CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

A comprehensive literature review is carried out to demonstrate the technical feasibility of DEE-kerosene-diesel blends used in CI engine and use of proper techniques to improve performance and emission characteristics. The outcomes of literature review are discussed here.

In a compression ignition engine, the fuel injected during the ignition delay period is atomised, vaporised, mixed with air, ignited through auto-ignition mode and burned in premixed burning phase. Once combustion has started, the fuel discharging from the injector is evaporated and ignited almost immediately, burning it in the diffusion burning phase. The peak cylinder pressure depends on the burned fuel fraction during the premixed burning phase (Heywood, 1984).

The diesel engines have several advantages like high thermal efficiency, torque capacity, reliability, adaptability, low HC and CO emissions and cost effectiveness, but they suffer from high concentration of NOx and particulate emissions. The primary contributing factors for the particulate matters are rich mixture and heterogeneous combustion, sulphur content, lubricating oil, unburned HC and dominant diffusion combustion phase. The NOx formation in diesel engines is a function of higher temperature, oxygen concentration and residence time.

Simultaneous reduction in NOx and particulate matter is quite difficult in diesel engines due to the trade-off between PM and NOx, which is often accompanied by fuel consumption
penalty (Nylund et al., 2005; Chang et al., 2014). Hence, it is more difficult for diesel engines to meet stringent emission norms by the use of conventional neat diesel fuel through engine design or control parameters alone. The diesel engine technology is being upgraded in order to meet stringent emission norms as well as fuel economy requirements. The various methods like EGR, dual fuel mode, catalytic converters, retarding the injection timing, use of high injection pressure, split injection and modifying the combustion chamber geometry to enhance the swirl and squish are being tried to reduce emissions but problems are still prevailing in the operation of these techniques (Mohanamurugan et al., 2011; Lounici et al., 2014).

2.2 ALTERNATIVE OXYGENATED FUELS USED IN DIESEL ENGINES

Global and urban environmental problems are being caused by a rapid increase in carbon dioxide (CO2) and harmful exhaust emissions due to the burning of fossil fuels. The remaining available oil deposits and the growing cost of conventional fuels for automotive engines have spurred the research for alternative fuels. The introductions of oxygenated compounds into diesel fuel especially those that are originally bio-resources are the best ways to reduce emissions of diesel engines (Nigam, 2011). Bio-fuels made from agricultural products which are oxygenated by nature, not only reduce the exhaust emissions, but also reduces the world’s dependence on oil imports. These oxygenates are classified as –

- Alcohols (R-OH)
- Ethers (R-O-R)
- Esters (R-C-O-O-R)
- Carbonates (R-O-C-O-O-R)

Item “R” represents a hydrocarbon chain. Among all oxygenates, a worldwide trend towards the application of bio-fuels and mainly biodiesel and alcohols have been observed for the last two decades as a clean alternative fuel for compression ignition engines without large sacrifice in vehicle performance (Xing-cai et al., 2004). The various oxygenated fuels which are investigated by researchers for I C Engines are listed in Table 2.1 and arranged orderly by their oxygen content.
Table 2.1 Oxygenated fuels studied in I C Engines (Tree et al., 2007; Thipse, 2010; Nigam et al., 2011; Agarwal, 2007; Sezer, 2011; Chang, 2014; Rakopoulos et al., 2014).

<table>
<thead>
<tr>
<th>Oxygenated Fuel</th>
<th>Structural Formula</th>
<th>Molecular Formula</th>
<th>Oxygen Content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl carbonate (DMC)</td>
<td>(CH₃O)₂CO</td>
<td>C₃H₆O₃</td>
<td>53.3</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>CH₃O</td>
<td>50.0</td>
</tr>
<tr>
<td>Dimethoxy methane</td>
<td>CH₃OCH₂OCH₃</td>
<td>C₃H₆O₂</td>
<td>42.1</td>
</tr>
<tr>
<td>Diethyl carbonate</td>
<td>(C₂H₅O)₂CO</td>
<td>C₅H₁₀O₃</td>
<td>40.7</td>
</tr>
<tr>
<td>Diethyl succinate</td>
<td>C₂H₅O₂CCH₂CH₂CO₂C₂H₅</td>
<td>C₈H₁₄O₄</td>
<td>36.8</td>
</tr>
<tr>
<td>Diethyl maleate</td>
<td>C₂H₅O(CO)CH=CH(CO)OC₂H₅</td>
<td>C₈H₁₂O₄</td>
<td>36.8</td>
</tr>
<tr>
<td>Propylene glycol methyl ether acetate (1-methoxy-2-propanol acetate)</td>
<td>CH₃CO₂CH(CH₃)CH₂OCH₃</td>
<td>C₆H₁₂O₃</td>
<td>36.4</td>
</tr>
<tr>
<td>Tetra(ethylene glycol) dimethyl ether (tetraglyme)</td>
<td>CH₃(OCH₂CH₂)₄OCH₃</td>
<td>C₁₀H₂₂O₅</td>
<td>36.0</td>
</tr>
<tr>
<td>Di(ethylene glycol) dimethyl ether (2-methoxymethyl, diglyme)</td>
<td>(CH₃OCH₂CH₂)₂O</td>
<td>C₆H₁₄O₃</td>
<td>35.8</td>
</tr>
<tr>
<td>Ethylene glycol dimethyl ether (monoglyme, 1,2-dimethoxy ethane)</td>
<td>CH₃O(CH₂)₂OCH₃</td>
<td>C₄H₁₀O₂</td>
<td>35.6</td>
</tr>
<tr>
<td>Dimethyl ether (DME)</td>
<td>CH₃-O-CH₃</td>
<td>C₂H₆O</td>
<td>34.8</td>
</tr>
<tr>
<td><strong>Ethanol</strong></td>
<td><strong>C₂H₅OH</strong></td>
<td><strong>C₂H₆O</strong></td>
<td><strong>34.8</strong></td>
</tr>
<tr>
<td>Tri(propylene glycol) methyl ether</td>
<td>CH₃(OC₃H₆)₃OH</td>
<td>C₁₀H₂₂O₄</td>
<td>31.1</td>
</tr>
<tr>
<td>Ethylene glycol monobutyl ether acetate (2-butoxyethyl ether)</td>
<td>CH₃CO₂CH₂CH₂O(CH₂)₃CH₃</td>
<td>C₈H₁₈O₃</td>
<td>30.0</td>
</tr>
<tr>
<td>Di (ethylene glycol) diethyl ether (2-ethoxyethyl ether)</td>
<td>(C₂H₅OCH₂CH₂)₂O</td>
<td>C₈H₁₈O₃</td>
<td>29.6</td>
</tr>
<tr>
<td>Chemical Name</td>
<td>Molecular Formula</td>
<td>Molecular Weight</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------------</td>
<td>------------------</td>
<td></td>
</tr>
<tr>
<td>Tetraethoxypropane</td>
<td>(C₂H₅O)₂CHCH₂CH(OH)₂C₂H₅</td>
<td>C₁₁H₂₄O₄</td>
<td>29.1</td>
</tr>
<tr>
<td>Dibutyl maleate</td>
<td>CH₃(CH₂)₃O₂CCH=CHCO₂(CH₂)₃CH₃</td>
<td>C₁₂H₂₀O₄</td>
<td>28.1</td>
</tr>
<tr>
<td>Ethylene glycol mono-n-butyl ether</td>
<td>CH₃(CH₂)₃O(CH₂)₂OH</td>
<td>C₆H₁₄O₂</td>
<td>27.1</td>
</tr>
<tr>
<td>Ethylene glycol mono-t-butyl ether</td>
<td>t-C₄H₉O(CH₂)₂OH</td>
<td>C₆H₁₄O₂</td>
<td>27.1</td>
</tr>
<tr>
<td>Propylene glycol mono-t-butyl ether</td>
<td>t-C₄H₉O(CH₂)₃OH</td>
<td>C₇H₁₆O₂</td>
<td>24.2</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>CH₃CH₂OCH₂CH₃</td>
<td>C₄H₁₀O</td>
<td>21.6</td>
</tr>
<tr>
<td>Pentyl ether</td>
<td>(CH₃(CH₂)₄)₂O</td>
<td>C₁₀H₂₂O</td>
<td>18.4</td>
</tr>
<tr>
<td>Ethylene glycol di-t-butyl ether</td>
<td>(CH₃)₃CO(CH₂)₂OC(CH₃)₃</td>
<td>C₁₀H₂₂O₂</td>
<td>18.4</td>
</tr>
<tr>
<td>Methyl t-butyl ether (MTBE)</td>
<td>(CH₃)₃COCH₃</td>
<td>C₅H₁₂O</td>
<td>18.2</td>
</tr>
<tr>
<td>Octyl alcohol</td>
<td>CH₃(CH₂)₇OH</td>
<td>C₈H₁₈O</td>
<td>12.3</td>
</tr>
<tr>
<td>Butyl ether</td>
<td>(CH₃(CH₂)₃)₂O</td>
<td>C₈H₁₈O</td>
<td>12.3</td>
</tr>
<tr>
<td>2-Ethylhexyl acetate</td>
<td>CH₃CO₂(CH₂)₄CH(C₂H₅) CH₃</td>
<td>C₁₀H₂₀O₂</td>
<td>10.3</td>
</tr>
<tr>
<td>Bio-diesel (KOME)</td>
<td>C₁₂ - C₂₂</td>
<td>C₁₂ - C₂₂</td>
<td>10 - 12</td>
</tr>
</tbody>
</table>

### 2.3 BIOFUELS

Alcohol fuels can substitute for gasoline in spark-ignition engines, while biodiesel, green diesel, diethyl ether (DEE) and dimethyl ether (DME) are suitable for use in compression ignition engines. The various technologies that can be used for production of biofuels are fermentation of sugar substrates, catalytic technology to convert ethanol to mixed hydrocarbon, hydrolysis of cellulose, biobutanol by fermentation, transesterification of natural oils and fats to biodiesel, hydrocracking of natural oils and fats, pyrolysis and gasification of various biological materials etc. (Nigam et al., 2011).

Biofuels are broadly classified as primary and secondary biofuels. The primary biofuels such as fuelwood, wood chips, pellets etc are used primarily for heating, cooking or electricity
production in an unprocessed form. The secondary biofuels are produced by processing of biomass e.g. ethanol, biodiesel, diethyl ether, dimethyl ether, etc. that can be used in vehicles and various industrial processes. The secondary biofuels are further divided into first, second and third-generation biofuels on the basis of raw material and technology used for their production (Nigam et al., 2011). The classification of Biofuels is shown in Figure 2.1.

Biodiesel is considered as a clean fuel which reduces unburned hydrocarbon, CO and particulate matter. It has almost no sulfur, no aromatics and has about 10% inherent oxygen, which helps it to burn fully. Its higher cetane number than diesel fuel improves the ignition quality even when blended with petroleum diesel (Kegi et al., 2008). However, it suffers from cold starting problems, higher viscosity and increasing NOx emission as compared to petroleum diesel (Rakopoulos et al., 2014).

Di-methyl ether (DME) is one of the promising alternative fuels for diesel engines. DME is the simplest ether expressed by its chemical formula CH₃OCH₃, consisting of two methyl groups bonded to a central oxygen atom. It has a low carbon-to-hydrogen (C:H) ratio. The chemical structure of DME is somewhat similar to methanol; it contains oxygen and no carbon-carbon bonds, thus limiting the possibility of forming carbonaceous particulate emissions during combustion (Youn et al., 2011). DME is a synthetic fuel can be made from
a variety of fossil feedstock including natural gas and coal as well as from renewable feedstock and waste. The most cost effective feedstock for both DME and methanol is natural gas at remote locations. The researchers Wang et al. (2014) have also studied the feasibility of DME as port premixing fuel in a diesel engine.

The bond breaking energies of DME fuel contains C–O bond is lower than with conventional fuel, which has C–C and C–H bonds. For this reason, the ignition delay of DME is much shorter and the auto-ignition temperature is lower than those of other hydrocarbon fuels. The short ignition delay and low auto-ignition temperature of DME contribute to the high cetane number. Cetane number is a measure of the fuel's ability to auto-ignite. Cetane number of DME (55-60) is higher than diesel fuel which leads to fast ignition and short ignition delay, which in turn lowers the premixed burning of the fuel, results in low NOx and noise emission. DME vaporizes easily in the cylinder when injected in a liquid phase due to its low boiling point (248 K) which yields better atomization and improved combustion. Also it leads to easier starting of engine during cold weather conditions. The viscosity of DME is very low, which reduces the effort in delivering the fuel supply into the engine cylinder during cold weather conditions. The exhaust gas reactivity of DME is very low. DME displays a visible blue flame similar to natural gas when burning over a wide range of air–fuel ratios, which is an important safety characteristic. DME is non-toxic and environmentally benign (Ismet et al., 2011).

The vapor pressure of DME (530 kPa at 298 K) is low but comparable to LPG hence it liquefies easily at relatively low pressurization (0.5 MPa). So, it can be easily handled and stored like LPG as liquefied gas, however, due to its low vapor pressure and low boiling point a pressurized fuel system is required to maintain liquid state of fuel. Corresponding high pressure on the back of the needle would decrease the injection rate and consequently hamper the engine performance. Also it increases the overall cost of the DME engine (Su et al., 2011). Low viscosity of DME causes the leakage from the fuel supply system which relies on small clearances for sealing (Semelsberger et al., 2005). Low lubricity of DME can cause intensified surface wear of moving parts within the fuel-injection system and hence conventional fuel delivery and fuel injection systems are not compatible with dimethyl ether (Ismet et al., 2011; Goto et al., 2005). The lower calorific value and lower density of DME than the diesel fuel requires higher volumetric flow rate of DME than the diesel fuel in order to produce the same amount of input energy (Seung et al., 2010). DME is not compatible
with most elastomers including those used in conventional diesel fuel system due to its corrosiveness (Su et al., 2011; Ismet et al., 2011). Due to the wide flammability limits the operation of DME combustion system needs the adoption of rigorous procedures for safe operation. To potentially overcome the fuel property effects of diesel fuel and neat DME fuel, as well as reduce emissions of diesel engine, it is advantageous to blend DME with diesel fuel without much engine modifications. Thus, the relative benefits of each fuel might be utilized. The blended fuel retains the desirable physical properties of diesel fuel but includes the cleaner burning capability of DME (Su et al., 2011).

Wang et al. (2008) experimentally demonstrates that the DME and diesel blend well with each other without any solvent. Xiaoming et al. (2005) experimentally demonstrated that the critical solubility temperatures of DME/diesel blended fuel are below 273.15 K and the critical solubility temperature decreases gradually with the increase of DME mass fraction in blend. Wang et al. (2008) have shown that the vapor pressure of DME-diesel blends is lower than that of pure DME at the same temperatures and it increases with an increase of DME mass fraction in blends but it is lower than that for pure DME. Due to lower vapor pressure of blend fuels, the low pressure fuel supply system can be used to keep blends in the liquid state. This lower fuel supply pressure is beneficial for the fuel transportation and storage safety of the blend fuels (In et al., 2011).

Ethanol is another promising oxygenated alternative fuel because it is a renewable bio-based resource and highly oxygenated (34.7% by weight), thereby providing the potential to reduce particulate emissions in CI engines and shows promise as a future fuel for spark ignition (SI) engines due to its high octane quality. However, there are many obstacles in the use of ethanol in CI engines such as very low cetane number (8), poor ignition characteristics and limited solubility in diesel fuel. Phase separation and water tolerance in ethanol-diesel blend fuels are crucial problems (Xing-cai et al., 2004). The dynamic viscosity of ethanol is much lower than diesel fuel. Thus, the lubricity is a potential concern of ethanol-diesel blend fuels (Rakopoulos et al., 2010). To overcome these problems, ethanol can be converted easily into diethyl ether through a dehydration process. Some important physicochemical properties of the base fuels and oxygenated fuels are shown in Table 2.2.
Table 2.2 Physical and Chemical Properties of diesel, kerosene and oxygenated fuels (Nigam et al., 2011; Thipse, 2010; Venkanna et al., 2011; Rakopoulos et al., 2014).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Diesel</th>
<th>Kerosene</th>
<th>Bio-Diesel (KOME)</th>
<th>DEE</th>
<th>DME</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure</td>
<td>C_{10} - C_{25}</td>
<td>-</td>
<td>C_{12} - C_{22}</td>
<td>C_{2}H_{5}-O-C_{2}H_{5}</td>
<td>CH_{3}-O-CH_{3}</td>
<td>CH_{3}-CH_{2}-OH</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>190-220</td>
<td>-</td>
<td>-</td>
<td>74</td>
<td>46</td>
<td>46</td>
</tr>
<tr>
<td>Oxygen content (mass %)</td>
<td>0</td>
<td>0</td>
<td>10-12</td>
<td>21.6</td>
<td>34.8</td>
<td>34.7</td>
</tr>
<tr>
<td>Cetane number</td>
<td>40-55</td>
<td>41.4</td>
<td>48-60</td>
<td>&gt;125</td>
<td>&gt;55</td>
<td>8</td>
</tr>
<tr>
<td>Auto-ignition temp. (°C)</td>
<td>250</td>
<td>-</td>
<td>-</td>
<td>160</td>
<td>235</td>
<td>420</td>
</tr>
<tr>
<td>Boiling point at 1 atm (°C)</td>
<td>180-360</td>
<td>148-282</td>
<td>182-337</td>
<td>34.6</td>
<td>-25.4</td>
<td>78</td>
</tr>
<tr>
<td>Lower calorific value (MJ/kg)</td>
<td>42</td>
<td>41.78</td>
<td>38.3</td>
<td>33.9</td>
<td>27.6</td>
<td>27</td>
</tr>
<tr>
<td>Stoichiometric A/F mass ratio</td>
<td>14-14.7</td>
<td>14.94</td>
<td>13.8</td>
<td>11.1</td>
<td>9.0</td>
<td>9.06</td>
</tr>
<tr>
<td>Vapour pressure(at 298 K) kpa</td>
<td>&lt;&lt;10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>530</td>
<td>-</td>
</tr>
<tr>
<td>Liquid density at NTP (kg/m³)</td>
<td>815-860</td>
<td>797</td>
<td>875-885</td>
<td>713</td>
<td>667</td>
<td>785-789</td>
</tr>
<tr>
<td>Viscosity of liquid at NTP (cSt)</td>
<td>2.6</td>
<td>1.15</td>
<td>1.9-6</td>
<td>0.23</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>Flammability limit in air (vol %)</td>
<td>1.4-7.6</td>
<td>-</td>
<td>-</td>
<td>3.4 - 18.6</td>
<td>-</td>
<td>4.3-19</td>
</tr>
</tbody>
</table>
2.4 DIETHYL ETHER (DEE)

2.4.1 Historical Background

Diethyl Ether (C₂H₅-O- C₂H₅) is a promising oxygenated renewable bio-base resource fuel for CI engines owing to its high ignition quality. Diethyl ether, also known as ethyl ether, sulfuric ether, simply ether, or ethoxyethane, is an organic compound in the ether class. DEE was first synthesized in 1540 by Valerius Cordus, who called it "oil of sweet vitriol" (oleum dulcis vitrioli). This name was chosen because it was originally discovered by distilling a mixture of ethanol and sulfuric acid (then known as oil of vitriol) and noted some of its medicinal properties. Furthermore, Theophrastus Bombastus von Hohenheim, better known as Paracelsus, discovered ether's analgesic properties. The name ether was given to the substance in 1730, by August Siegmund Frobenius.

Diethyl ether is a common laboratory solvent often used for liquid-liquid extractions (generally called solvent extractions). It has limited solubility in water (6.05 g/100 ml at 25 °C). It is the simplest ether expressed by its chemical formula CH₃CH₂-O-CH₂CH₃, consisting of two ethyl groups bonded to a central oxygen atom as shown in Figure 2.2.

![Figure 2.2 Chemical structure of DEE molecule](image)

2.4.2 DEE Production

Diethyl ether is one of the most important commercial ethers. In industry, DEE is often used as a solvent of organic reactions such as oil, fat, latex, micro cellulose, perfume, alkaloid solvent. This is also used as a separator of organic compound from its natural material sources. In addition, diethyl ether is identical to anesthesia in medical science (Widayat et al., 2013).
Diethyl ether can be produced using homogenous catalyst (sulfuric acid/Barbet process) and heterogeneous catalyst. The difficulty of Catalyst separation becomes the weakness of Barbet process. Furthermore, the corrosive behavior of Barbet process causes this process becomes costly. The second process, heterogeneous catalyst, uses alumina catalyst. In this process, ethanol conversion per pass and its yield is 60-80 and 90% respectively (Widayat et al., 2013). Evidently, the use of alumina catalyst in ethanol dehydration process produces a low ethanol conversion and diethyl ether yield. Hence, researchers develop the type of catalyst that can be used for ethanol hydration and dehydration process such as Alumina, MgO, alumina silica and WO₃ catalyst (Smith, 1981).

DEE can be produced both in the laboratory and on an industrial scale by the distillation of ethanol with sulphuric acid (acid ether synthesis). Initially, ethanol (CH₃CH₂OH) is mixed with a strong acid, typically sulphuric acid (H₂SO₄). The acid dissociates in the aqueous environment producing hydronium ions, H₃O⁺. A hydrogen ion protonates the electronegative oxygen atom of the ethanol molecule, giving it a positive charge as shown in Equation 1.1.

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{CH}_2\text{OH}_2^+ + \text{H}_2\text{O}
\] (1.1)

A nucleophilic oxygen atom of unprotonated ethanol molecule displaces a water molecule from the protonated (electrophilic) ethanol molecule producing water, a hydrogen ion and diethyl ether as in Equation 1.2 (Karas et al., 2004; Nigam et al., 2011).

\[
\text{CH}_3\text{CH}_2\text{OH}_2^+ + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H}_2\text{O} + \text{H}^+ + \text{CH}_3\text{CH}_2\text{O} \text{CH}_2\text{CH}_3
\] (1.2)

The above reaction must be carried out at lower than 150°C temperatures in order to ensure that an elimination product (ethylene) is not a product of the reaction. At higher temperatures, ethanol will dehydrate to form ethylene. The reaction to make diethyl ether is reversible; hence eventually equilibrium between reactants and products is achieved. Getting a good yield of ether requires that ether be distilled out of the reaction mixture before it reverts to ethanol (Karas et al., 2004). A schematic diagram for production of Diethyl ether from Bio-ethanol is shown in Figure 2.3. In this figure process simulation shows that hydrous ethanol (ethanol diluted with water) could be converted in to Diethyl ether.
Bailey et al. (1997) have reported regarding the production and cost analysis of DEE from biomass via bio-ethanol and mentioned that the National Renewable Energy Laboratory (NREL) conducted an exercise on process simulation which showed that hydrous ethanol could be converted to DEE and resulting liquid/liquid phases of water–ethanol/ethanol–DEE could be easily separated in a simple decanter. Ideally, at the end of biomass ethanol production process and subsequent rectification, hydrous ethanol would be generated. However, the conversion of ethanol to ether could take place before final drying of the alcohol. This analysis shows that the net conversion cost for producing DEE in this manner is similar to the cost of the final drying process step, which means that the cost of fuel-grade DEE would be only slightly higher than that of anhydrous ethanol. Although, more detailed cost analysis for DEE production is needed.

**Figure 2.3** Schematic diagrams for production of DEE from bio-ethanol

### 2.4.3 DEE Utilization in Diesel Engines

DEE has several favorable properties for CI engines such as high cetane number (>125), low auto ignition temperature, high oxygen content, reasonable energy density for on-board storage, broad flammability limits, high miscibility with diesel fuel and renewable bio-fuel (Rakopoulos et al., 2012). It is a liquid at ambient conditions, which makes it attractive fuel
for handling and infrastructure requirements. Diethyl ether is a pungent, volatile, highly flammable liquid derived from the distillation of ethyl alcohol with sulfuric acid and widely used as a common solvent. Its flammability limits are broader than those of many fuels. DEE is attractive for fuel handling compared to DME because it is a liquid at ambient conditions (Masoud et al., 2008). Burning velocity of DEE is 13% greater than normal heptanes, about the same as benzene, and much less than that of propyne (Sezer, 2011; Karas et al., 2004). However, storage stability of DEE and blends of DEE are of concern because its tendency to oxidize and forming peroxides in storage (Karas et al., 2004).

Intersolubility of DEE with diesel is the prerequisite for the engine’s stable working. Physical and chemical properties of DEE and diesel display mutual solubility at any ratio. DEE is completely miscible with diesel fuel (Mohanan et al., 2003). Hence, it can be mixed in any proportion in diesel fuel. There are many limitations of DEE-diesel blends such as low kinematic viscosity, low density, low boiling point, storage stability due to its tendency to oxidize and forming peroxides in storage (Bailey, 1997), safety due to low flash point, lubricity and material compatibility, which need to be studied in detail. There are some studies focused on the use of DEE-diesel blends in direct injection diesel engines and that too with less fraction of DEE in the blends. Therefore, there is a need to extend this study for high DEE fraction in the blends. Before commercializing the DEE-diesel blended fuel, it is needed to check the kerosene adulteration effect on DEE-diesel blends, which is not yet studied. Theoretical and computational analysis of combustion process in DI diesel engine, in support with experimental investigations is needed to understand the effect of adverse properties of DEE-diesel blends of high DEE fraction on performance and emissions characteristics of engine.

The physicochemical properties of DEE are well-described in chemical databases, but the knowledge about DEE as an alternative fuel for diesel engine still seems to be inadequate. Bailey et al. (1997) have presented the first results of the literature search to identify the potential of DEE as a transportation fuel. Cheng et al. (1999) have conducted engine tests using DME and DEE blended with diesel fuel. They reported that the particulate matter levels reduced drastically (by as much as 76%) during higher power test modes and for lower power modes PM emissions were often unchanged. Increased CO₂ emission and higher fuel consumption were also reported with DME and DEE blends when compared with that of diesel alone.
Subramanian et al. (2002) have studied the use of DEE as an ignition improver for diesel fuel by its addition to diesel-water emulsions and reported the reduction in smoke, NOx, HC, and CO emissions without adverse effect on brake thermal efficiency. Miller et al. (2006) have used DEE with LPG in a diesel engine. Subramanian et al. (2002) have experimentally investigated the effect of DEE-diesel blend with 5, 10 and 15% DEE by weight in diesel in CI engine. The optimum quantity of DEE in DEE-diesel blend was found to be 10% based on the thermal efficiency, along with advanced injection timing, They showed that the blend decreased the smoke and CO level drastically at all loads and increased the brake thermal efficiency at high load without affecting NOx emissions. The peak heat-release, peak pressure and maximum rate of pressure rise are also increased.

Anand et al. (2007) have experimentally achieved a simultaneous reduction of smoke and NOx by blending 10 to 30 % DEE by volume with diesel fuel along with 5 to 15% EGR in diesel engine. They found that 20 vol% DEE–diesel blend resulted in the optimum performance and emission characteristics. When the DEE proportion was at or above 30 vol %, there was severe knocking in the engine. They found that the 5% EGR operated with 20% DEE-diesel blend to be favourable.

Mohanan et al. (2003) have been evaluated a number of DEE- diesel blends in a single cylinder diesel engine and found that at higher blends of DEE-diesel, engine emits more smoke at full load than other blends and neat diesel and reported that this may be due to phase separation of the blend, which results in incomplete combustion of the blend fuel. They have also mentioned that the blends of DEE up to 25% were possible, the most favourable blend was 5% resulting in low smoke, high brake thermal efficiency and low brake specific fuel consumption.

Wu et al. (2006) and He et al. (2008) have reported that the density, viscosity and bulk modulus properties of the oxygenated fuel play a significant role on the improvement of atomisation behaviour. They also found that the spray quality of low viscosity oxygenated blended fuels improves and a finer droplet, a stronger interface between fuel spray and surrounding gas perform well as compared to neat diesel. Thus, the combustion efficiency enhances because of heat losses in the cylinder are decreased due to lower flame temperature of DEE blend than that of neat diesel.
Clothier et al. (1990) have experimentally demonstrated that DEE ignition was inhibited by diesel fuel and that adding DEE to diesel fuel actually decreased the cetane number of the diesel fuel. They have suggested that DEE may interact with aromatics in diesel fuel, delaying the onset of ignition. It is also in agreement with the findings reported by Hess et al. (2001), where they have used an oxygenated cetane improver having cetane number more than 100 as an additive to diesel fuel.

Iranmesh et al. (2008a) have carried out experimental investigation on DI diesel engine for the blends of 5%, 10%, 15% and 20% DEE (by vol.) with diesel and reported that the 5% DEE-diesel blend was found to be optimum one in terms of performance and emissions behaviour. They reported that higher than 15% DEE blend with diesel showed some instability and fluctuations in engine speed and power output.

Rakopoulos et al. (2012) have carried out performance and emissions experiments on high speed direct injection diesel engine blended with 8%, 16% and 24% DEE by volume with diesel at a speed of 2000 rpm and at three loads. They found that DEE in blend with diesel fuel decreases emissions of smoke, CO, and NOx and increases emission of HC. They have mentioned that there is no unstable operation of the engine at least for up to 24% addition of DEE. Furthermore, Rakopoulos et al. (2013) have carried out investigation on combustion and cyclic variability of 24% addition of DEE with diesel and reported that neither the injection process (through the dynamic injection timing), nor the kind of DEE/diesel fuel blend used (through the cetane number) have any practical effect on the cyclic variations (irregularity) and hence, there is no unstable operation of the engine.

Gorski et al. (2014) have experimentally examined the effect of blending DEE to diesel on the physicochemical properties of the mixture. DEE was added in diesel with volumetric proportion of 5, 10, 15, and 20 %. They reported that a higher content of DEE (>20% DEE by vol.) in a blend with diesel causes hard-starting and poor engine performance, because of the lower viscosity of DEE and increased leakages in the fuel supply system. They also mentioned that it is also possible that the hard-starting problem is caused by vapour locks in the injection system.

As it is well known that biodiesel fuelled CI engines are more prone to cold-starting problems, especially in winter seasons. Hence to overcome these problems many researchers
have focused on the blending of DEE with biodiesel in CI engine to reduce emissions and the results of these works showed that DEE-biodiesel blends resulted in better engine performance and lower emissions (Anand et al., 2007; Iranmesh et al., 2008b; Imtenan et al., 2014).

2.5 DIESEL ADULTERATION WITH KEROSENE

In India along with automotive vehicles the population of the stationary engines is increasing at rapid rate. The most popular applications are gensets due to uncertain supply of electricity and agriculture water pumps. These gensets and pumps use gasoline, diesel, kerosene and adulterated fuels. Fuel adulteration by blending kerosene with gasoline or diesel is becoming a widespread problem because of financial benefit resulting from the price difference between two fuels (Baral et al., 2009). Although, adulteration is being a widespread problem, the effects of kerosene fuel adulteration have not been assessed adequately.

Pathak et al. (2005) conducted engine tests for the detailed investigation on the effects of kerosene on SI engine gensets and reported that the kerosene run gensets are cost effective than gasoline gensets and produces less noise in comparison to diesel gensets. Ziegier et al. (2000) have reported that kerosene improves the cold flow characteristics of diesel fuel by simply diluting the problematic paraffin waxes present in the diesel fuel distillation curve.

Yadav et al. (2005) have experimentally demonstrated that the percent opacity value decreased sharply even at small adulteration level of kerosene with diesel. They have reported that density of the kerosene-diesel fuel tests is within the prescribed value even at higher blend, while considerable decrease in kinematic viscosity than baseline diesel is observed with increase in blend ratio.

Bergstrand (2007) has also reported that the kerosene has lower cetane number than diesel, thus giving a longer ignition delay, making it viable for lower emissions and observed the lower soot emissions with the blends of kerosene with diesel at low load as compared to neat diesel while soot emission was similar to that of diesel fuel at high load. Roy et al. (2014) have experimentally investigated the effect of kerosene addition on biodiesel and reported that a kerosene–biodiesel blend reduces HC only under heavy load condition, while a NOx emission reduces at all load conditions.
In this study, before going for the commercial use of optimum DEE-diesel blend, considered more practical approach to check the adulteration effect of kerosene on optimum DEE-diesel blend. However, initially the adulteration effect of kerosene with diesel is first investigated. In this context, the detailed literature survey is carried out to investigate diesel/gasoline fuel adulteration by kerosene. While considering more practical approach, till date no research work is found related to effects of kerosene adulteration on DEE-diesel blend.

The main purpose of this research work is to find out the optimum performance DEE-diesel blend and check it for the adulteration effect with kerosene. The adulteration effect of kerosene with diesel is also investigated before blending it with optimum DEE- diesel blend.

2.6 REMARKS FROM LITERATURE REVIEWED

A summary of literature reviewed shows that the diesel engines have several advantages like high thermal efficiency, torque capacity, reliability, adaptability, low HC and CO emissions and cost effectiveness, but they suffer from high concentration of NOx and particulate emissions.

The survey highlighted the limitations of diesel engines and demonstrated that the simultaneous reduction in NOx and particulate matter is quite difficult due to the trade-off between PM and NOx, which is often accompanied by fuel consumption penalty. Hence, it is more difficult for diesel engines to meet stringent emission norms by the use of neat petroleum diesel through engine design or control parameters alone.

Based on the literature reviewed it is observed that the introductions of oxygenated compounds into diesel fuel especially those that are originally bio-resources are the best ways to reduce emissions of diesel engines. Among all oxygenates, a worldwide trend towards the application of bio-fuels and mainly biodiesel and alcohols have been observed for the last two decades. Alcohol fuels can substitute for gasoline in spark-ignition engines, while biodiesel, green diesel, DEE and DME are suitable for use in compression ignition engines. The oxygenated fuels like DEE and DME are attracting notable attention of researchers as a clean alternative fuel for compression ignition engines without large sacrifice in vehicle performance.
Ethanol is promising alternative fuel because it is a renewable bio-based resource and highly oxygenated fuel. However, there are many obstacles in the use of ethanol in CI engines such as very low cetane number, poor ignition characteristics and limited solubility in diesel fuel. Phase separation and water tolerance in ethanol-diesel blend fuels are crucial problems. The dynamic viscosity of ethanol is much lower than diesel fuel. Hence, the lubricity is a potential concern of ethanol-diesel blend fuels.

The research studies indicate that the limitations of ethanol can be overcome by converting it easily into diethyl ether (DEE) by dehydration process. This is the easiest way to use ethanol in diesel engine. DEE has several favorable properties for CI engines such as high cetane number, low auto ignition temperature, high oxygen content, reasonable energy density for on-board storage, broad flammability limits and high miscibility with diesel fuel. DEE is renewable bio-based fuel and widely used as a common solvent. It is easy for handling because it is a liquid at ambient conditions and has lower flammability leading to higher safety as compared to dimethyl ether.

There are some studies focused on the use of DEE-diesel blends in direct injection diesel engines and that too with less fraction of DEE in the blends. As DEE is completely soluble with diesel, the relative benefits of each fuel might be utilized by blending DEE with diesel fuel. The result of DEE-diesel blends shows reduction in smoke emissions. Meanwhile NOx, HC and CO emissions are reduced in some cases and increased in others. Some researchers have reported that 5 % DEE-diesel blend as an optimum performance blend. Therefore, there is a need to extend this study for high DEE fraction in DEE-diesel blends with various techniques particularly different injection timings.

There are many limitations to DEE-diesel blends such as low kinematic viscosity, low density, low boiling point, storage stability due to its tendency to oxidize and forming peroxides in storage, safety due to low flash point, lubricity and material compatibility, which need to be studied in detail.

Some studies highlighted a widespread problem of diesel and gasoline adulteration by kerosene due to financial benefit resulting from the price difference between two fuels. The effects of kerosene adulteration with diesel have not been assessed adequately. This needs to be also investigated. Before commercializing the optimum DEE-diesel blend fuel, it is needed
to check the kerosene adulteration effect on DEE-diesel blends, which is not yet studied by any researcher.

So far, no research has been reported on the computational study of DEE-diesel blends in DI diesel engine for analysis of experimental investigations. The effects of fuel properties of DEE-diesel blend of high DEE fraction on combustion, performance and emissions characteristics of diesel engine with the help of computational model need to be studied.

Research studies clearly indicate the potential of bio-based renewable oxygenated fuels like diethyl ether for simultaneous reduction of particulate matter and NOx, which is still a problem in a diesel engine. Recent studies suggest that further comprehensive investigation is required for suitable higher percentage of DEE in DEE- diesel blends with proper techniques.

2.7 RESEARCH GAPS FOR THE PRESENT RESEARCH

An overview of the literature illustrates some gaps among the research works regarding utilization of DEE-diesel blend in compression ignition diesel engine are as follows:

1. Less attention has been paid to higher percentage of DEE in DEE-diesel blend CI engine.
2. Further comprehensive investigations are needed for the optimization of higher percentage of DEE in DEE- diesel blends by using various techniques to obtain simultaneous reduction of NOx and smoke emissions.
3. An elaborate investigation about blending of DEE to diesel to improve combustion and emission characteristics of diesel is required.
4. Optimal injection timing for DEE-diesel blends has not been investigated for different engine loads and its effect on combustion and emission characteristics of CI engine.
5. Effect of DEE addition on diesel fuel properties have not been investigated adequately.
6. Before commercializing the optimum DEE-diesel blend fuel, it is required to check the kerosene adulteration effect on DEE-diesel blends for combustion, performance and emission characteristics, which is not yet studied by any researcher. Accordingly the effects of kerosene adulteration with diesel need to be assessed adequately.
2.8 OBJECTIVES

Keeping in view the research gaps and need for the research work, the present investigations have been undertaken to accomplish the following objectives:

- To investigate the potential of DEE-diesel blends of high DEE fraction, as an alternative fuel for compression ignition engines.
- To evaluate the blended fuel properties to analyze the experimental investigations of various fuel combinations.
- To study the effect of different injection timings and optimize it for the optimum selected fuel combinations.
- To recommend a suitable DEE-diesel blend of high DEE fraction as a diesel engine fuel and investigate it for adulteration effects with kerosene.

2.9 SCOPE OF PRESENT WORK

In order to achieve the above mentioned objectives the scope of present study decided is as follows:

- To find the limiting proportion of DEE in DEE-diesel blends and kerosene in kerosene-diesel blends through fuel properties investigations.
- To design and develop the testing facility for the measurement of performance, emission and combustion parameters of naturally aspirated, single cylinder, direct injection diesel engine.
- To test initially the kerosene-diesel blends for the adulteration effects of kerosene on diesel on naturally aspirated, single cylinder DI diesel engines.
- To carry out tests at different engine loads for the investigation of combustion, performance and emission characteristics of DEE-diesel blend with high DEE fraction.
- To study the effect of different injection timings on optimum DEE-diesel blend and optimize the injection timing for the optimum blend.
- To analyse the results and recommend suitable DEE-diesel blend based on combustion, performance and emission parameters.
To check the recommended suitable DEE-diesel blend for the adulteration effects with kerosene at different engine loads for the combustion, performance and emission characteristics.

To meet above objectives a research scheme has been developed, which is shown in Figure 2.4 as layout of the present work.

2.10 RATIONALE OF THE STUDY

The literature showed that DEE is one such oxygenated, renewable, bio-base resource fuel that can be used as a clean alternative fuel for compression ignition engines. DEE is completely miscible with diesel and DEE-diesel blends retain the desirable physical properties of diesel fuel but include the cleaner burning capability of DEE and hence reduce the exhaust emissions of diesel engine. Before going for the commercial use of desirable DEE-diesel blend, it needs to be checked for the adulteration effects with kerosene. The extensive use of DEE in diesel engines will lead to the benefits such as reduction in petroleum fuel consumption, reduction in exhaust emissions and hence air pollution reduction to a greater extent, boost to rural economy and energy security.
Investigation on Performance and Emission Characteristics of DEE-Diesel Blended CI Engine

- Literature review

- Experimental study
  - Single cylinder 4-stroke cycle naturally aspirated CI engine

- Evaluation of fuel properties of various blends

- Engine tests with DEE-Diesel blends
  - Adulteration effects - Engine tests with Kerosene-Diesel blends
  - Engine tests with optimised DEE-Kerosene-Diesel blends

- Parameters of
  - Combustion
  - Performance
  - Emissions

- Engine tests with optimised DEE-Diesel blend for different injection timings

- Analysis of experimental results

Conclusions

Figure 2.4 Layout of Present Work