel engines are:

2.5.1 Injection Timing
This technique is used to control NO\textsubscript{X} emission. Retarding the injection timing of fuel is an effective method used to decrease NO\textsubscript{X} emissions from a diesel engine. Thus, combustion events are shifted towards the expansion stroke, causing a reduction in peak flame temperature and in-cylinder pressure that results into slowing down the reactions of the NO\textsubscript{X} formation. However, this technique also causes an increase in PM emissions and fuel consumption. The reason could be due to delaying the fuel injection the duration of the diffusion combustion phase is extended and the resulting lower temperatures during the expansion stroke leads to impair the oxidation of the soot. The change in fuel injection timing provides a classic example of the NO\textsubscript{X}-PM trade-off which is a characteristic of diesel engines.
2.5.2 Exhaust Gas Re-circulation (EGR)

In this technique re-circulating part of the exhaust gases helps in reducing NO\textsubscript{x} emission. However, appreciable particulate emissions are observed at high loads, thus there is a trade-off between NO\textsubscript{x} and smoke emission. Hence, this technique is mainly used in low-load and low-speed conditions. When a part of this exhaust gas is re-circulated to the cylinder, it acts as diluent to the combusting mixture. This also helps to reduce O\textsubscript{2} concentration in the combustion chamber.

Thus, the challenge is to minimize the pollutants by manipulating the thermodynamic properties and the oxygen concentration of the cylinder charge whilst keeping minimum degradations in the power and efficiency, which is the principal reason to apply EGR in diesel engines.

At stoichiometric combustion, very small fraction of oxygen is left as a combustion product while at idle load conditions about 20\% oxygen is available at the tail pipe of modern diesel engines. Thus, with the increase in the engine load, concentration of CO\textsubscript{2} and H\textsubscript{2}O and specific heat of exhaust gases increases. The flame temperature and the maximum temperature of the working fluid will be lowered with the increase in CO\textsubscript{2} and H\textsubscript{2}O. Therefore, at low engine load operation, higher rates of EGR can be tolerated by the engine whereas small rate of EGR is sufficient at high engine load operation.

The effect of increasing EGR leads to lower combustion temperatures and reduce oxygen availability. The decrease in oxygen concentration and combustion temperatures reduces the rate of oxidation of species including soot, UHC and CO (Jacobs and Bohac 2005).

Studies conducted on diesel engines have shown that the EGR can reduce NO\textsubscript{x} substantially (Lapuerta and Hernandez 2000).

Ladommatos et al. (Ladommatos and Abdelhalim 1996a; Ladommatos and Abdelhalim 1996b; Ladommatos and Abdelhalim 1997) worked extensively on the effect of EGR and have published three papers which suggested the following mechanism responsible for NO\textsubscript{x} control:
i. Dilution mechanism: Increased level of inert gas concentration in the charge increases ignition delay or greater time for premixing and long burn duration which is known as EGR’s dilution effect. This results in lowered flame temperatures. Moreover, the partial pressure of oxygen reduces at low temperatures and availability of less oxygen is expected to suppress the NO\textsubscript{x} formation.

ii. Thermal Mechanism: Higher specific heat capacity and thermal mass of recirculated CO\textsubscript{2} and H\textsubscript{2}O compared to oxygen and nitrogen present in the fresh air. Thus, it decreases the temperature rise in the combustion chamber after the same heat release. This also helps to reduce heat transfer losses, which occurs during and after the combustion event, at that time the surface area and volume ratio of the engine is a maximum. Thus, the heat loss to the coolant reduces due to low peak combustion temperature.

iii. Chemical Mechanism: As the combustion process progresses water vapor and carbon dioxide molecules undergo dissociation (endothermic dissociation of water vapour), and as the rate of heat release is modified. Thus, it leads to affects NO\textsubscript{x} formation and heat absorbed during dissociation result in a decrease in the flame temperature.

### 2.6 DIESEL EXHAUST AFTER-TREATMENT TECHNOLOGIES

Available technology and measures used to control combustion inside the cylinder and hence to cut-down emissions could not provide large reduction in harmful pollutants. So, to meet the stringent emissions norms after-treatment of exhaust gases has been used for efficient conversion of harmful pollutants into harmless substances. Therefore, in compression ignition engines to reduce emissions of harmful pollutants like carbon monoxide, unburned hydrocarbons and nitrogen oxides and also soot or particulates different techniques are used. Thus, diesel oxidation catalyst (DOC), the diesel particulate filter (DPF) as well as highly efficient NO\textsubscript{x} after-treatment technologies will become mandatory in the future.
2.6.1 Diesel Particulate Filter

This method is based on filtration of particulate matter by using ceramic materials such as cordierite ($2MgO_2, Al_2O_3, 5SiO_2$), aluminum titanate and silicon carbide ($SiC$).

Fig. 2.5 shows honeycomb ceramic monolith that traps the particulate matter as the gas flows through porous walls of its cells, thus it is also known as ceramic wall flow filters. The flow channels are arranged in such a manner that alternate ends of these cells plugged at one end and kept open at opposite end. Therefore, exhaust gas enters from the upstream end while flowing along the length of the channel flow direction is changed and it enters into adjacent channel to leave from the filter. It is evident that long time application of DPF lead to produce back pressure due to blockage of passage by particulate matter and in turn it manifests in terms of fuel penalty. So there is need to clean accumulated particulate matter by burning or oxidizing it also known as regeneration. Hot burn gas raise the temperature of the DPF which converts soot into $CO_2$.

![Figure 2.5: Ceramic wall flow filter for diesel particulates.](image)

2.6.2 Diesel Oxidation Catalysts

Since early 1990’s diesel oxidation catalysts (DOC) have been widely used in the light-duty diesel commercial vehicles in the European countries. Diesel oxidation catalysts consists of ceramic honeycomb monolith which has a large number of
parallel and straight open channels for flow of exhaust gases. The flow through these
channels is laminar. The inorganic material (Al$_2$O$_3$, SiO$_2$, TiO$_2$), ceramic or metal with
dispersed Pt, Pd or Rh are used on its surface (Handbook 2004). It allows a large reaction
surface within a small space. The reactions of the oxidation of UHC and CO are as follows

\[ C_{y}H_{n} + \left(1 + \frac{n}{4}\right)O_{2} \rightarrow yCO_{2} + \frac{n}{2}H_{2}O \]  \hspace{1cm} Eqn. (1.14)

\[ CO + \frac{1}{2}O_{2} \rightarrow CO_{2} \]  \hspace{1cm} Eqn. (1.15)

\[ CO + H_{2}O \rightarrow CO_{2} + H_{2} \]  \hspace{1cm} Eqn. (1.16)

2.6.3 NO$_x$ Reducing After-treatment Technologies

Two after-treatment methods could be used to reduce NO$_x$ emissions from
compression ignition engines. As the diesel engines operate with excess air, thus
exhaust gas is oxygen rich. Therefore in the oxygen rich environment conversion of
NO$_x$ needs additional reducing agents termed as reductants. So, selective catalytic
reduction and lean NO$_x$ trap are discussed hereunder.

Selective catalytic reduction of NO$_x$ employed anhydrous ammonia or urea as
reducing agent. Urea is injected into the exhaust, which undergoes thermal
decomposition and hydrolysis to get converted into ammonia.

Urea Hydrolysis

\[ (NH_{2})_{2}CO + H_{2}O \rightarrow CO_{2} + 2NH_{3} \]  \hspace{1cm} Eqn. (1.17)

NO$_x$ conversion

\[ 4NO + 4NH_{3} + O_{2} \rightarrow 4N_{2} + 6H_{2}O \]  \hspace{1cm} Eqn. (1.18)

\[ 6NO_{2} + 8NH_{3} \rightarrow 7N_{2} + 12H_{2}O \]  \hspace{1cm} Eqn. (1.19)

Lean NO$_x$ trap is used to reduce NO$_x$ emission also known as NO$_x$ storage converter
(NSC) or a NO$_x$ absorber. This converter mostly catalyzes the reduction of nitrogen
oxides to nitrogen. Hence, platinum is used as catalyst; the NSC converter also
contains storage components with high affinity to NO$_x$ like Barium compounds.
2.7 EMISSIONS AND THEIR HEALTH EFFECT

Diesel engine exhaust is a complex mixture of hundreds of constituents in either a gas or particle form. Gaseous components of diesel engine exhaust include carbon dioxide, oxygen, nitrogen, water vapor, carbon monoxide, nitrogen compounds, sulphur compounds, and numerous low-molecular-weight hydrocarbons. Among the gaseous hydrocarbon components some have toxicologic relevance are the aldehydes (e.g., formaldehyde, acetaldehyde, acrolein), benzene, 1,3-butadiene, and polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs.

PM consists of fine particles (fine particles have a diameter <2.5 µm), including a subgroup with a large number of ultrafine particles (ultrafine particles have a diameter <0.1 µm). Collectively, these particles have a large surface area which makes them an excellent medium for adsorbing organics. Also, their small size makes them highly respirable and able to reach the deep lung. Available evidence indicates that there are human health hazards associated with exposure to diesel exhaust. The hazards include acute exposure-related symptoms; chronic exposure related non-cancer respiratory effects, and lung cancer.

NOₓ react with ammonia, moisture, and other compounds to form small particles. These small particles penetrate deeply into sensitive parts of the lungs and can cause or worsen respiratory disease, such as emphysema and bronchitis, and can aggravate existing heart disease, leading to increased hospital admissions and premature death. Some reported works are given hereunder to discuss the health hazard due to diesel engine exhaust.

Study (Nightingale and Cullinan 2000) found that sulphur oxides (SOₓ), nitrogen oxides (NOₓ) when mixed with water vapour (H₂O) present in the air forms sulphuric-acid and nitric-acid results in acid rain. Thus, it cause air pollution and adversely affects the respiratory system prone to diseases like chronic Obstructive Pulmonary disease (Pulmonary ventilation provides the air flow function between atmosphere and lungs), Asthma, Pneumonia, Tuberculosis and lung Cancer. Kahn et al. (Kahn and Weeks 1988) found severe effects from the NOₓ and sulphur compounds on the nervous system, increase in chronic bronchitis and asthma. Also, in another
study (Gamble and Jones 1987) breathing problem, nausea, increase in sensation and burning of eyes observed.

Study (Edling and Axelson 1984) revealed that PM with the metal composition of Iron, Zinc, Vanadium and Nickel has the direct effect on the pulmonaries, cardiovascular, variations in the heart rate, formation of arrhythmias that may leads to ultimately death due to blockage of atrioventricular. Ultrafine particles (<100 nm) present in the PM cause severe effects on inflammation, it damages epithelium and phagocytosis inhibition.

2.8 ADDITIVES FOR DIESEL ENGINE

Oxygen-containing compounds have been used as fuel oxygenates to reduce soot emission or to supply oxygen to form CO₂ and reduce carbon rich particles. Various oxygenates generally used along with diesel are

- Alcohol (Atcilla and Orhan 2002; Huang and Lu 2004; Zuohua Huang and Hongbing Lu 2004)
- Methyl or ethyl esters or bio-diesel (Sharp and Howell 2000; Jiménez-Espadafor and Francisco J. Torres 2012; Pandey Shyam and Sharma Amit 2012)
- Ethers (Liotta and Montalvio 1993; Youn and Su Han Roh 2011)
- Ethylene glycol monoacetate (Lin CY and JC 2003)

Oxygenates capability to reduce smoke opacity, PM, CO and NOx emissions depend on the chemical structure and amount of oxygen in the fuel.

Bio-diesel: Straight chained vegetable oils have long been considered as alternative fuel to replace diesel (Shahid and Jamal 2008). The beginning was made by Dr. Rudolf Diesel when he demonstrated use of 100% peanut oil to run his engine in an exhibition at Paris. Since Vegetable oils are usually triglycerides (having branched hydrocarbon chain of fatty acids), they possess some unfavourable physico-chemical properties which impede their path to be directly used as fuel of compression ignition engine. Viscosity of vegetable oils (35 cSt to 60 cSt at 40 °C) is much higher as
compared to that of diesel (4 cSt at 40°C) and this is due to large molecular weight and complex molecular structure of vegetable oils.

To overcome above difficulties to use it successfully in diesel engines vegetable oils or triglycerides undergo dilution, pyrolysis, microemulsions, and transesterification process (Ali and Hanna 1994). Transesterification is the process of splitting vegetable oils into light molecules. Therefore bio-diesel is derived from vegetable oils or animal fats made up of (m) ethyl esters. These vegetable oils are renewable biological sources. The merits of using bio-diesel instead of conventional diesel are its comparable energy density, cetane number heat of vaporization, higher combustion efficiency, low sulfur and aromatic content, renewability, and stoichiometric air/fuel ratio (Agarwal 2007). Bio-diesel is also non-toxic and rate of its biodegradation is much faster than conventional diesel. Greenhouse gas effects are least observed in case of bio-diesel (Alat and Balat 2008; Murugesan A and Umarani C 2009).

Although oxygenates are usually used in the form of blends with diesel fuel, alcohol for instance, can also be used in other forms. Depending on the level of engine modifications required alcohol can be used through the fumigation, dual fuel injection and even by neat alcohol. However, last option requires extensive engine modification includes injection system, fueling and injector.

It may be noted that fumigation is a particularly attractive method because it allows the utilization of alcohol in engines with little modification and without the issues associated with the limited miscibility of alcohol (methanol and ethanol in particular) with diesel fuel.

2.8.1 OXYGENATES AND Diesel COMBUSTION

Literature showed that extensive investigation has been done to understand the effect of oxygenates on the performance and emissions of diesel engine. Researcher (Mišosšaw Kozak and Merkisz 2008; Miloslaw Kozak and Merkisz 2009) have evaluated potential of oxygenates to reduce PM emissions. Investigators have found that molecular structure and oxygen content of oxygenate primarily control the PM emissions. Ironically, there is still lack of clarity regarding the parameter (molecular
structure or oxygen content) plays dominating role to reduce PM emissions. The actual mechanisms through which oxygenated compounds affect pollutant formation in diesel engines are still widely debated by researchers.

Nabi et al. (Nabi and Minami 2000) investigated the effect of oxygen content on smoke emissions. Six different oxygenates have been studied to understand their effect on emissions of single cylinder diesel engine. It was found that smoke emissions decrease linearly with oxygen content of oxygenate and it reaches almost zero level at oxygen contents of 38% (wt.) or more. Investigators have (Miyamoto and Ogawa 1998; Cheng and Dibble 2002) reported that the reduction in PM level was largely influenced by the oxygen content of the blends rather than the chemical structure of the oxygenates. However, several investigators believe that in addition to oxygen content, the chemical structure of an oxygenate plays significant role in determining its effectiveness in reducing PM emissions.

Yeh et al. (Yeh and Rickeard 2001) examined the effect of molecular structure on PM emissions by using fourteen different oxygenates, the blends were prepared keeping same oxygen content. Oxygenates found to be more effective were alcohol and more volatile compounds showed superior performance than heavier ones. They found that ethers, esters, and carbonates outperformed in PM reductions.

The effect of fuel bound oxygen on NO\textsubscript{x} emissions is not very clear. Some studies report a small increase in NO\textsubscript{x} whereas others conclude that the emissions of oxides of nitrogen remain essentially un-changed. Again, the addition of oxygen modifies the fuel as a whole, and these changes in NO\textsubscript{x} formation cannot be attributed solely to oxygen content. In addition to that, testing conditions and engine characteristics probably have a significant influence on NO\textsubscript{x} emissions.

2.9 COMBUSTION CONTROL STRATEGIES IN HCCI

The research and development of HCCI diesel engines has been pursued along three main technical routes, depending on the mixture preparation process involved: the first approach involves injecting the fuel into the intake air, upstream of the intake valve, similar to a conventional port-fuel injection (PFI) SI engine. However, it was not until the mid-1990s that systematic investigations began on the potential for diesel fueled HCCI
engines for automotive applications, due to the need for substantial reductions in both NO\textsubscript{x} and PM emissions. The second approach was early direct injection into the cylinder which increases ignition delay, thus improving premixing. The third technique, developed by Nissan Motors, is late direct injection or modulated kinetics.

The above discussion lays emphasis on the hurdles to accomplish advanced combustion technology. Recent publications showing increased interest amongst the scientific community have appeared especially in India, China, Indonesia and Brazil to explore premixed techniques to reduce emissions from diesel engines.

2.9.1 Early Direct Injection HCCI

In this technique homogenous mixture can be prepared by injecting fuel during the early part of compression so that the time available between the start and end of compression can be utilized effectively. Homogenous mixture is prepared during the time interval between the end of the injection and the on-set of combustion, which necessitates injection to be timed meticulously. The advantage of this technique is that in this process air is slightly compressed, as compared to when it is inducted into the cylinder, and the pressure and temperature are higher compared to inlet conditions. Although, wall wetting due to the over penetration of the fuel, less time available for fuel-air mixing, and also combustion phasing control would be critical issues.

Compared to premixing by air intake manifold fuel injection, this technique offers some inherent advantages, namely once the compression begins, movement of piston increases in-cylinder pressure and temperature of the air which helps in vaporization of the fuel being injected, as well as, it improves the mixing prior to initiation of combustion. Moreover, there is no additional requirement for inlet air preheating, which often requires electric heating system. However, researcher also attempted to explore early direct injection along with conventional direct injection (dual injection), and a brief review of that work is presented hereunder.

2.9.1.1 PREDIC

One of the most significant contributions in early direct injection HCCI was done at New ACE institute in Japan by Yoshinaka et al. (Yoshinaka and Nakagone 1996) and
Nakagome et al. (Nakagome K and Shimazaki N 1997). Three alternate fuel injection techniques were tried to better distribute the fuel, and to minimize over penetration and wall wetting that can occur when the fuel is injected well before the top dead center. Since the in-cylinder pressure and densities are low as compared to TDC conditions, conventional injectors designed for TDC conditions will not be able to produce good results. The three major techniques adopted were follows.

i) In this first technique, central injector with 6 holes of size 0.17 mm and spray angle (155°) were replaced by 16 holes of size 0.08 mm and the same spray angle without changing position of the injector.

ii) In this technique, three stage spray angle nozzle with 32 holes, were staggered in the three sets, i.e., two sets of 0.08 ×12 at spray angle of 155° and 105° respectively and another with 0.08 ×6 at 55°.

iii) In this technique, to reduce possibility of wall wetting, two injectors were mounted diametrically opposite, with two sprays each, positioned in such a way that they collide at the middle of the chamber.

The reported work used the base fuel have higher cetane number (CN) 62 , at compression ratio of 16.5, it resulted in over advanced combustion, therefore new fuel blends with CN 19 and 40 were developed and used along with changes in intake temperature and compression ratio. Charge dilution was also tried, CO2 was found to be the most effective diluent gas to control the combustion phasing. Harada et al. (Harada and Shimazaki 1998) carried out follow-up study and examined the effect of swirling flow pintle-nozzle injector that helps to produce more uniform mixture which in turn reduces wall wetting (evaluated by reduction in lube-oil dilution), thus improving combustion efficiency.

The early HCCI-DI, work further expanded by Hashizume et al. (Hashizume and Miyamoto 1998). Dual injection strategy was adopted to accomplish this objective, side mounted injectors were used to produce lean premixed fuel while the central injector was used to inject the additional fuel near TDC. Various combinations of injection timing and fuel cetane number were tried to optimize performance and emissions. As the second injection lead to produce diesel like combustion, therefore
NO\textsubscript{x} and PM emissions were much higher as compared to pure HCCI. However, NO\textsubscript{x} emissions were reduced to about half without substantial increase in BSFC. However, PM decreases but UHC emission increases compared to pure diesel combustion.

Akagawa et al. (Akagawa H and Miyamoto T 1999) further extended the work mainly to solve the shortcomings of PREDIC, i.e., high UHC and CO emissions. They found that UHC and CO emissions could be decreased by adopting a pintle type injection nozzle, or a reduced top-land-crevice of piston. Fuel consumption was also improved by application of EGR, or addition of an oxygenated component to the diesel fuel. Following techniques were presented broadly

i) Crevice volume was reduced by raising top piston ring - shown to be beneficial to reduce UHC and by small extent CO.

ii) Cooled EGR was used- it is known to be beneficial in retarding the HCCI combustion phasing, hence it occurs near TDC.

iii) Several fuel additives like dimethyl carbonate, diethylene glycol dimethyl ether, methyl tertiary butyl ether (MTBE) and ethanol were blended with diesel fuel to determine their effects on combustion phasing. MTBE and ethanol, which have low Cetane number, were found to be advantageous for preventing overly advanced HCCI combustion.

Significant reduction of NO\textsubscript{x} emission was recorded but the maximum IMEP could be achieved is limited to about 50% of that of conventional diesel combustion.

2.10 PREMIXED TECHNIQUES

Port Fuel Injection (PFI) is perhaps the most straightforward approach while to obtain a pre-mixed charge. Experimental study conducted by Osses et al. (Osses and Andrews 1998) on diesel fumigation to achieve partial premixed charge of vaporized fuel with air and remaining fuel is directly injected into the combustion chamber. It was observed by using this technique, 20% of port injected diesel lead to lower the NO\textsubscript{x} and soot emissions but at the same time BSFC, CO, UHC and VOF (volatile organic fraction of the PM) was increased.
Conventional diesel combustion could be considered to be replaced by partial HCCI or PCCI-DI combustion. Horng-Wen Wu et al. (Horng-Wen Wu and Ren-Hung Wang 2011) investigated combustion and emission of a partial HCCI engine using ethanol and gasoline as a premixed fuel and diesel as a directly injected fuel in a single cylinder compression ignition engine. Concentrations of NO\textsubscript{x} and smoke were lower in case of premixed ethanol as compared to premixed gasoline. They have found NO\textsubscript{x} concentration decreases with increase in premixed fuel ratio. Nevertheless, unburned HC emission was increased with increase in premixed fuel ratio.

The effect of bowl shape on PCCI combustion was studied using 3D-CFD software and ECFM-3Z combustion model (Juttu and Thipse 2008). Both, simulation and experimental results were compared and found close resemblance. It was concluded that performance characteristics of engine not much dependent on geometry of bowl and at part load operations turbulence zone inside the bowl plays critical role in control of soot and CO emissions. In an another study effect of injection timing and injection pressure was studied (S Juttu and S S Thipse 2011) by using four cylinder diesel engine equipped with CRDI fuel injection system. As per the results reported NO\textsubscript{x} emissions and low soot emissions were observed with high injection pressures and combined PCCI-DI could be economical solution to meet Euro-IV emission norms. Moreover, results from visualisation study showed higher injection pressures promotes PCCI combustion compared to lower injection pressures.

Kaneko et al. (Kaneko and Ando 2002) conducted study using pintle nozzle injector (12 MPa injection pressure) mounted on the intake manifold. In this study, the intake air temperature was maintained at 20 °C, i.e., no heat was supplied to assist vaporization. When diesel fuel was used, UHC emission increased dramatically and the lubricating oil become diluted, presumably due to diesel fuel adhering to the cylinder wall. Some NO\textsubscript{x} and notable smoke emissions were also present with diesel fuel, indicating that the mixture was not sufficiently homogenous.

Olsson et al. (Olsson and Tunestal 2001) presented a strategy for closed-loop control of a multi-cylinder turbo charged HCCI engine. A dual fuel port injection system was applied to control the combustion timing and load individually for each cylinder. For
a better range of auto-ignition properties, isoctane and n-heptane were used as a fuel. Cylinder pressure sensors was used for feedback and for information regarding combustion. The crank angle of 50% heat release was calculated in real time for each cycle and used for timing feedback. Also, inlet air preheating was used at low loads to maintain high combustion efficiency.

Kim et al. (Kim and Lee 2006) experimented partial HCCI combustion as an effective way to control HCCI combustion. A DI (Direct injection) diesel engine was modified to operate on partial HCCI, port fuel injection mechanism was used to inject either diesel or gasoline or n-heptane. The combustion and emission study showed reduction in NO\textsubscript{x} and soot emission simultaneously. NO\textsubscript{x} and soot emission decreases when diesel were used as a port fuel at room temperature, however, at elevated temperature it results in deterioration of combustion, lead to narrowed operating limit at higher premixed ratio. Gasoline as a port fuel showed remarkable improvement in the emissions as compared to other fuels.

In an experimental study conducted based on the control of fuel ignition timing and suppression of rapid combustion in a partially premixed charge compression ignition (PCCI) engine. They attempted injection of water directly into the cylinder as a reaction suppressor. The possible engine operating range with ultra-low NO\textsubscript{x} and smokeless combustion was extended to a higher load range with the water injection (Naoyam and Hirokazu 2002).

### 2.10.1 Alcohol and HCCI Combustion

Application of alternative fuels, e.g., alcohol, natural gas, and bio-diesel considered to be effective method to control the PM and NO\textsubscript{x} emissions (Wang and Clark 1997). Because of limitations on the development of dedicated compression ignition engine operate on alcohol. Researchers have shifted their focus on the partial replacement of diesel fuel, which could be done by two ways: either alcohol premixed with diesel or injected into air intake manifold. As we know, alcohol has higher self-ignition temperature, therefore, it is difficult to utilize in HCCI combustion mode, Yap et al. (Yap and Megaritis 2004) utilizes exhaust gas trapping techniques along with
moderate intake air heating of bio-ethanol fueled HCCI engine, the combustion results showed very low NO\textsubscript{x} emissions.

It has been shown that removal of water from bio-ethanol found to be very energy-extensive process therefore authors (Megaritis and Yap 2007) have thought of converting this demerits into merits. A diesel engine was modified to operate on HCCI mode, fueled with bio-ethanol and bio-ethanol and water blends (up to 20%) together with residual gas trapping was done by negative valve overlap. Earlier investigators (Iwashiro and Tsurushim 2002) have shown blending water with diesel successfully reduces NO\textsubscript{x} emissions. Addition of water tends to cool down the in-cylinder gas at inlet valve, hence for stable combustion fueling rate need to be increased and, lambda decreases with increase in water blending. Thus, increase in maximum in-cylinder pressure rise rates was observed which in turn significant rise in NO\textsubscript{x} emissions was found at more than 10% of water content in the fuel. Thus, fixed rate of water bending found to be counter productive to control the NO\textsubscript{x} emissions.

2.10.2 Alcohol and Fumigation

The process used to atomized the fuel into the air, prior to induction in the engine cylinder, is known as fumigation (Abu-Qudais and Haddad 2000). Initially, fumigation was thought of as a means to enhance the power. German engineers employed this concept on numerous aircraft, which were used in Second World War during 1940’s. (Gunston and Bridgman 1994).

The researchers worked on fumigation, prior to 1980’s, did not emphasize on the emission characteristics; they rather focused on the usage of alternate fuel and power boosting system. However, later on 80’s more than three decades fumigation have been widely explored by researchers to reduce NO\textsubscript{x} emissions (Jiang and Ottikkutti 1990). Perhaps, it helps in two ways-one it can reduce the temperature of the flame, which, in turn, increases the density of the air that improves the performance, one more advantage of using alcohol as an alternative fuel is that it requires minimum modifications in the engine (Abu-Qudais and Haddad 2000). It could be possible to use widely available bio-fuels, like ethanol and methanol and, recently butanol showed relatively better alcohol after Butamx (ButamxTM 2013) has come out.
manufacturing facility from bio-resources. It has much better physico-chemical properties as compared to other counter parts; therefore it’s also considered as another alternative out of alcohol which is available as fumigants.

### 2.10.2.1 Methanol Fumigation

Dedicated methanol fueled buses were tried by USA, however, due to operational problem later on they were phased out. Gradually R-&-D interests have been shifted towards partial replacement of diesel by methanol. Two possible methods were studied: one by preparing methanol and diesel blends and, another by injecting directly into the intake air.

Baranescu (Baranescu 1986) experimentally examined the effect of fumigation of alcohol (methanol and 190, 160 proof ethanol) on six-cylinder, turbocharged, direct-injection, diesel engine’s (7.1 L) combustion and emission pattern. The results showed fumigation of alcohol causes considerable increase in peak in-cylinder pressure and maximum rates of in-cylinder pressure rise as compared to pure diesel combustion. The maximum replacement of diesel fuel by methanol and ethanol together was about 30%, in terms of fuel energy liberated. Considerable increase in UHC and CO emissions were reported due to fumigation of alcohol, especially, at low engine loads. Moreover, NOx emission was decreased.

Since the fumigation of alcohol significantly changes combustion characteristics (high latent heat of vaporization by cooling effect) so it is advantageous to optimize the injection timing to produce best results from the fumigation combustion mode. To explore complete harnessing possibility by improvised injection mechanism, system complexity needs to be increased, in terms of injection timing and injection duration. The effect of varying injection timing with the help of electronically controlled, multipoint ethanol injection system was studied by Savage et al. (Savage and White 1986). A turbocharged six cylinder (7.1 L Navistar DT-436B) diesel engine was selected to operate in fumigation mode. Experimental results revealed that by varying fumigants (methanol and 190-proof ethanol) injection timing (different crank angle position in the cycle-via induction air) makes remarkable difference in alcohol tolerance level and knock threshold. Therefore, up to 90 and 35% replacement of
diesel fuel energy was possible by alcohol at low and high engine loads respectively, without any significant change in thermal efficiency.

Blending of diesel and methanol needed additive to prepare a stable blend (Chao and Lin 2001; Huang and Lu 2004). Moreover, it does not require any engine modification. Fumigation or injecting methanol into the intake air requires minor modification (Cheng and Cheung 2008; Yao CD and Cheung CS 2008) in the induction manifold, low-pressure gasoline injectors along with electronic controller was used. However, the major drawbacks of methanol fumigation were considerable increase in UHC and CO emissions, which have been reported by Yao et al. and Cheng et al. (Yao and Cheung 2007; Cheng and Cheung 2008). Hosoya et al. (Hosoya and Shimoda 1996) used diesel oxidation catalyst (DOC) to reduce UHC, CO and PM emissions.

Cheng et al. (Cheng and Cheung 2008) examined the performance and emission analysis of in-line four cylinder water cooled diesel engine (4.334 L) with fumigation methanol into the air intake at each cylinder. The experiments were done on 1800 rev/min engine speed and 0.08 MPa, 0.19 MPa, 0.38 MPa, 0.56 MPa and 0.67 MPa brake mean effective pressure (BMEP). For instance fueling the engine with diesel until 90% load and fumigating methanol until the engine reaches 100% load, creating a 10% replacement by load. Fumigation of methanol is done in such a way that it can top up the load by respective percentage (10%, 20% & 30%) at various loads. They have found that maximum amount of diesel could be replaced by methanol was about 43% of the total mass of fuel consumed. At all loads except, 0.67 MPa, brake thermal efficiency decreases with increase in fumigation methanol, however, it increases in the case 0.67 MPa load with an increase in fumigation methanol. UHC and CO emissions were increased, considerably, at all loads. CO₂ emissions increase at low and medium engine loads but no significant change was found at high engine loads. However, it was found that at high loads, smoke opacity and particulate mass concentration decreased considerably with increase in fumigation methanol.

Cheung et al. (Cheung and Chuanhui Cheng 2008) investigated effect of methanol fumigation along with bio-diesel on performance and emissions, they have used all equipment as discussed above. It was found brake thermal efficiency decreases with
increase in fumigation ratio at low engine load (0.19 MPa), it changes from 27% to 23.2% which corresponds to fumigation ratio 0 to 0.55. At medium engine load (0.38 MPa), initially slight increase in brake thermal efficiency was seen but after 0.26 fumigation ratio it starts decreasing, however the changes were very small only 2%. At higher engine load (0.56 MPa), only 1% variation in BTE was found and no deterioration was observed within 0.2 fumigation ratio. The variation in thermal efficiency was found due to cooling effect of methanol, since methanol has a much higher latent heat of vaporization (1178 kJ/kg) as compared with that of bio-diesel (250 kJ/kg), they have found this phenomenon dominating at low engine load (due to low gas temperature) whereas, at high engine load higher gas temperature overcome cooling effect up to a higher extent. Moreover, homogenous mixture of air and ethanol burns faster, which increases brake thermal efficiency at high engine load. Therefore, not an obvious reduction in the brake thermal efficiency was observed at high engine load. At all engine loads increase in fumigation ratio resulted into drops in CO₂ concentration. It ranged from 3.47% to 3.21%, 5.55% to 4.99% and 7.96 to 7.59% associated with engine load of 0.19 MPa, 0.38 MPa and 0.56 MPa, respectively. At any fixed engine load (0.19 MPa, 0.38 MPa, 0.56MPa) both CO and UHC increased with fumigation ratio. For three engine loads CO increased by ratio 4 and UHC increased by a ratio 2.5, also the rate of increase was significantly higher at low engine loads. All fixed engine load (0.19 MPa, 0.38 MPa and 0.56 MPa) NOₓ emission decreases with increase in fumigation ratio. The relatively significant reduction was found at low engine load. However, they explained three distinct mechanisms which control the NOₓ emissions (oxygen content of fuel has been used, intake charge cooling due to methanol and ignition delay) and these factors compete with each other. The maximum reduction in NOₓ emission was reported at low engine load (0.19MPa/0.38 MPa) about 20% and at high engine load (0.56 MPa) it reduces to about 10%. The particulate number concentration and size distribution showed the total no of particles decreases by about 30% (at 0.19 MPa and 0.38 MPa) but it reduces less than 10% in the case of 0.56 MPa. PM mass concentration reduces significantly due to increased oxygen content in the fuel, thus higher amount of fuel was burnt in the premixed phase and diffusion combustion phase becomes cleaner due to presence of methanol.
In spite of biodegradable and nontoxic nature of bio-diesel, researcher (Sharp and Howell 2000) found that at higher loads application of bio-diesel in diesel engine may increase the NO\(_x\) emissions. Engine experiments were performed at constant engine speed of 1800 rpm and at three different engine loads (0.19 MPa, 0.38 MPa and 0.56 MPa). In this study, the fumigation ratio defined as the ratio of volume of methanol to the total volume of methanol and bio-diesel being burnt, the values selected were 0 (pure bio-diesel), 0.27, 0.37, 0.43 and 0.55.

Cheng et al. (Cheng and Cheung 2008) compared emissions from ULSD, bio-diesel, biodiesel and 10% methanol blends and bio-diesel and 10% methanol fumigation in the 4 cylinder direct injection diesel engine same as used for methanol fumigation (Cheng and Cheung 2008). In the blending mode, methanol tends to increase ignition delay therefore higher percentage of fuel was burnt in premixed phase together with increase in peak net heat release rate. Fumigation mode, also, showed longer ignition delay (cooling effect produced by methanol) period and hence greater amount of bio-diesel and methanol burns in the premixed mode. Thus, shorter diffusion controlled combustion and bio-diesel combus in the environment of air and methanol instead of air alone. At 10% fumigation or blending minimum BSFC was associated with ULSD, whereas, fumigation mode has lower value compared to blending but, higher than that associated with bio-diesel. ULSD showed lowest brake thermal efficiency at all loads, contrary to the lowest BSFC, whereas maximum brake thermal efficiency (39.6%) was attained with 10% methanol premixed mode at 0.67 MPa. Both ULSD and bio-diesel showed almost similar BSCO2 emissions, however, 10% methanol, either in blending or premixed mode, resulted into marginal reduction of about 2.5%. Nevertheless, UHC and CO emissions increased significantly when engine was operated under fumigation mode, NOx emissions reduces by about 5% due to cooling effect of methanol. Compared to ULSD both Bio-diesel and methanol are able to reduce particulate emission. Relatively, methanol seems to be more effective due to oxygen content in the fuel and relatively longer premixed mode of combustion. Nevertheless fumigation mode, compared to blending mode, has less potential to reduce particulate. The reason behind is higher hydrocarbon in fumigation mode condenses into particulate. Submicron size of particles was found to reduce when engine was operated with 10% methanol.
In an another study (Cheung C S and Zhang Z H 2009) authors have analyzed performance and emissions of fumigation methanol under different engine speeds (1280, 1920 and 2560 rpm). Fumigation % represents portion of engine loads takes up by the methanol. The brake thermal efficiency decreases with engine speed but increases with engine load for diesel fuel and fumigation methanol. At each engine speed corresponding to the 20% and 40% engine load, the brake thermal efficiency decreases with increasing level of fumigation methanol. At high engine loads, no significant change was found with level of fumigation methanol. At high engine speed BTE deteriorates due to incomplete combustion. UHC and CO emissions increased to more than two times, whereas, NOx emissions decreased from 5.6% to 27.5% (averaged at different loads) as compared to baseline fuel. At high engine loads CO2 emission decreases with increase in fumigation methanol whereas no significant change was recorded at low loads. Maximum reduction in particulate mass concentration was found at 2560 rpm ranges from 19-48% (different level of fumigation methanol and engine loads) compared to baseline fuel. Significant increase in unburned hydrocarbon was the result of higher unburnt methanol. However, unburnt methanol decreases with increase in engine loads but less dependent on engine speed. DOC helps to reduce further PM. At all engine speeds, BTE decreases with increase in premixed methanol.

The experimental investigation (Zhang and Cheung 2009) was carried out to understand the performance and emission characteristics of naturally aspirated, 4-cylinder direct injection diesel engine fueled with diesel and methanol used as fumigants. To evaluate the full range of operating conditions, five loads (0.08 MPa, 0.19 MPa, 0.39 MPa, 0.58 MPa & 0.70 MPa) were selected and engine speed was maintained constant at 1800 rpm with and without DOC. The methanol accounted for 10% to 30% of the engine loading. At low to medium loads brake thermal efficiency decreases with increase in fumigation, however, small positive change was observed at higher loads. The maximum reduction and increase in BTE was observed at 30% (methanol displacement ratio) fumigation, it was about 11.2% and 1.8% at BMEP of 0.08 MPa and 0.7 MPa respectively. BSCO and BSHC decrease with increase in load but increases with increase in fumigation. As compared to baseline results, at 30%
Fumigation the maximum increase in BSHC was 7 times (at 0.08 MPa) and 3 times respectively (at 0.7 MPa), whereas, the maximum increase in BSCO was observed about 5.5 times. BSNO\textsubscript{x} and BSNO\textsubscript{2} decrease with increase in engine load, despite an increase in NO\textsubscript{x} concentration in the engine exhaust with increase in engine load. The maximum increase in BSNO\textsubscript{2} was 7.8 times at 30% fumigation methanol. DOC helps to reduce BSNO\textsubscript{x} with a very small magnitude of only 2% for the entire range of fumigation methanol. CO\textsubscript{2} concentration increases with engine load but the BSCO\textsubscript{2} decreases with engine load. The maximum decrease of BSCO\textsubscript{2} occurred at high engine load with 30% fumigation methanol of about 7.2 times. After DOC, there is a slight increase in BSCO\textsubscript{2} was observed, which is the result of conversion of CO into CO\textsubscript{2}. The smoke opacity increases with load, however considerable reduction in smoke opacity and particulate mass concentration was discovered by fumigation methanol, the relatively higher reduction was found at medium to high engine load and very small at low engine load. Also, the particulate mass concentration could be reduced further by DOC. Thermal efficiency was found to be reduced at low engine load whereas there was no substantial change observed at medium to high engine load.

To explore further, authors (Zhang and Cheungb 2010) carried out fumigation methanol study on 4 cylinder direct injection diesel engine aimed to know regulated and un-regulated (benzene, toluene, formaldehyde and methanol) emissions and performance. The experiments were performed at constant speed of 1920 rpm and five engine loads (BMEP) of 0.13 MPa, 0.27 MPa, 0.40 MPa, 0.53 MPa and 0.63 MPa. At low engine loads of 0.13 MPa and 0.27 MPa they observed there was reduction in brake thermal efficiency by 11% and 10% corresponds to 30% fumigation methanol. However, at high engine loads (0.40 to 0.63) slight increase in brake thermal efficiency were recorded. At 0.13 MPa and 0.63 MPa engine load with 30% fumigation methanol, BSHC emissions increased by 9.6 and 3 times respectively as compared to pure diesel. Moreover, under the similar conditions BSCO emissions increased by 4.5 and 6.2 times. At all engine loads except 0.63 MPa there was a reduction in NO\textsubscript{x} emissions with increase in level of fumigation, maximum reduction were recorded at 0.4 MPa (about 20.8%) at 30% fumigation methanol. At 0.13 MPa
engine the brake specific unburned methanol increased from 0.1 \( gkW^{-1}h^{-1} \) (at baseline engine or pure diesel) to 25.3 \( gkW^{-1}h^{-1} \) (at 30% fumigation methanol). Moreover, with increase in engine loads the unburnt methanol decreases but still higher than the pure diesel combustion. Similar to brake specific formaldehyde emission increases with increase in fumigation methanol, the maximum rise was about 3.4 -4.5 times at 30% fumigation methanol. It was concluded that fumigation methanol decreased the emission of ethylene, ethane, 1-3 butadiene, as a drawback there was significant increase in unburnt methanol, formaldehyde and BTX (Benzene, toluene and xylene) was reported.

In another investigation (Zhang Z.H. and Tsang 2011) they had analyzed the effect of fumigation methanol and ethanol on the gaseous and particulate emission on the similar set-up and experimental condition as discussed above. The results showed that BTE decreases by 2-5% and 3 -8% in the load range of 0.08 MPa- 0.39 MPa, whereas at higher engine load (0.7 MPa) it was increases by 10% and 9% when engine was operated at 10% and 20% fumigation methanol respectively as compared to Euro-V diesel. At 10% fumigation ethanol in the load range (0.08 MPa - 0.39 MPa) showed reductions within 2-4%, whereas at 20% ethanol fumigation level it increased to 7%. Similar to fumigation methanol at higher engine load (0.7 MPa) and 20% ethanol fumigation brake thermal efficiency increased by 3% and no significant change was observed at 10% ethanol fumigation. Both UHC and CO emissions increase with increase in level of fumigation. At low engine load range (0.08 MPa-0.39MPa) BSHC and BSCO emissions were higher in case of fumigation methanol compared to fumigation ethanol, however at high engine loads no significant difference was observed from two alcohols. BSNO\textsubscript{x} emission decreases with increase in level of fumigation methanol or ethanol. At all the loads methanol fumigation leads to higher NO\textsubscript{x} emissions reduction compared to ethanol. Moreover, at low engine loads NO\textsubscript{x} emissions reduction was higher as compared to high engine loads. BSPM decreases with increase in fumigation of either alcohol, similar to BSNO\textsubscript{x} it also showed higher reduction when methanol was used as a fumigants. The maximum reduction corresponds to 20% methanol fumigation of about 20-41% compared to pure diesel
combustion. Particulate number concentration also decreases with increase in level of fumigation methanol or ethanol.

2.10.2.2 Ethanol Fumigation

Historically, Havemann et al. (Havemann and Rao 1954) thought of utilization of ethanol in diesel engine. Initially, they tried blending of ethanol with diesel, due to poor miscibility of ethanol in diesel it could not produce satisfactory results. Therefore, they attempted to utilize it by fumigation technique. The fumigation tests were carried out on a Ricardo research engine and on a Petter AV1 Series II production engine. They found at full load the maximum fuel energy that could be provided by ethanol was limited up to 36% (Ricardo engine) and 70% (Petter engine), in addition to it, the maximum limit of ethanol fumigation strictly controlled by knocking (Ricardo Engine) and misfire (Petter engine). Results from the study showed, in both engines ethanol fumigation led to high air utilization, which made it possible to use ethanol to provide a power boost (over fueling) without sacrificing the smoke limit, moreover, smoke density was reduced considerably also it was in proportion of amount of ethanol fumigation. In case of Ricardo engine the thermal efficiency was improved slightly at higher engine loads.

Ethanol fumigation was explored by Alperstein et al. (Alperstein and Swim 1958) in 1957. They examined combustion in single cylinder (swirl-chamber and open-chamber) naturally aspirated diesel engines. Results reveal that smoke reduction up to 70%, increase in smoke-limited power output up to 18.5%, and decrease in specific fuel consumption up to 9.8%.

Barnes et al. (Barnes and Kittelson 1975) examined alcohol (methanol, ethanol and isopropanol) fumigation on six cylinder (5.1 L), turbocharged direct injection diesel engine. Single atomizing nozzle was fitted in the upstream of turbocharger compressor instead of six (one each for cylinder). The results revealed that engine efficiency decreased with increasing flow of alcohol. The loss of efficiency was the result of insufficient compression heating and evaporation of alcohol which leads to considerable reduction in the intake manifold temperature. Smoke density decreases with increase in alcohol fumigation, whereas, other emissions largely remain
unaffected. The rate of in-cylinder pressure rise was increased sharply at high engine loads, without any indication of engine knocking.

Bro and Pedersen (Bro and Pedersen 1977) examined the effect of ethanol fumigation on combustion, performance and emissions of single cylinder natural aspirated direct injection diesel engine. The results revealed improved thermal efficiency and reduction in smoke at high engine loads, however, UHC emissions increased with ethanol fumigation. Uncontrolled combustion or engine knock limits the maximum amount of ethanol fumigation.

Chen et al. (Chen and D. Gussert 1981) performed experimental investigation in order to study combustion, performance and emission of 4-cylinder (5.5 L, turbocharged) direct injection diesel engine which was modified and simple atomizing nozzle fitted in the induction air channel downstream of the compressor to inject alcohol. Ethanol (200 and 160 proof) was selected as fumigants. Results showed 160 proof ethanol mixture was able to substitute up to 25% of diesel. They observed variation in the exhaust port temperature at different conditions affect vaporization of ethanol and in turn results in to non-uniform distribution of ethanol in different cylinder. Combustion study showed that rates of cylinder pressure rise and ignition delay increased due to ethanol fumigation, whereas, thermal efficiency fluctuates at high and low engine loads in the positive and negative direction respectively. However, performance of the engine could not be changed considerably by different ethanol proofs. Smoke and NOx emissions were decreased with increase in ethanol fumigation, perhaps UHC and CO increased.

Heisey and Lestz (Heisey and Lestz 1981) performed comparative study on performance and emissions of single cylinder diesel engine operated on fumigation ethanol and methanol. Thermal efficiency under ethanol fumigation mode showed marginal improvement compared to methanol at 1/3 of maximum engine load, however, between 2/3 to full maximum load condition no significant difference was observed. The ethanol in different proofs (200, 180, 160, and 140) was used and simple atomizing nozzle was used to inject in the intake air. They concluded that lower proofs helps to reduce NOx emissions without significantly affecting thermal efficiency and rate of cylinder pressure rise. However, relatively longer ignition delay was found in case of lower ethanol proofs.
Authors (Broukhian and Lestz 1981) examined effect of fumigation ethanol on engine fuel efficiency, gaseous emissions, smoke, raw particulate and engine knocking by using indirect injection, naturally-aspirated light-duty automobile diesel engine. Simple air-atomizing nozzle was used and fitted with specially designed mixing chamber to fumigate ethanol among eight cylinders. The results showed that thermal efficiency increases with ethanol fumigation at higher engine loads, however, the quantity of ethanol fumigated limits by engine roughness (occurrence of knock). Particulate matter (mass basis) and NO\textsubscript{x} emissions decrease from the reference diesel level with increase in ethanol fumigation.

Sullivan and Bashford retrofitted fumigation kit on an Allis-Chalmers 7040 diesel tractor (Sullivan and Bashford 1981). Ethanol was sprayed into the upstream side of turbocharger compressor and flow rate was regulated by boost pressure. Reported results showed improved diesel fuel economy but very high rotational speed of compressor blades could not sustain impingement of ethanol fuel droplets that leads to considerable damage on the blades within thirty hours of operation.

Goering and Wood (Goering and Wood 1981) investigated the effect of ethanol (100- and 160-proof) fumigation on performance and emission of 3-cylinder, naturally-aspirated tractor engine. The aim of this investigation was to understand how ethanol fumigation helps in augmentation of the total engine power (over-fueling) instead of replacing diesel fuel. Nevertheless, intake air was needed to be heated to vaporize lower ethanol proofs. Results showed that at idle condition and full engine load ethanol was able to add up to 40% and 16% of the total energy, respectively. It was found that engine power output increased, however, thermal efficiency decreased. The emissions of smoke, UHC and CO increased.

Ethanol fumigation tests were performed (Shropshire and Goering 1982) on a four-cylinder, DI diesel engine. Three different ethanol proofs (100, 150, and 190) were selected for the study and four injection nozzles was mounted on each induction manifold of the engine. They showed up to 66% and 30% of energy replacement could be achieved by ethanol (190 proof) fumigation at high and low engine loads, respectively. Thermal efficiency (BTE) was increased slightly at full engine loads, however, adverse effect was observed at lower engine loads. Nevertheless, premixed
of ethanol results in to reduction in smoke levels at all engine loads but, on the other hand, UHC and CO were increased.

A long-term endurance and tribological testing was done by Allsup (Allsup 1983) on three engines for five hundred hours. Two engines were tested with fumigation technique and one with ethanol diesel blends (E-diesel). The results showed remarkably clean combustion zones, piston rings and exhaust valves were found for engines running on fumigants whereas other engine using an emulsified fuel had a premature engine failure.

A comparison of various fumigation systems was done (Shropshire and Bashford 1984). Abnormal combustion was found when using air atomizing nozzle which creates fine spray. Thermal efficiency deteriorated at low loads but maintained at high loads. Single nozzle could not produce better results compared to multiple nozzles.

Lower proof ethanol could be produced from distillation facility without much effort, whereas higher proof ethanol was more cost extensive due to dehydration process which consumes lots of time. It is always desirable to use lower proof ethanol. To understand and analyze the effect of different ethanol proofs, Hayes et al. (Hayes and Savage 1988) conducted experimental investigation on six cylinder, turbocharged, direct injection diesel engine (7.1 L Navistar DT-436B) fitted with multipoint electronic ethanol injection system. Engine testing was performed at constant engine speed of 2400 rpm and 0.2, 0.5 and 0.8 MPa BMEP. Optimum ethanol proof which produces better results are fall within 100 to 150 proof. They observed reduction in peak cylinder pressure and the maximum rate of in-cylinder pressure rise was reduced up to 20% as compared to absolute ethanol (200 proof). NO emissions reduced as compared to diesel fuel for hydrous ethanol (150 proof), however, UHC and CO emissions were increased several times as compared to diesel only combustion.

Griffith et al. (Griffith and Savage 1988) examined the effect of ethanol fumigation on Harvester farm tractor engine (6-cylinder, turbocharged, direct injection, 7.6 L diesel engine) by both laboratory and field testing. Ethanol fumigation was achieved by installing electronically controlled multi-point fuel injection system. Experimental results revealed that maximum 28% of fuel energy could be supplied by ethanol at low engine loads and 13% at full load. Lubricating oil and cylinder walls optical borescopic analysis indicates greater degree of engine wear due to fumigation. The
reason of abnormal wear could be dilution of lubricating oil due to ethanol which inducted with air and in turn affected the lubricating oil film at the cylinder walls.

A study was conducted (Jiang and Ottikkutti 1990) to explore potential of ethanol fumigation to address the problem of NO\textsubscript{x} emissions with the help of reducing adiabatic flame temperature. A four cylinder, turbocharged, direct injection diesel engine (4.5 L John Deere 4276T) was selected to perform investigation of performance, emission and adiabatic flame temperature. Minor modification was done in the induction manifold for ethanol fumigation. They showed stoichiometric adiabatic flame temperature reduces as the water in the mixture vaporized, however thermal efficiency was not affected till the water flow reaches 2.5 times the diesel flow rate. UHC and CO emissions tend to increase due to ethanol fumigation, whereas substantial reduction in the NO\textsubscript{x} emissions was found. Using lower ethanol proofs was found to be more beneficial, since higher water content reduces peak combustion temperature. Hence, as the thermal NO\textsubscript{x} emissions largely depend on the peak combustion temperature tends to reduce drastically.

Ethanol fumigation was studied at G. B. Pant University of agriculture and Technology, Pantnagr India (Ajav E. A. and Bachchan Singh 1998). A single cylinder direct injection, constant speed, water cooled diesel engine, 1.102 L was used to study their performance and emissions under fumigation mode at 20 °C and 50 °C inlet temperatures of mixture. A solex down drought carburetor was used to vapourize ethanol, EGR device was employed to preheat air-ethanol mixture. Small variation in engine speed was found at maximum brake power developed by the engine under pure diesel and fumigation mode. BSFC decreases with increase in load but small increase was reported after 75% of the engine load. At low loads (0-50%) fumigation ethanol had higher BSFC than diesel. The reason could be explained by reduction in quantity of diesel displacement when operation moved towards higher engine loads. At 66% engine load both diesel and fumigation mode had equal BSFC. The maximum percentage replacement (mass basis) of diesel under preheated/unheated condition was about 33.6% at low loads (0-50%), whereas at full load it reduces up to 15%. The maximum brake thermal efficiency was found at 75% load and fumigation without preheating mode showed relatively higher (27%) value as compared to pure diesel combustion (25.7%). Exhaust gas temperature and lubricating oil temperature
increased with increase in load. CO and NO\textsubscript{x} emission increases slightly at full load. However, no detailed study was conducted on emissions.

Abu-Qudais et al. (Abu-Qudais and Haddad 2000) conducted comparative analysis of ethanol fumigation technique and ethanol as a blend with diesel fuel. A single cylinder, naturally aspirated, four stroke, direct injection, 0.582 L diesel engine, and for ethanol fumigation at low pressure single hole spraying nozzle was selected for the study. The testing was done in the engine speed range of 1000 rpm to 2000 rpm, total energy kept fixed (baseline fuel) and ethanol supplied in terms of energy flow rates 5%, 10%, 15% and 20%. Both fumigation and blending showed slight gain in brake thermal efficiency, however, relatively more favorable results were achieved by ethanol fumigation which produces 7.5% gain while operating at 20% fumigation. Whereas, optimum percentage for ethanol diesel blends (15%) produces an increase in thermal efficiency was about 3.6%. The reason could be explained by the increase in ignition delay period that results in rapid heat release rates and hence less time was available to transfer the heat from the engine to coolant which saves loss of energy. Results showed optimum percentage of ethanol fumigation rate was 20%, and blending ethanol with diesel fuel was 15%. UHC emission ranges from 20% to 36% under different operating condition when using 20% ethanol fumigation, however, it increased from 25% to 49% under ethanol diesel blends. Moreover, at 20% ethanol fumigation leads to produce a reduction of engine smoke by 48%. CO emissions were increased by 55% and 43.4% under fumigation (20%) and blending (15%) condition respectively.

Leahey et al. (Leahey and Jones 2007) adopted several strategy to use oxygenates (bio-diesel and ethanol) with diesel in a single-cylinder CFR engine. They used different injection strategy (bio-diesel & diesel with advanced injection timing and ethanol diesel blends with late injection timing). Blending of bio-diesel and ethanol with diesel showed small reduction in the soot emissions. However, fumigation of ethanol successfully reduces up to 50% of soot emissions without adversely affecting lubricity which was one of major concerns when ethanol was used in the form of blend. Thermal efficiency improved by about 3% with all combination of biofuel and diesel as a fuel as compared to pure diesel.
K. S. Tsang et al. (Tsang and Zhang 2010) studied fumigation of ethanol on 4-cylinder direct injection diesel engine (4.334 L, Isuzu 4HF1) fueled with Euro-V diesel. They examined various performance, combustion and emission parameters on five different BMEP (0.08, 0.19, 0.39, 0.58 and 0.70 MPa) at constant engine speed of 1800 rpm. BSFC decreases with increase in engine load but increases with increase in fumigation ethanol. BTE was reduced at low and medium loads but there no significant change was observed at high engine loads. At low load (0.08 MPa) peak in-cylinder pressure decreases with increasing fumigation ethanol but at medium and high load (0.39 and 0.70 MPa) the trend was exactly reversed. The peak heat release rate increases with increase of fumigation ethanol irrespective of engine load. Start of combustion was retarded due to fumigation ethanol, thus it increases ignition delay. Maximum increase in ignition delay corresponds to 20% fumigation ethanol of about 2° CA. Premixed combustion phase increases with increase in fumigation ethanol at high engine loads. At engine load of 0.08 MPa and 0.70 MPa, the maximum increase in BSCO was associated with 20% fumigation ethanol were 1.3 and 2.7 times as compared to diesel fuel respectively. Moreover, BSHC increased by 3.3 and 2.4 times in the similar condition as stated above. The reduction in BSNOx with reference to pure diesel combustion was more significant at low engine loads compared to high engine loads. At engine load of 0.39 MPa and 0.70 MPa the maximum reduction associated with 20% fumigation ethanol was 14.7% and 3.9% respectively with reference to diesel fuel. Smoke opacity decreases significantly at medium and high engine loads with increase in fumigation ethanol. The maximum reduction was reported at 0.58 MPa was about 56% associated with 20% fumigation ethanol. PM concentrations were reduced up to 27% under different percentage of fumigation ethanol and it was more obvious at medium and high engine loads. The maximum reduction in particle number concentration was about 30% associated with 20% fumigation ethanol at 0.39 MPa engine load.

Ethanol fumigation was studied at the Delhi Technical University, Rohini New Delhi India in 2008 (Bhupendra Singh Chauhana and Naveen Kumar 2011). Ethanol was fumigated by using a carburetor. Quantity of ethanol was controlled by butterfly valve of CV (constant velocity) carburetor and quantity of diesel injected was regulated by
speed governor of the engine. Interestingly air box has two outlets-one was directly connected with the induction manifold and another with carburetor which further rejoined to the induction manifold. The emissions study was performed on single cylinder (10 HP), constant speed direct injection, and water cooled Kirloskar diesel engine with displacement volume of 0.78 L. At no load CO emissions increases, however at low and high load it decreases with increase in fumigation ethanol. The maximum reduction in CO was recorded at 20% and 45% of full load that was associated with 20% fumigation ethanol. Similarly, CO₂ emission decreases with increase in fumigation ethanol at 20% and 45% of full loads and remains constant at no load condition. At no load NOₓ emission increases with increase in fumigation ethanol, however at 20% and 45% of full load it decreases up-to certain level of fumigation ethanol (20-22%) and again starts increasing. Considerable amount (up to 7 times) of UHC emissions was observed at no load and small load with increase in fumigation ethanol, nevertheless at full load the maximum substitution was limited up to 20% fumigation ethanol and it showed relatively lower emissions. Reduction in smoke opacity was higher in the medium and high engine load conditions. At 70% and full load maximum reduction in smoke opacity was found at 14% of fumigation ethanol.

Ethanol fumigation with hot and cold EGR was studied at the Christ University, Bangaluru Karnataka India (Hebbar and Anantha 2012). A small DI, water cooled four-strokes Kirloskar diesel engine (0.624 L, AV 1) was used for the study. At 50% EGR brake thermal efficiency drops by 20% and 40% with fumigation and without fumigation respectively. However at low level of fumigation (10%) and EGR (30%) measured loss was very low around 5% and further increase in fumigation leads to enhance brake thermal efficiency by around 20%. CO₂ emissions showed insignificant change with increasing EGR under fumigation ethanol associated with EGR mode, whereas, it increases with EGR without fumigation ethanol. Pure diesel combustion along with EGR emits higher smoke compared to fumigation ethanol mode, also considerable reduction they had measured when fumigation ranges from 5% to 15%. NOₓ emission reduced from 10% to 15% by fumigation ethanol. UHC emissions increase with EGR rate and level of fumigation ethanol.
The role of injection timing on performance of dual fueled operation was demonstrated by Padala et al. (Padala and Woo 2012) by using small single cylinder common rail DI engine. In-cylinder pressure decreases at TDC whereas net heat release rate increases with increase in fumigation ethanol. Brake thermal efficiency increased during fumigation ethanol as compared to diesel fuel for the same combustion phasing. They showed stable combustion could be achieved up to 40% fumigation ethanol, also engine delivers higher IMEP while running on fumigation ethanol compared to diesel fueling. One interesting observation was made that increase in fumigation ethanol leads to reduce premixed phase and late cycle burning duration.

Surawski et al. (Surawski and Miljevic 2010) conducted a study in order to investigate the effect of ethanol fumigation on PM emissions, volatility, and toxicity. Their experiments were carried out on a four-cylinder Ford diesel engine (2.7 L) and the fumigation system featured an electronically-controlled ethanol injector. A Scanning Mobility Particle Sizer (SMPS) was used to analyze particle-size distributions. They showed reductions in total particle mass concentrations compared to baseline diesel. However, the particle size distributions also exhibited a shift towards smaller particle diameters (nucleation-mode particles), with a corresponding increase in total particle number concentrations with ethanol fumigation.

2.11 ETHANOL PRODUCTION FROM RENEWABLE SOURCES
Ethanol is derived from renewable sources feedstock, locally grown plants such as wheat, sugar beet, corn, straw, and wood (Gray and Zhao 2006). It is possible that wood, straw and even house-hold wastes may be economically converted to alcohols. Nevertheless, largely ethanol is produced by fermentation; it is an anaerobic biological process in which the sugars are converted to alcohol by the action of microorganisms, usually yeast (Demirbas 2007). It is envisaged that long-term, economical and environmentally friendly production of bio-ethanol is via carbohydrates (hemicelluloses and cellulose) in lignocellulosic materials. The lignocellulose is subjected to delignification, steam explosion and dilute acid pre-hydrolysis, followed by enzymatic hydrolysis and fermentation into bio-ethanol (Satgé de Caro and Mouloungui 2001; Fahd and Ebna Alam Wenming 2013). In
India, ethanol is produced from conventional feedstocks, such as sugar cane/beet juice and molasses or from starch based feedstocks like wheat, corn or even tubers like cassava.

As the agricultural research demonstrated that tropical sugar beet and sweet sorghum are cost effective feedstocks, recently sweet sorghum also accepted commercially (Praj Industries) to produce bio-ethanol that would cater to the growing need of ethanol as a fuel. India is the world’s largest sugar consumer and currently producing 4% of global bio-ethanol from sugar cane. Praj industry at Pune in India (Praj Industries) emerged as the first company in South Asia to set up an integrated second generation (2G) cellulosic ethanol plant. Table 2.1 (Imran and Varman 2013) shows increasing ethanol production to justify the ethanol demand as a fuel.

Table 2.1: Bio-ethanol production annually (millions of U.S. liquid gallons per year)

<table>
<thead>
<tr>
<th>Country or region</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>6485</td>
<td>9235</td>
<td>10,938</td>
<td>13,231</td>
<td>13,900</td>
</tr>
<tr>
<td>Brazil</td>
<td>5019.2</td>
<td>6472.2</td>
<td>6577.89</td>
<td>6921.54</td>
<td>5573.24</td>
</tr>
<tr>
<td>European Union</td>
<td>570.30</td>
<td>733.60</td>
<td>1039.52</td>
<td>1176.88</td>
<td>1199.31</td>
</tr>
<tr>
<td>China</td>
<td>486.00</td>
<td>501.90</td>
<td>541.55</td>
<td>541.55</td>
<td>554.76</td>
</tr>
<tr>
<td>Canada</td>
<td>211.30</td>
<td>237.70</td>
<td>290.59</td>
<td>356.63</td>
<td>462.3</td>
</tr>
<tr>
<td>Thailand</td>
<td>79.20</td>
<td>89.80</td>
<td>435.20</td>
<td>270.13</td>
<td>289.29</td>
</tr>
<tr>
<td>India</td>
<td>52.80</td>
<td>66.00</td>
<td>91.67</td>
<td>110</td>
<td>135</td>
</tr>
<tr>
<td>Colombia</td>
<td>74.90</td>
<td>79.30</td>
<td>83.21</td>
<td>73.96</td>
<td>79.26</td>
</tr>
<tr>
<td>Australia</td>
<td>26.40</td>
<td>26.40</td>
<td>56.80</td>
<td>66.04</td>
<td>87.2</td>
</tr>
</tbody>
</table>

2.12 EFFECT OF EGR ON HCCI COMBUSTION

Despite the large differences in the auto-ignition characteristics of gasoline and diesel fuels, most applications of HCCI for SI and diesel engines use some form of exhaust gas re-circulation (EGR) to help control the combustion phasing.

The (Sjöberg and Dec 2011) results have showed that the single-stage ignition fuel ethanol is quite sensitive to the reduction of compression heating that occurs with EGR due to the higher heat capacity of the EGR gases compared to air. This high sensitivity to the cooling effect of EGR is similar to that of gasoline and iso-octane,
which also are single-stage ignition fuels under these conditions. On the other hand, ethanol is very insensitive to the reduction of O₂ concentration associated with the addition of EGR. Both of these characteristics relate to ethanol’s molecular stability – it does not react much until just before the hot-ignition point is reached. Consequently, ethanol has a low intermediate-temperature heat-release rate, which leads to a low temperature-rise rate prior to hot ignition, and therefore a high sensitivity to the cooling effect of EGR. Also, the relative lack of intermediate-temperature heat release prevents [O₂] from having much influence on the temperature rise prior to hot ignition, leading to a low sensitivity of the auto-ignition timing to changes of [O₂]. Finally, both H₂O and trace species have significant ignition-enhancing effects for ethanol that to some degree counter the retarding effect of EGR.

Study (Ryan III and Callahan 1996) carried out on a single-cylinder, direct-injection diesel engine, which was modified to operate on compression ignition of homogenous mixtures of diesel fuel and air. The limitations of HCCI mode of combustion which happens to be misfire and knock could be overcome. To control the auto-ignition, the variables examined in this study included air-fuel ratio, compression ratio, fresh intake air temperature, exhausts gas re-circulation rate, and intake mixture temperature. The results suggested that controlled homogeneous charge compression ignition is possible. It is found that satisfactory power settings are possible with high EGR rates and stoichiometric fuel-air mixtures. Successful HCCI operation results in near zero smoke emissions.

Follow-up research on the same engine (Gray III and Ryan III 1997) it was observed that for diesel fueled HCCI combustion, premature ignition and knocking occurs if normal diesel compression ratios were used. Compression ratios in the range of 8:1 to 13:1 produces satisfactory results, together with intake temperatures and the amount of EGR also plays important role. Compression ratios of 9:1 to 11:1 provide acceptable combustion over the largest range of fueling rates. However, combustion phasing was still advanced even at low compression ratios. Also, relatively high intake temperatures (135 ºC to 205 ºC) were required to minimize the accumulation of liquid fuel on the surface of intake system. When intake temperatures were reduced
below 130 °C, smoke emissions was increased significantly. Authors suggested that this owing to combustion occurring in scattered diffusion flames around large droplets. Further, UHC emission tended to be very high. As a result of poor combustion efficiency, reduced compression ratios, and non-optimal combustion phasing, fuel consumption increased by an average of about 28% over normal direct-injection (DI) diesel combustion.

Mingfa Yao et al. (Mingfa and Zheng Chen 2006) experimentally examined the HCCI combustion fueled by DME and methanol, two injectors were mounted near the port of water cooled diesel engine modified to operate on HCCI mode. Quantity of DME and methanol were regulated by electromagnetic valve and electric controller respectively. The percentage of DME was expressed in terms of amount of energy released by DME to the total energy released by DME and methanol together. It was found that HCCI combustion could be controlled by regulating percentage of DME and EGR. However EGR is not able to enlarge the maximum IMEP but it can be increased the higher % of DME at normal combustion. Ultra-low NOx emission was reported at normal combustion, CO emissions found to be closely related with the peak mean temperature in the cylinder. UHC emissions found to be reaching a lowest value by adjusting percentage of EGR and DME.

Simescu et al. (Simescu and Ryan 2002) carried out partial HCCI combustion in heavy duty engine along with cooled and hot EGR. The lowest weighted BSNOx achieved was 2.55 g/kW-hr using cooled EGR and 20% port fuel injection (PFI). This corresponds to 54% reduction compared, however, BSHC and BSCO emissions increased by a factor of 8 and 10, respectively, compared to the stock engine.

Qiang et al. (Qiang and Junhua 2012) investigated the influence of pilot injection and exhaust gas re-circulation (EGR) on combustion and emissions in a HCCI-DI combustion engine and observed that, NOx emission decreased with increase in pilot quantity. In addition, substantial reduction in NOx emission was found with low level of EGR as compared to without EGR. Nevertheless, smoke opacity was increased because of EGR.
Xing-Cai et al. (Xing-Cai Chen and Lü 2005) used single-cylinder four stroke high speed diesel engine to investigate the effect of RON (research octane number) fuels, EGR rate, intake charge temperature, equivalence ratio, coolant temperature, and engine speed on the HCCI ignition timing, combustion duration, cycle-to-cycle variation, and emissions. Moreover, minor modifications were done in the intake, exhaust and fuel injection system to successfully operate on HCCI mode of combustion. The fuels selected for different set of operating conditions were n-heptane and iso-octane and their blends with RON25, RON50, RON75, and RON90. The results revealed that the cumulative heat release in the first-stage combustion was strongly dependent on the concentration of n-heptane in the mixture. The start of ignition of the second-stage found to be linear with the start of ignition of the first-stage.

In continuation to the first part Xing-Cai (Xing-Cai Chen and Lü 2005) author studied the effect of EGR rate, intake temperature, coolant temperature and engine speed on the HCCI combustion characteristics of a single-cylinder HCCI engine. The ignition timing for the both first and second stage of combustion was found to be retarded along with combustion duration, and it increases with the use of cooled EGR. High octane fuel showed considerable change in the emissions of CO and UHC whereas moderate effect was found in case of n-heptane and RON25.

Shi et al. (Shi and Cui 2006) used combined internal EGR with the help of variable valve timing (VVT) and external cooled EGR. Early direct injection of diesel fuel was done to enhance the fuel vaporization by the hot EGR trapped into the cylinder by negative valve overlap. This helps to prepare homogenous mixture, which in turn reduces NOx and soot emissions. Cooled external EGR was effective to control the start of ignition; this basically delayed the start of combustion, and as the diesel has high cetane number shows early start of ignition (SOC) at elevated temperature.

Machrafi et al. (Machrafi and Simeon Amouroux 2008) performed parametric study by using mono-cylinder cooperative fuel research engine on the emission of HCCI combustion fueled with primary reference fuel. The parameters selected for this purpose were inlet temperature, it changed from 30 to 70 ºC. In addition to that, equivalence ratio (0.28 to 0.41), compression ratio (6 to 14), together with thermal and chemical effects of exhaust gas re-circulation was analyzed. A higher dilution due
to EGR, decreases the peak temperature, and incomplete combustion can take place when the dilution is too strong, increasing the CO concentration.

The experimental work (Miguel Torres García and Francisco José Jiménez-Espadafor Aguilar 2009) conducted on single cylinder HCCI engine fueled by diesel. They have studied the effect of injection timing and EGR on start of combustion and emissions. Results were revealed that an increase of inlet temperature at constant EGR rate has a large effect on the start of combustion in HCCI mode, and advances it. Soot emissions are negligible in the HCCI combustion mode, and are independent of the EGR rate. Engines running in the HCCI combustion mode with EGR reach ultra-low NOx emissions.

2.13 EMISSION STANDARDS

The emissions and fuel regulations for four-wheeled light-duty, heavy-duty vehicles are one of the motivation to improve diesel combustion. Table 2.2, shows emissions standards for light-duty vehicles propelled by diesel engines. Initially, Euro-I norms was implemented first in the year 2000 (DieselNet 2013) and named as India 2000. Progressively the emission limits becomes more stringent and currently a mixed of BS-III and BS-IV are applicable across the nation. However, BS-IV is still applicable in National capital regions and eleven major cities of the country.

Table 2.2: Emission standards for Light-Duty vehicles (DieselNet 2013)

<table>
<thead>
<tr>
<th>Standard</th>
<th>CO</th>
<th>UHC</th>
<th>UHC+NOx</th>
<th>NOx</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>-</td>
<td>17.3-32.6</td>
<td>2.7-3.7</td>
<td>-</td>
<td>-</td>
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<tr>
<td>1996</td>
<td>-</td>
<td>5.0-9.0</td>
<td>-</td>
<td>2.0-4.0</td>
<td>-</td>
</tr>
<tr>
<td>2000</td>
<td>India 2000</td>
<td>2.72-6.90</td>
<td>-</td>
<td>0.97-1.70</td>
<td>-</td>
</tr>
<tr>
<td>2005</td>
<td>Bharat Stage II</td>
<td>1.0-1.5</td>
<td>-</td>
<td>0.7-1.2</td>
<td>-</td>
</tr>
<tr>
<td>2010</td>
<td>Bharat Stage III</td>
<td>0.64-0.80</td>
<td>-</td>
<td>0.56-0.72</td>
<td>0.50-0.65</td>
</tr>
<tr>
<td>2010</td>
<td>Bharat Stage IV (Only in selected regions)</td>
<td>0.50-0.63-0.74</td>
<td>-</td>
<td>0.30-0.39-0.46</td>
<td>0.25-0.33-0.39</td>
</tr>
</tbody>
</table>
Nevertheless, advanced combustion systems with increased injection pressure, EGR, improved piston-bowl geometries, and improved in-cylinder flows have resulted in substantial reductions in emissions, and research efforts continue. Despite these efforts, it appears highly unlikely that conventional jet-mixing controlled diesel combustion can meet future emission requirements without being fairly expensive after-treatment systems.

2.14 PHYSICOCHEMICAL PROPERTIES OF ALCOHOL AS FUEL

It has been established by various studies (Alan and Hansen 2005; Demirbas 2007) that alcohol along with diesel fuel produces satisfactory results with compression ignition engine. Alcohol fuels, methanol and ethanol have similar physicochemical properties and emission characteristics as that of petroleum fuels.

i) The role of fuel viscosity and lubricity is very vital for the injection system, especially, when the engine is operating on rotary distributor injection pumps or common rail injection system, however, it is not very serious when inline fuel pumps and unit injectors are sued. Addition of ethanol to diesel lowers the fuel viscosity and lubricity (Wrage and Goering 1980) that results into increase the leakage from the pump and injector and it leads to reduce the maximum fuel delivery and ultimately power output. Fuel viscosity also affects the atomization and spray characteristics (smaller Sauter mean droplet diameter) in the combustion chamber.

ii) Power output from the engine directly depends on the energy content of the fuel, since alcohol has low heating value as compared diesel fuel. Therefore, addition of each 5% ethanol decreases the energy content of E-diesel blends by approximately 2%. This indicates that to get the same power output from the E-diesel compared to diesel more alcohol is required by mass and volume.

iii) Solubility ethanol-diesel blends is mainly affected by two factors, temperature and water content (small trace amount of water also leads to separation of blends) of the blend. Therefore, a higher percentage of alcohol is not allowed for they could not mix with diesel fuel homogeneously. The aromatic content of the diesel fuel also affects solubility of ethanol in diesel (Gerdes 2001). Prevention
of separation can be possible by two ways either by adding emulsifier (to suspend small droplet of ethanol in diesel) or by adding co-solvent that acts as a bridging agent through molecular compatibility (Letcher 1983).

iv) As per ASTM standard D975-02, the specified minimum cetane number for No. 2 diesel fuels is 40. Typically no. 2 diesel fuels have cetane number of 45-50. Since ethanol has higher octane no which is inversely related with cetane no therefore ethanol has extremely low CN (between 5 and 15). Higher cetane number leads to increase ignition delay period which provides more time for fuel vapourization before combustion starts. However, it increases initial burn rate (constant volume heat release) which is more efficient conversion process of heat to work. Sometimes poor ignitability may lead to rapid burning of vapourized alcohol and sever knock which may damage the engine.

v) Alcohol has higher stoichiometric fuel/air ratio (methanol -0.15393 and diesel - 0.06924) than diesel this is due to the partially oxidized state or it is an oxygenated fuel. Thus, blending alcohol into diesel fuel leads to leaner operation. Also, alcohol has negligible sulfur content and high H/C ratio.

vi) As alcohol (methanol and ethanol) has higher latent heat of vaporization as compared to diesel fuel, therefore E-diesel leads to longer ignition delay period. Also, when alcohol is injected into the intake manifold (fumigation) it cools down the air which is inducted and increased volumetric efficiency (reduces compression work done) and similarly this cooling effect reduces temperature of air-fuel after compression.

vii) Alcohol burning produces higher laminar flame propagation speed which completes the combustion process faster and thus improves engine thermal efficiency (Adelman H 1979; Wagner and Zarah 1979)

viii) As the high flammability of alcohol is one of the major concerns during handling and storage while implementing their application in existing infrastructure.

ix) In addition to lower calorific value, very high latent heat of vaporization, there is a serious health hazard associated with methanol which limits use of methanol over ethanol as an automotive fuel.
Methanol is a highly toxic substance used as an alternative fuel, industrial solvent and automotive antifreeze. Moreover, it is extremely dangerous in case of human consumption, since it leads to severe visual disturbance.

Methanol is more toxic than ethanol. The key reason behind this when methanol converted in to aldehyde, it leaves the by product of formaldehyde which is toxic.

Robert and Nauss examined methanol toxicity on humans (Robert Kavet and Nauss 1990) specially due to automotive methanol vapour. They reported that consequences of acute exposures of methanol leads to un-compensated metabolic acidosis with superimposed toxicity to the visual system.

### 2.15 CONCLUSIONS FROM THE LITERATURE REVIEW

Based on the literature review above, it is clear that lot of emphasis is given on development of alternate diesel combustion technology and application of alternate fuel in diesel engine has increased significantly. Alcohol increasingly being used as a replacement to diesel fuel compared to other fuels.

After reviewing the literature few gaps are clearly visible and need extended research work. These are mentioned hereunder:

- Partially premixed charge compression ignition study which was carried out in China (Tsang and Zhang 2010; Zhang Z.H. and Tsang 2011) and other parts of world is being done on multi-cylinder engines. Only few researcher (Abu-Qudais and Haddad 2000; Padala and Woo 2012) worked on single cylinder engine and especially in India (Ajav E. A. and Bachchan Singh 1998; Bhupendra Singh Chauhana and Naveen Kumar 2011; Hebbar and Anantha 2012) and reported premixed ethanol.

  i) All the reported work does not includes optimization of injection timing for premixed fuel (ethanol) and DI (diesel) fuel.

  ii) Reported studies (Ajav E. A. and Bachchan Singh 1998; Bhupendra Singh Chauhana and Naveen Kumar 2011; Hebbar and Anantha 2012) were used carburetor or single hole atomizing nozzle to create premixing of ethanol with
air. So it was felt to study the effect of electronically controlled multipoint fuel injection system for ethanol which creates premixing of ethanol with the air.

iii) Hebbar et al. (Hebbar and Anantha 2012) is only the single work reported effect of EGR on premixed ethanol. However, it could not include combustion study and effects of injection timing. So there is a need to explore premixed ethanol on small capacity diesel engines which are used for agricultural and decentralized power generation purpose in rural India.

iv) Effect of intake air-preheating is not explored in great details.

v) Effect of combustion geometry (toroidal shape) on emissions is not reported.

vi) Effect of altering the injection spray pattern also not reported. So in this case instead of three holes nozzle is replaced with four holes nozzle.

2.16 OBJECTIVES OF THESIS

1. Modification of an existing single-cylinder four stroke direct injection diesel engine to operate on the partially premixed charge compression ignition combustion mode.

2. Study the effects of varying mixture compositions of premixed ethanol combustion at different engine loads.

3. Comparative performance, emission and combustion analysis of the developed PCCI engine fueled with ethanol and diesel in different proportions.

4. To achieve simultaneous reductions of NOx and smoke with the help of premixed ethanol and EGR.