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Investigating the Effects of Alternative Fuels with Different Aromatic Species on Compression Ignition Engine Emissions and Performance

By

Bandar Awadh A Almohammadi

Supervisors

Dr Bhupendra Khandelwal

Dr Robert Wooley

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ABSTRACT

Harmful emissions are the major challenge for combustion systems and continuously increasing with the use of fossil-based feedstock around the globe. Compression ignition engine (CI) is one of the main emitters of harmful pollutants. As compared to spark ignition (SI) engine, CI engine produces high particulate matter (PM) and nitrogen oxides (NO_x) emissions. The need for the improvement of engine performance; fuel consumption and thermal efficiency is another challenge. Investigating the effect of fuel components is one of the approaches that can be used to reduce exhaust emissions and improve performance.

knowledge gaps need to be completed in how different aromatic species of the same type impact the engine performance and emissions. The contributions of the present study are in the detailed investigations reporting and analyzing the role of different alkylbenzenes and polycyclic aromatics in surrogate fuels on emissions and engine performance. This knowledge would help the future fuel industry to produce future fuels with appropriate alkylbenzenes and polycyclic aromatics for lower emissions and improved performance. In addition, the study provides more details about the influence of different aromatic concentrations in the fuel on emissions and performance.

To attain the aims of the current study, different alkylbenzenes and polycyclic aromatics were blended with surrogate fuel at three different contents. The blended fuels were tested experimentally using a direct injection (DI) CI engine at two different load conditions. Appropriate sampling line, particulate and gaseous species measurement instrumentation were integrated with the engine rig in order to take measurements accurately. Impact of different properties of aromatic species on PM, NO_x UHC's, CO and engine performance has also been investigated and forms a part of contribution to knowledge.

The overall results show that increasing aromatic content in fuel contributes to high levels of exhaust emissions and impacts engine performance. Comparison among alkylbenzenes surrogate blends presents that blends containing ethylbenzene produce low exhaust emissions and better performance because of its properties; high calorific value, cetane number, low density and hydrogen-to-carbon (H/C) ratio. While, indane surrogate blends have better results as compared to other polycyclic aromatics. Finally, optimum surrogate blend is formed with appropriate aromatics (ethylbenzene and indane). Operating the engine with optimum blend results in significant reduction of PM, smoke, unburned hydrocarbons (UHC) as compared to commercial diesel fuel. However, increase of brake thermal efficiency (BTE), reduction of NO_x and brake specific fuel consumption (BSFC) are insignificant. NO_x and PM correlations are developed as a function of significant impacted fuel properties. The prediction models developed are highly agreeing with experimental results. Overall, this work would provide basis for selection of aromatic species in future fuels, as not all aromatic species lead to higher PM, NO_x or give the optimal engine performance.

NOMENCLATURE

CI	Compression Ignition
SI	Spark Ignition
DI	Direct ignition
BTE	Brake thermal efficiency
BSFC	Brake specific fuel consumption
TDC	Top dead centre
BDC	Bottom dead centre
IDI	Indirect Injection
nvPM	Non-volatile PM
vPM	Volatile PM
LII	Laser-Induced Incandescence
TEM	Transmission electron microscope
DPF	Diesel Particulate Filter
DOC	Diesel Oxidation Catalyst
EPA	Environmental Protection Agency
FC	Fuel consumption
BP	Brake power
Q	Calorific value
LCCC	Low Carbon Combustion Centre
DME	Dimethyl ether
ASTM	American Society for Testing and Materials
PPME	Pongamiapinnata methyl ester
CME	Castor methyl ester
CNG	Compressed natural gas
LNG	Liquefied natural gas
HPDI	high pressure direct injection
IC	Internal combustion
LPG	liquefied petroleum gas
IDA	International DME Association
ULSD	Ultra-low sulfur diesel
EGR	Exhaust gas recirculation

TDI	Turbocharged Direct Injection
T90	90% distillation temperature
MEL	Mobile emissions laboratory
Ppm	Part per million
(Nd:YAG	Neodymium-doped yttrium aluminium garnet
R_s	Absolute reflectance of the stained filter
R_w	Absolute reflectance of clean filter

CHEMICAL ABBREVIATION

PM	Particulate matter
NO_x	Nitrogen oxides
H/C	Hydrogen-to-carbon
UHC	Unburned hydrocarbon
CO	Carbon monoxide
CO_2	Carbon dioxide
SO_2	Sulfur dioxide
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
O_2	Oxygen
N_2	Nitrogen gas

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In preparation

1. Bandar Awadh Almohammadi, Paramvir Singh and Bhupendra Khandelwal. The Effect of Different Alternative Fuels on Performance and Emissions of Compression Ignition Engines, Review

1. INTRODUCTION

1.1 Motivation

The transportation sector is primarily based on internal combustion engines. The implementation of stringent new emission standards on a global scale necessitates better fuel efficiency and lower emissions from combustion engines [1]. Higher efficiency, lower fuel consumption and heavy-duty applications of DI CI engines make them more impactful in some places as compared to gasoline operated vehicles. Many new approaches for DI CI engine have been proposed in recent times for reducing the harmful pollutants from diesel operated engines. Some authors suggested different combustion strategy, minor tweaking in engine parameters and parts to reduce the harmful emissions. On the other hand, fuel companies are continuously working on the components of diesel fuel and try to make them more compatible with existing engine technology for better performance. Although typical pollutants such as carbon monoxide (CO), carbon dioxide (CO_2) and UHCs which result from CI engine combustion are lower than those from SI engines. CI engine emissions are still the main source of PM and NO_x emissions [2]. Human health and ecosystem are significantly affected by hazardous substances in PMs such as inorganic ions, organic carbon and trace elements [3]. Furthermore, half of NO_x emissions in urban environments are emitted from the CI engines and highly impact the respiratory system [4].

Investigating the effect of fuel composition is one of the feasible approaches that are being used to increase the performance and reduce the emissions in CI engine. Sulfur concentration highly impacts exhaust emissions and is responsible for the production of high PMs that are main contributor to air pollution and also increase the corrosion of engine part [5]. For this reason, in many countries, it has been reduced to be less than 15 ppm in diesel fuel [6]. The role of oxygenates was also investigated in many studies in the literature such as Choi [7], Xue et al. [8] and Beatrice et al. [9]. It was recommended that the addition of sufficient oxygen content to diesel could help improve combustion efficiency as well as reducing emissions. These implementations have been encouraged many researchers to study the role of other fuel components such as aromatics.

1.2 Types of CI Engines

It is commonly accepted that CI engines are mainly classified into two categories, two- and four-stroke engine [10]. For two-stroke engine, one crankshaft cycle or two piston strokes are needed to complete combustion. Air is introduced into the combustion chamber just before the beginning of compression and emissions are exhausted just before the end of expansion stroke. Two-stroke engines consume high volumes of fuel as compared to four-stroke engines due to poor scavenging [11].

As illustrated in figure 1.1, a four-stroke engine needs two crankshaft cycles or four piston strokes to complete a cycle. The intake stroke relies on moving the piston from top-dead-center (TDC) to the bottom-dead-center (BDC) and air is induced. After that, during the compression stroke, induced air is compressed and heated up to be higher than fuel autoignition temperature just before TDC [11]. As fuel starts burning and the heat energy releases, pressure is significantly increased and then, applied to the piston. This applied pressure causes piston movement from TDC into BDC. This is known as the expansion stroke or sometimes power stroke because the output power of engine is produced in this stroke by pushing the piston downwards [11]. The combustion products are rejected as the exhaust valve opens.

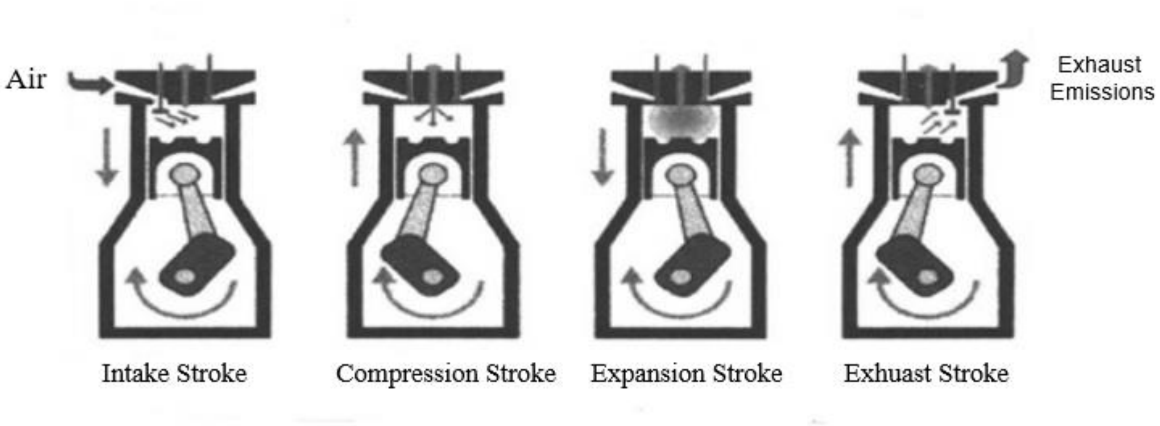


Figure 1.1 Combustion process of four-stroke CI engine [11]

Four-stroke CI engines can be classified into indirect (IDI) and DI engines. The later relies on injecting fuel into the main chamber, whereas, in IDI engines, fuel is injected into a pre-chamber. At cold starting, fuel ignition is enhanced by a glow plug that is fitted in the pre-chamber [11, 12]. DI engines are commonly used as compared to IDI engines because of their simple design. In the present study, a DI four-stroke CI engine is used to test the fuel blends.

1.3 Diesel Injection and Combustion Process

Before TDC, the fuel introduced is atomized as small droplets and absorbs heat from heated compressed air. The fuel-air mixture temperature increases over the auto-ignition temperature of the fuel at TDC [10]. Hence, the combustion starts when the premixed fuel-air instantaneously ignites. The time between start of fuel injection and the combustion start is defined as ignition delay time. As illustrated in figure 1.2, the pressure in the chamber reaches a peak **exactly** after the ignition delay time because the premixed combustion plays a role in heating up and compressing unburned fuel-air mixture [13]. Consequently, the remaining fuel-air mixture is vaporized and then, burned.

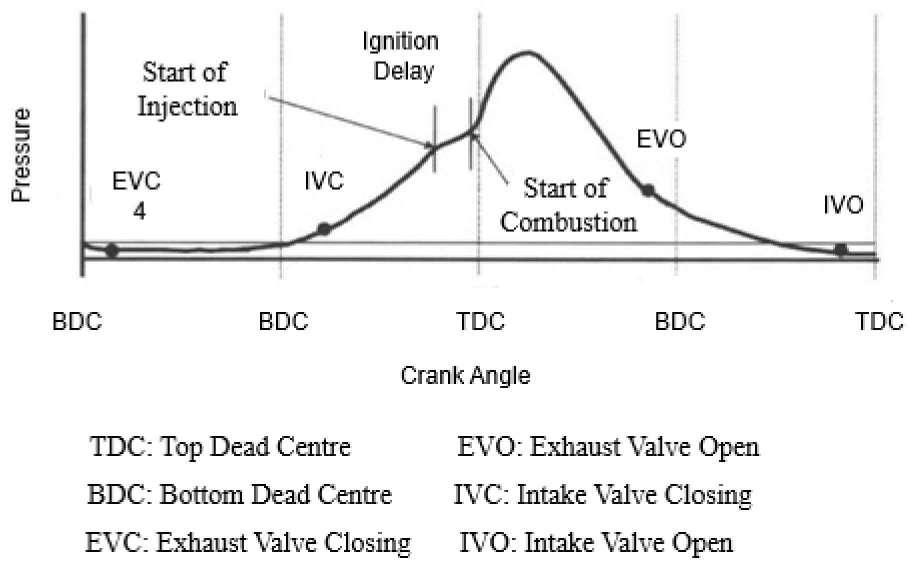


Figure 1.2 Pressure characteristics vs crank angle [13]

1.4 Formation of CI Engine Emissions

Water vapour, hydrogen and CO_2 are not the only CI engine exhaust products. Other emissions are resulted such as NO_x, CO, UHC, PM and sulfur dioxide (SO_2) emissions as illustrated in figure 1.3. Exhaust emissions from CI engines consist of many pollutants differing in size, structure and toxic properties. There are two emissions classes which are based on their physical phases or their causes. Zhao [12].categorized the exhaust emissions resulting from the combustion of diesel-air mixtures into three groups depending on their causes. First, NO_x emissions produce from a secondary chemical reaction. Second, UHC, CO and soot emissions are formed because of incomplete combustion. Finally, the reaction among impurities in diesel fuel results in SO_2. On the other hand, Merker [14] classified the exhaust emissions into particulate matter and gaseous emissions according to their physical phases. PM emissions are known as all the particles exhausted from CI engine [14]. Even though numerous particles that are formed, soot is the dominant particle. While, CO_2, NO_x, CO, UHC and SO_2 represent gaseous emissions. The latter classification is used in the present study.

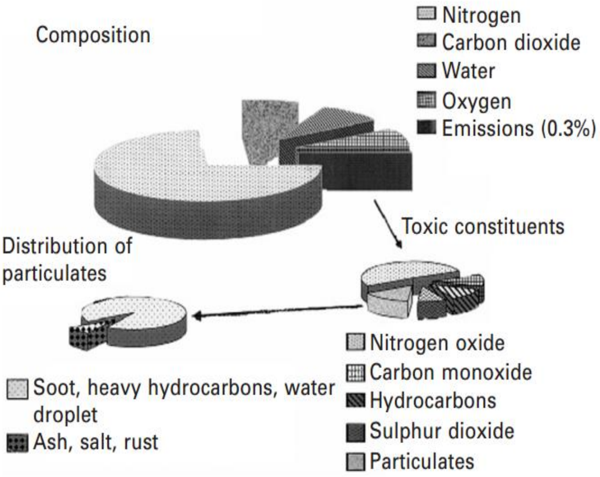


Figure 1.3 Components of exhaust CI engine emissions [12]

1.4.1 CO Formation

CO is considered a toxic gas at low level [13]. It is results as a product of an intermediate oxidization because of incomplete combustion. The incomplete combustion is caused by a lack of air (mainly oxygen), temperature and resident time. In other words, CO is mainly formed because a lack of air-fuel mixture homogeneity as illustrated in figure 1.4. firstly, it is produced at injection flame edges before dominant CO_2. It is also formed near the combustion chamber walls due to low temperature. However, CO can be converted into CO_2 through the reaction of recombination between different oxidants and CO or there is sufficient air [13]. High CO levels usually are resulted from the combustion of rich fuel-air mixtures. While, in case of CI combustion, air-fuel mixture is lean which there is an oxygen. Therefore, the production of CO emissions from CI engine is very low and considered to be insignificant[13].

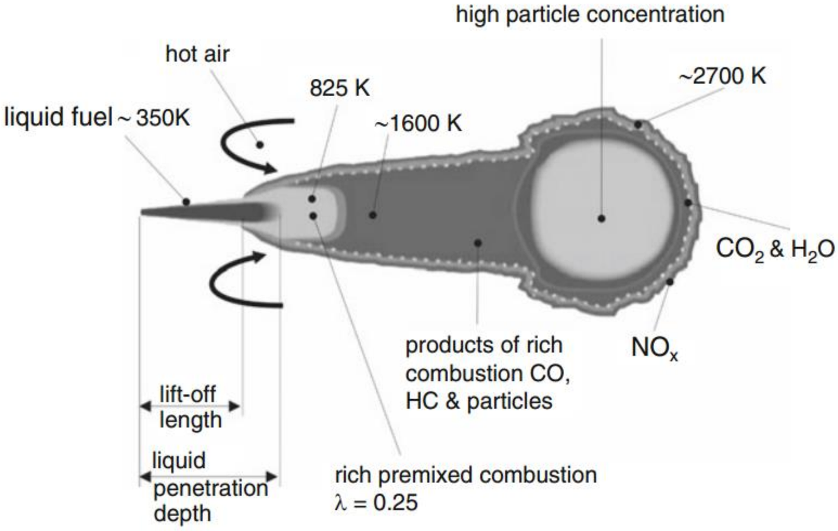


Figure 1.4 Combustion model of the formation of diesel emissions [13]

1.4.2 UHC Formation

UHC emissions result from the combustion of diesel-air mixtures consisting of either recombined intermediate compounds or decomposed fuel molecules [13]. Lubricating oil is another source of UHC emissions. Two main paths are behind the formation of UHC emissions; the mixture of air-fuel may be too lean to autoignite or the mixture may become too rich to autoignite. The fuel can be consumed by a slower reaction of thermal oxidation later in the expansion process when mixing the fuel with additional air. Consequently, hydrocarbons remain unburned due to incomplete mixing or quenching of the oxidation. In conclusion, production of UHCs may relate with the fuel portion on the chamber wall, spray core and spray tail.

1.4.3 NOx Formation

The term NO_x denotes to nitrogen monoxide (NO) and nitrogen dioxides (NO_2). NO represents more than 90% of total NO_x [12]. For this reason, NO formation was primarily addressed in the literature rather than other NO_x components. Three different methods are identified for NO formation, namely fuel NO, prompt NO and thermal NO [12, 13]. First, fuel NO is produced from the nitrogen molecules in the fuel. Nitrogen in the fuel is converted to compounds or radicals of cyano compounds (carbon triple bonded to nitrogen) before entering the combustion zone. In the flame zone, the particles then partially oxidize to produce NO. But, the content of nitrogen in diesel fuel composition is very low therefore, it is less likely to contribute to NO formation [12, 13]. Second, prompt NO is formed from nitrogen in the air inside the reaction zone of the enriched hydrocarbon flame. The local temperature is likely to be similar to the temperature under adiabatic combustion conditions reaching up to 2800 K with a stoichiometric ratio [12].

Third, thermal NO is produced from the nitrogen molecules in the induced air at high temperatures (2200 K). This is initiated by oxygen radicals and enhanced by OH radicals. According to the Zeldovich mechanism, an oxygen atom is exposed to high temperature in a region with high nitrogen concentration [12, 13]. NO is formed and a nitrogen atom is left in an unstable state (Eq. 1.1). This atom is stabilized by reacting with an oxygen molecule when enough heat energy is available from the process of combustion. As a result, NO forms and an oxygen atom leave in an unstable state (Eq. 1.2). Zhao [13] stated that a modified Zeldovich mechanism exists where OH radicals react with nitrogen atoms to produce more NO and a hydrogen atom in rich or near-stoichiometric mixtures (Eq. 1.3).

$$\mathrm{N_2 + O \rightarrow NO + N} \qquad \text{Eq (1.1)}$$

$$\mathrm{O_2 + N \rightarrow NO + O} \qquad \text{Eq (1.2)}$$

$$\mathrm{OH + N \rightarrow NO + H} \qquad \text{Eq (1.3)}$$

According to the Zeldovich mechanism, nitrogen atoms do not start the reaction, due to low equilibrium concentrations during the process of combustion, as compared to oxygen atom equilibrium concentrations [13, 15]. Consequently, the formation of local NO in the spray is associated with the concentration of local oxygen atoms and the local temperature. NO_2 results from the reaction of NO with excess oxygen. NO levels are frozen above equilibrium concentrations, due to quenching by excess air. NO concentration does not decrease when the temperature during the expansion stroke decreases. Newhall and Starkman [16] indicated that NO concentration was constant, because of the slow removal processes of NO during the expansion stroke. Komiyama and Heywood [17] also revealed that NO concentration was constant in lean air-fuel combustible mixtures.

1.4.4 PM Formation

PM is one of most harmful emissions produced by CI engines. In contrast to gaseous emissions, PM is not a well-known chemical species. The definition of PM extends to any liquid (condensate) and solid materials present in cooled and diluted diesel exhaust [13]. The mass of PM emissions is determined by the PM collected on the sampling filters. Any change in dilution parameters or filter types may result in different results. Exhaust particles from CI engines include many elemental carbons, sulfur, poly-aromatic and HC compounds. Toxic PM properties are varied because of size, solubility and composition [18]. Soot represents a main component of PM because of oxygen deficiency [12, 19].

PM emissions consist of accumulation and nuclei mode particles. The diameter of the nuclei particles is between 0.007 and 0.04 μm. However, some studies have redefined the size range of nuclei particles to be smaller, between 0.003 to 0.03 μm [20]. However, in this study, PM mass (mg/m^3) are measured instead of particulate sizes.

In the fact, there are many terms relating to PM emissions such as total PM, non-volatile PM (nvPM) and volatile PM (vPM) emissions. In this study, PM emissions used in literature review chapter were nvPM emissions. Moreover, for measurements of test fuel blends, nvPM mass was measured using the Laser-Induced Incandescence (LII) instrument. However, in future work, PM size and number will be measured when appropriate instruments are available. Smoke density is another term relating to PM emissions. In this study, smoke density term was measured which was based on ARP 1533. The smoke density was expressed as smoke number which was obtained by drawing a fixed sample volume through a filter paper and recording the reflectance before and after sampling.

1.4.4.1 Soot Formation Process

Soot formation from a liquid or vapor phase to solid particulates can involve five steps; as described in figure 1.5 [21, 22]. However, oxidization may occur at any time during soot processes by converting hydrocarbons to CO_2, CO, and H_2O. Sometimes, the net soot formation term is used to describe the combination of oxidization and soot formation [21]. However, in this section, oxidization is provided as a process which is similar to the study by Tree and Svensson [21].

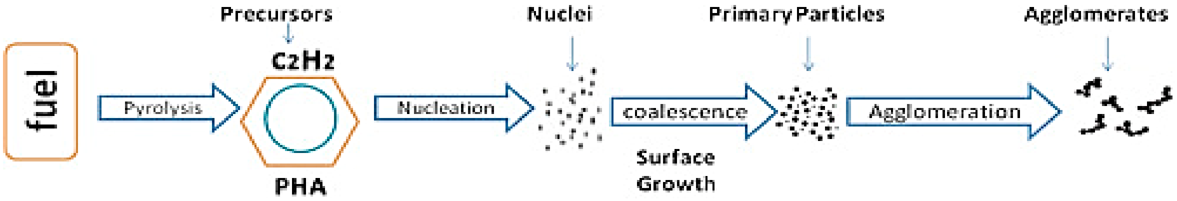


Figure 1.5 Soot formation process [22]

1.4.4.1.1 Oxidation

As mentioned above, oxidation may occur at any time during the processes of soot formation to form combustion products such as CO_2, CO, and H_2O. It is usually influenced by the state of air-fuel mixture at that time. Oxidation of small soot particulates associates with two oxidation processes; absorption and desorption [21]. Absorption process is a chemical oxygen attachment to the surface and desorption process take place when oxygen is desorbed by the attached fuel component from the soot surface. The dominant soot oxidation is by OH radicals at stoichiometric and fuel-rich mixture conditions while, both OH and oxygen are more likely to be oxidized at lean mixture condition [21]. The oxidation of soot occurs when the temperature is more than 1300 K.

1.4.4.1.2 Fuel Pyrolysis

Fuel pyrolysis is the process of degradation of organic compounds of the fuel which alters its molecular structure at high temperature [23]. This occurs without oxidation although oxygen may be present. High in-cylinder temperature and the state of the air-fuel mixture are significant contributing factors for pyrolysis reactions [21]. The results of the pyrolysis process are considered to be the building blocks or precursors for soot formation. In fact, both pyrolysis and oxidation play an important role in the precursors of soot formation due to the presence of OH radicals [21, 23]. Although, both share a proportional relation with temperature, pyrolysis rate is slower than oxidation. Therefore, in the case of premixed flames, more oxygen content is present, which results in reduced soot formation, however, in a diffusion flame, more soot is produced because insignificant oxygen content is available in pyrolysis region with increased temperature. OH radicals are also important; especially in diffusion flame because they accelerate the pyrolysis process [23].

Polycyclic aromatic hydrocarbons, acetylene and polyacetylenes are the main products of the pyrolysis process. In addition, a study by Haynes and Wagner [24] indicated that benzene, CH_4, C_2H_4, C_3H_6, and C_2H_2 are typical pyrolysis products in the case of laminar diffusion flames.

1.4.4.1.3 Nucleation

The formation of soot particles from gas-phase reactants is known as soot particle inception or nucleation. These particles, also termed as nuclei are ranged between 1.5 and 3 nm in size. The process of particle inception relies on the addition of small hydrocarbon and aliphatic radicals into large aromatic molecules at temperatures of 1300-1600K. Although particle nuclei do not result in the total soot mass, they play the main role in affecting the mass that is added later. This is because they are the building blocks for surface growth.

Soot nucleation has three routes; cyclization, direct path of aromatic rings, and breakup and recyclization of rings which are influenced by the fuel composition and temperature [21]. Chain molecules are cyclized into a ring structure. For instance, the benzene ring is formed due to the combination of acetylene molecules. Aromatic rings dehydrogenate directly at low temperature to produce polycyclics. However, at high temperature, rings are formed due to break up and recyclization of molecules.

1.4.4.1.4 Surface Growth

Surface growth is the addition of mass to the soot particle surface resulting from nucleation. However, the fact is that the distinction between the start of the surface growth process and the nucleation is not clear. Tree and Svensson [21] claimed that both processes concurrently occur. During the surface growth process, the reactivity of hot surface of soot particles absorbs hydrocarbons in gas-phase, which contributes to an increase in the mass of soot particles. However, the number of particles is still constant. As the radical sites of small soot particles are more reactive, their surface growth rates are higher than that for large particles

1.4.4.1.5 Coalescence and Agglomeration

Coalescence sometimes called coagulation occurs when soot particles collide and coalesce. Consequently, the number of primary particles decreases and a fractal particle are formed as the combination of small particles [21, 25]. However, the combined mass holds constant. Agglomeration is known as the combination of large groups of particles to form chain-like structures. Exhaust soot particles from CI engines are likely to be fractal in shape and their size depends on the type of fuel injector, operating conditions, and measurement methods as shown in figure 1.6 [21, 22]. Lee et al. [26] reported primary particles ranges from 20 to 50 nm and about 30 nm as an average diameter using sampling probe and optical-scattering technique, respectively. Bruce et al. [27] used the in-cylinder light-scattering method and found that the average particle size ranges between 30 nm and 70 nm.

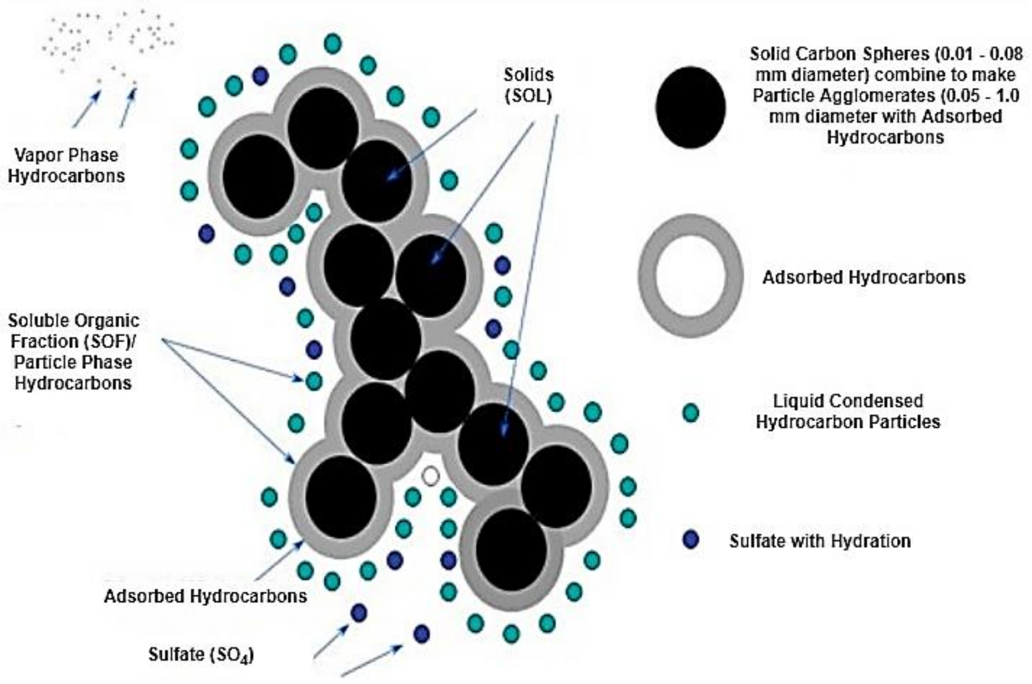
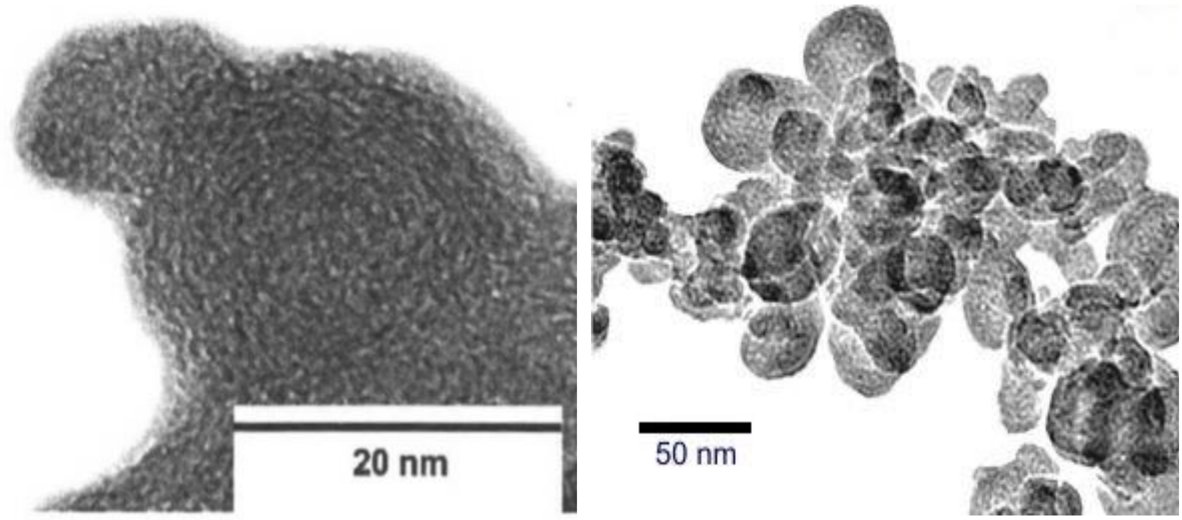


Figure 1.6 Schematic representation of PMs [22]

Figure 1.7 shows the structures of soot exhausted form CI engine in transmission electron microscope (TEM) image [11]. The principle of the TEM relies on a beam of electrons which is transmitted through a specimen in order to form an image. As shown in figure 1.7a, the Agglomerated particles are shaped as graphite crystallites that are small in size with a few nanometres. In figure 1.7b, the agglomerated particles show a fractal cluster-like structure which is formed of hundreds of nuclei mode particles.



(a) (b)

Figure 1.7 The TEM of agglomerated diesel soot [11]

1.4.4.2 Diesel Particulate Filter

PM emissions from CI engines continue to be reduced throughout the world such as Euro 6 standards. Therefore, the use of diesel particulate filter (DPF) is essential after-treatment device that can reduce particulate size and number concertation [28, 29]. DPFs can typically be made from silicon carbide, cordierite and aluminum titanate [30]. Particulates are captured by DPF's porous wall as the exhaust emissions are forced through the inlet channels [31]. The design of DPF can be coated with a catalyst such as NOx abatement catalyst. The filtered particulates are removed from the device using passive or active regeneration or both together. In a passive regeneration, NO_2 emissions are used to oxides the particulates to CO_2 and CO emissions. In order to increase the concentration of NO_2 in the exhaust emissions, NO is converted to NO_2 using a Diesel Oxidation Catalyst (DOC). In contrast, the performance of passive regeneration is low when, the exhaust temperature is low or there is a lack of NOx emissions. However, active regeneration can be used in this case. The active regeneration relies on the use of oxygen in the exhausts periodically. However, the temperature of exhausts could be maintained between 500 and 550°C to enhance oxidization of PMs [30]. However, in this study, there is no a DPF or catalyst equipped with the CI engine with an aim of comparing between different fuel blends. In this study, the LII instrument was used to measure nvPM mass. PM size and number were not measured due to unavailability of appropriate instruments, but they will be measured in future work.

1.5 Diesel Emissions Regulations

1.5.1 Europe Emissions Standards

Emissions regulations in different areas of the world are established in order to limit the impact of emissions from SI and CI vehicles. In Europe, many emissions standards are specified over the last three decades as provided in table 1.1. UHC’s, NOx, CO and total nvPM mass emissions and number are regulated for in-road vehicles such as light commercial vehicles.

From Table 1.1, it ca be observed that PM mass are reduced by 96% for Euro 6 as compared to that of Euro 1. PM number regulation have applied for Euro 5a. Diesel particle filter (DPF) was firstly used in Euro 5 standards in order to meet PM mass and number limits [32]. NOx emissions regulations were firstly applied for Euro 3 and are decreased significantly by 84% for Euro 6. Although diesel vehicles produce low CO emissions as compared to SI vehicles, CO emissions are regulated and reduced to be 0.5 g/km for Euro 6.

Table 1.1 European emission standards for light commercial CI vehicles ≤1305 kg g/km [33]

Date Approval	**Standards**	**NOx (g/km)**	**THC (g/km)**	**HC+NO (g/km)**	**CO (g/km)**	**PM (g/km)**	**PN [No/km]**
Oct-93	**Euro 1**	**-**	**-**	**0.97**	**2.72**	**0.14**	**-**
Jan-97	**Euro 2**	**-**	**-**	**0.7**	**1**	**0.08**	**-**
Jan-00	**Euro 3**	**0.5**	**-**	**0.56**	**0.64**	**0.05**	**-**
Jan-05	**Euro 4**	**0.25**	**-**	**0.3**	**0.5**	**0.025**	**-**
Sep-09	**Euro 5a**	**0.18**	**-**	**0.23**	**0.5**	**0.005**	**-**
Sep-11	**Euro 5b**	**0.18**	**-**	**0.23**	**0.5**	**0.0045**	**6×1011**
Sep-14	**Euro 6**	**0.08**	**-**	**0.17**	**0.5**	**0.0045**	**6×1011**

1.5.2 Emissions Standards in the U.S

In the US, Tier 3 standards are the most recent Environmental Protection Agency (EPA) regulations for light-duty vehicles following Tier 1 in 1990 and Tier 2 in 1999 [34]. Tier 1 standards were applied for only light duty vehicles (< 8500 Ib) whereas, Tier 2 standards extended to include medium duty vehicles (8500-10,000 lbs). Heavy-duty vehicles have included (up to 14000 Ibs) in Tier 3 which were singed to cover the period between 2017 and 2025. Tier 3 standards for light-duty vehicles are provided in table 1.2. The vehicles are classified into EPA's rating standards which is identified as bins. For example, the vehicle classified into Bin 125, must produce less than 0.125 g/mile of NOx + volatile organic compounds (NMOG), 0.004 g/mile HCHO, 0.003 g/mile PM mass and 1.2 g/mile CO.

Table 1.2 Tier 3 EPA's emissions standards for light-duty CI vehicles [34]

Classification	NOx + NMOG	HCHO	PM	CO
Bin 20	0.02	0.004	0.003	1
Bin 30	0.03	0.004	0.003	1
Bin 50	0.05	0.004	0.003	1.7
Bin 70	0.07	0.004	0.003	1.7
Bin 125	0.125	0.004	0.003	2.1
Bin 160	0.16	0.004	0.003	4.2
Fleet Average	0.03	--	--	--

1.5.3 Emissions Standards in Japan

The reduction of exhaust emissions from vehicles is a major environmental challenge in Japan [35]. Transport sector produces 18% of exhaust emissions in Japan and on-road vehicles contribute to 85% of total transport sector's emissions. In 1980s, emissions standards for light- and heavy- duty vehicles were introduced in Japan. Table 1.3 provides emissions standards for diesel light-duty vehicles over the last four decades [36]. NOx and nvPM mass emissions standards are reduced by 87% and 97%, respectively in 2009 as compared to 1993 standards.

Table 1.3 Japan emissions standards for light-duty CI vehicles (≤ 1700 kg) [36]

Date	Test	NOx (g/km)	PM (g/km)	CO (g/km)	HC (g/km)
1988	10-15 mode	0.90		2.1	0.40
1993		0.60	0.20	2.1	0.40
1997		0.40	0.08	2.1	0.40
2002		0.28	0.052	0.63	0.12
2005b	JC08c	0.14	0.013	0.63	0.024d
2009		0.08	0.005	0.63	0.024d

1.6 Engine Performance Parameters

The improvement of CI engine performance has become one of the essential tasks of vehicle manufacturing in recent years [37]. The performance of CI engines can be indicated by many parameters such as mean pressure, fuel consumption, mechanical and thermal efficiency. There are two methods to measure engine performance parameters, identical and brake methods. For example, identical power is considered as power exerted in piston due to burning fuel in cylinder without consideration of energy losses such as heat loss by cooling system, through cylinder walls and friction. While, energy losses are considered in the case of brake power [37]. In the present study, engine load is set by adjusting brake output power by using a dynamometer that is controlled electrically using control panel. Therefore, engine performance parameters are measured based on the brake method. Another point, this study focuses on the use of different fuel blends rather than engine parts and technology. Hence, performance parameters that associate strongly with fuel components are measured namely BSFC and BTE. Both parameters are affected by global fuel properties such as calorific value, cetane number and density. BSFC and BTE can be obtained from following equations (Eq 1.4 and Eq 1.5).

$$\mathrm{BSFC} = \frac{\mathrm{FC} \times 3600}{\mathrm{BP}} \quad (\mathrm{kg/kWh}) \qquad \text{Eq (1.4)}$$

$$\mathrm{BTE} = \frac{\mathrm{BP}}{\mathrm{Q} \times \mathrm{FC}} \times 100 \quad (\%) \qquad \text{Eq (1.5)}$$

Where,

FC: fuel consumption (kg/s)

BP: brake power (kW)

Q: calorific value of fuel (MJ/kg)

1.7 The Need for Surrogate Diesel Fuel

Diesel fossil-fuel is considered to be a complex hydrocarbon mixture consisting mainly of alkanes, sulfates and aromatics. As sulfur concentration leads to engine part corrosion and impact exhaust emissions, it has reduced in many countries to be less than 15 ppm [5, 6]. Different types of alkanes including iso-alkanes, n-alkanes, cyclo-alkanes form 60-80% of total diesel components. Earlier, blends of various alkanes have been formed into surrogate fuels in order to decrease the levels of exhaust emissions. However, recently, some researchers have recommended that blends of alkanes alone do not provide the actual picture of diesel fuel combustion. Therefore, aromatics should be included in surrogate diesel fuels. Main attention has been paid for aromatics since they represent 20-30% of diesel fuel components.

1.7.1 Aromatics in Diesel Fuel

Aromatics are known as compounds that include one or more closed benzene rings [38]. Aromatic structure can contain single or multiple rings as shown in figure 1.6. Aromatics are considered to be important fuel compounds representing 20-30% by mass of diesel fuel and highly influenced the PM formation [39, 40]. Alkylbenzenes and polycyclics form the majority of aromatics in diesel fuel. Two common terms namely aromaticity and aromatic content are used in the literature for aromatic blended fuels [38]. Aromaticity is subject to the percentage of carbon moles in a sample including an aromatic ring. Aromatic compounds on the basis of aromaticity were used in few studies such as Reijnders et al. [41]. While, most of the studies such as Ladommatos et al. [39], MI et al. [42] and Kidoguchi [43] used aromatic content as based on the volume or mass percentage of molecules containing at least one aromatic ring. For the present experimental investigation, the aromatic contents of varying structure and type were blended with the base fuel on a mass basis.

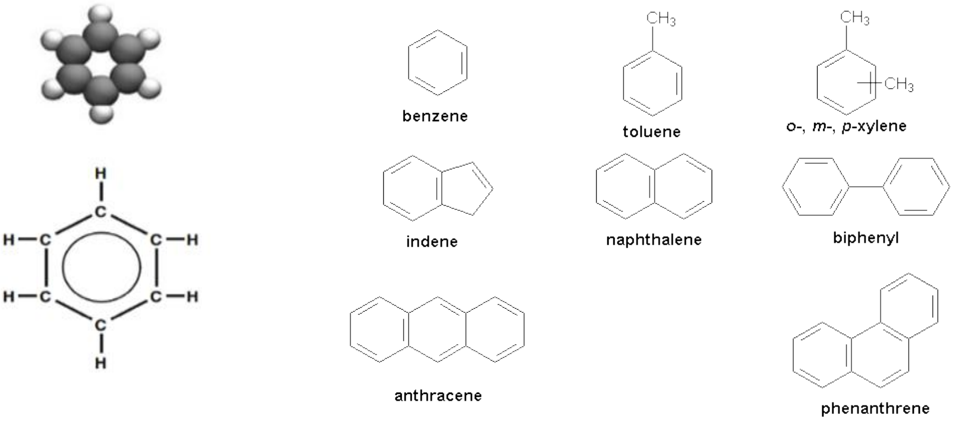


Figure 1.8 The structure of benzenoid ring [14]

1.8 Diesel Fuel Properties

Diesel fuels is the liquid hydrocarbon of choice for CI engines due to their higher specific energy content, long storage life, ease of transport and handling. Some of the fuel properties are known to affect the performance and emissions [44]. The criteria for the measurement of these properties have been standardized, for instance, by ASTM International or the International Petroleum (IP) test method established by the Energy Institute. In most cases, the both test methods have been matched so, IP test is likely to be equivalent to the ASTM test [45]. The European Committee for Standardization (CEN) provides some standards in Europe such as EN 590. Fuel quality is determined by selected fuel properties and composition. In some countries, fuel specifications at least could meet a minimum fuel quality. Generally, the aims of these standards are to ensure that an CI engine starts easily at cold conditions, warms up quickly, runs smoothly, delivers efficient power under all conditions. In this study, the properties of test fuel blends (e.g. cetane number, lubricity, boiling point and density) agree with EN 590-2004 standards. Densities of some fuel properties were less than the lower density limit specified in EN 590-2004, but these reductions were less than 1.3%.

1.8.1 Cetane number

Cetane number determines the autoignition quality. Cetane measurement of a fuel relies on comparing its ignition characteristics with known fuel cetane number using the ASTM D613 test method [44]. The reference fuel consists of normal cetane, heptamethyl nonane that is a highly branched paraffin with 15 cetane number and n-hexadecane that has cetane number of 100 [46].

The higher cetane number means shorter time of ignition delay contributing to easier fuel ignition. Generally, diesel fuels could be ranged from 40 to 60. Therefore, in the present study, cetane number for all fuel blends were set to be within this range. Cetane number of diesel fuel and based fuel were measured based on ASTM D613. A linear variation of cetane numbers of fuel blends, were estimated according to the compendium of experimental cetane number data by Murphy et al. [47].

1.8.2 Boiling Point

The performance and the safety of CI engines are affected by the volatility characteristics of fuels. The boiling range of fuel is determined by distillation at atmospheric pressure regarding to the procedure evaluated in ASTM D86. The volatility can be determined by the percentage of the total volume of the fuel evaporated at a certain temperature. Two measurement methods can be used; namely Txx whereby xx% fuel volume is evaporated at the temperature (T) [45] or Eyy being the percentage of fuel volume evaporated at yy temperature, for example,

$$E100 = 50\% \text{of fuel volume and } T50 = 100\ ^\circ C$$

Diesel fuel involves a mixture of hundreds of hydrocarbons that boil over a range as compared to pure compounds. The boiling point curve covers a temperature interval from initial boiling point to final boiling point. The initial boiling point is known as the evaporation of first diesel droplet, whereas, final boiling point is measured when compounds with high boiling points evaporate. In the present study, final boiling points of diesel fuel, base fuel and aromatic species were obtained based on IP 123.

1.8.3 Density

Fuel density is an important diesel property and it can be considered as a fuel quality indicator [48]. Particularly, diesel density depends on the proportions of different hydrocarbons that make up the fuel. Aromatics are heavy hydrocarbon compounds and have high densities compared to other diesel components. So, increasing aromatic content leads high global fuel density. The increased fuel density leads to a decreased cetane number and fuel consumption. Decreasing diesel density results in low exhaust emissions, especially for PM emissions. Therefore, in Europe, the diesel density ranged is specified to be between 820 and 845 kg/m3 at 15 °C. In the present study, global densities of fuel blends are ranged between 810 and 832 kg/m3. The densities of some fuel blends are less than diesel fuel density because of low densities of alkylbenzenes and the base fuel used. However, density reductions are less than 1.3% compared to the density of diesel fuel.

1.8.4 Lubricity

The fuel lubricity is an important property which can indicate wear or scaring amount occurring between two metal parts that are immersed in the fuel. According to IP 450 and ASTM D6709-11 tests, a steel ball is vibrated in loaded in a test fuel immersing with a steel plate. In this test, the wear scar is required to be less than 460 microns according to the European specification (EN 590) [45]. Low lubricity level in the fuel may contribute to high wear whereas, lower wear and long component life (e i. fuel pump and injection system) are achieved by higher lubricity.

For many years, diesel fuels had sufficient lubricity that are required to maintain adequate performance. However, recently, the change of fuel composition such as lowering sulfur content have been played a main role in reducing fuel lubricity. This is because hydrotreating process used to lower sulfur level removes some of naturally lubricants in diesel fuel. For example, in Sweden, a rapid injection pump failure was observed when the sulfur level was lowered in diesel fuel due to lower lubricity. Therefore, diesel fuel should have sufficient lubricity to avoid the failure of the fuel pump [45]. The natural lubricity is correlated with the presence of heterocyclic, polar, aromatic compounds [49]. Generally, lower aromatic content, sulfur content and acid content, result in removing some of the compounds that provide lubricity as lower lubricity is exhibited. As ensuring the operability and repeatability of CI engine rig is one of objectives of this study, the overall aromatic content of fuel blends are maintained to be more than 20% as agreed with the low limit of aromatic content in commercial diesel fuels to avoid failure of the fuel pump and injection system [39, 44].

1.8.5 H/C Ratio

H/C ratio is an important chemical property and an indicator of hydrogen and carbon contents in fuel. Increasing H/C ratio leads to low density which reduces fuel spray distance and enhanced atomization. Fossil base fuels consist mainly of carbon and hydrogen elements. In particular, diesel fuels are mainly composed of two hydrocarbons classes; aromatics and alkanes. Each hydrocarbon class has a range of H/C ratios, and hence global H/C ratio of diesel fuel is formed as a result of the concentrations of each class [50]. Aromatics have low H/C values in comparison to alkanes. In this PhD study, the H/C ratios of diesel fuel, base fuel and tested aromatic species are obtained using ASTM D5291.

1.9 Main Outlines of the Thesis

This thesis contains eight chapters that are divided mainly into three parts; introductory, main body and conclusion. Main body consists of six chapters' two to seven. While, chapters' one and eight represent introduction and conclusion. The main topics covered by the chapters of this thesis are concluded as below.

Chapter 1: Introduction

This chapter introduces the role of CI engines in transportation and industrial sector. It also provides challenges facing the continue of CI engines in near future such as human and environmental impacts. Basic concepts are overviewed such as types of CI engines and diesel combustion process. Exhaust emissions formation and classifications are discussed as well as performance parameters. Finally, emissions standards and CI engine fuel specifications are discussed.

Chapter 2: Literature Review

This chapter consists of three main sections; literature review, knowledge gaps and objectives and aims. The literature review section covers the effect of alternative fuels that can be used in CI engine. Promising fuels namely biodiesel, natural gas, alcohols, Dimethyl ether (DME**)**, hydrogen and aromatics-and alkanes-hydrocarbon fuels are briefly reviewed. The properties of each fuel are explained and how they impact exhaust emissions and performance. The first section of this chapter will be prepared as review manuscript. The second section highlights the knowledge gaps. The last section provides objectives and aims that need to be achieved.

Chapter 3: Fuel Selection and Analysis

This chapter provides a brief description about the method used to achieve study targets. It includes the categories used to select test aromatics. Verity in the properties and chemical structures of selected aromatics are explained. Furthermore, aromatic concentrations in test fuel blends are also discussed in this chapter. Correlation between properties of the fuel bends are analysed. This chapter also involves uncertainties of the experimental results.

Chapter 4: Experimental Setup

This chapter describes rig configuration and lab facilities. Rig test components are identified and how they are connected to build up rig configuration. A detailed description of operating principle and specifications of each instrument is discussed such as gaseous emissions and particulate analysers.

Chapter 5: Effect of Alkylbenzenes on CI Engine

This chapter concentrates on 12 different monocyclic aromatics (alkylbenzenes) that are investigated experimentally. Each alkylbenzene is blended with the base fuel at three contents, 5, 10 and 15% by mass in order to form 36 fuel blends. Resultant performance, gaseous and particulate emissions are provided with a deep discussion in first part of this chapter. This part has been published as technical paper, in the Fuel journal. While, in the second part, correlations are developed for NO_x and PM emissions as a function of significant impacted fuel properties. The second part of this chapter has published as technical paper in AIAA SciTech Forum and Exposition. Jan 6 – 10, 2020 Orlando, Florida, United States.

Chapter 6: Impact of Polycyclic Aromatics in CI Engine

This chapter provides the results of four polycyclic aromatics namely indene, indane, tetralin and methylnaphthalene. Resultant emissions and performance of fuel blends are discussed briefly. NO_x and PM correlations are created as function of H/C ratio, density and aromatic content. This chapter was submitted as a manuscript for Applied Energy and it is now under review.

Chapter 7: Comparison of Optimum Blend and Diesel Fuel

Based on the outputs of alkylbenzenes and polycyclic aromatics investigated in chapters' five and six, diesel surrogate fuel is reformed with optimum types of alkylbenzenes and polycyclic aromatics. The properties of optimum blend and diesel fuel are compared. The results from the burn of optimum blend in the CI engine are discussed and compared to those of commercial diesel fuel.

Chapter 8: Conclusion and Future Work

This chapter concludes contributions to knowledge from this study based on the implementations of the aims. Aromatics with significant effect on performance and emissions are determined**.** Some suggestions are shortly discussed that will be considered in future work.

2. LITERATURE REVIEW AND KNOWLEDGE GAP

2.1 Overview

Relating studies of CI engine have mostly focused on new engine technologies and alternative fuels approaches. In this chapter, the later approach is reviewed as it is strongly related to this PhD study. As illustrated in figure 2.1, topics covered in this review are illustrated with yellow colour.

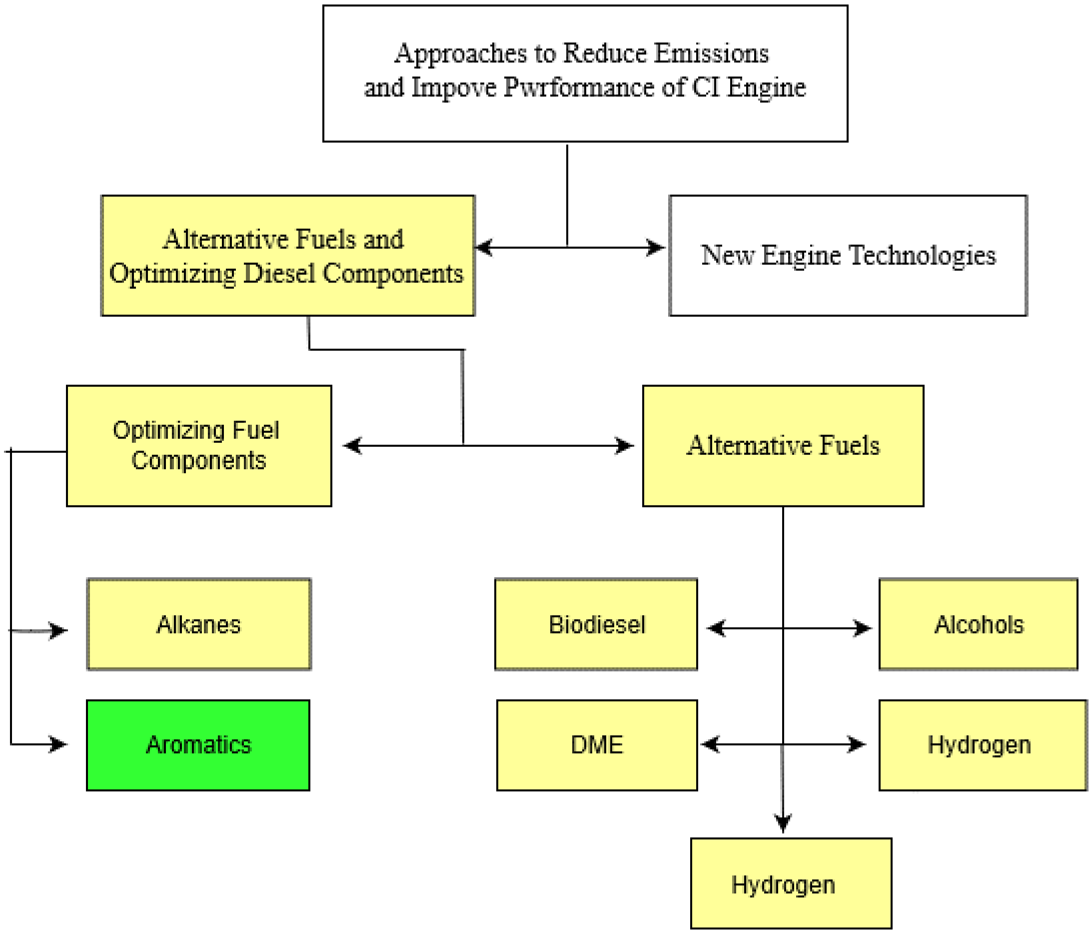


Figure 2.1 Schematic diagram of literature review

In the first part of this chapter, alternative fuels, namely different biodiesel fuels, three types from alcohols (methanol, ethanol and butanol), Dimethyl ether (DME), both compressed and liquefied natural gas, hydrogen, aromatics- and alkanes-hydrocarbon fuel blends are reviewed with a focus on their properties and effects on emissions and performance. Both the gaseous and particulate emissions of the alternative fuels are discussed. Many engine performance parameters are also covered such as BSFC, BTE and brake power. The second part presents knowledge gaps that need to be covered.

2.2 Biodiesel

2.2.1 Biodiesel Properties

A variety of feedstocks can be used to produce biodiesel fuel; animal fat, vegetable oil and waste cooking oil [51, 52]. Soybean and rapeseed oils are commonly used materials for biodiesel fuel for example. The American Society for Testing and Materials (ASTM) reported that biodiesel can be defined as mono-alkyl esters of long-chain fatty acids [53]. Operating CI engine with pure vegetable oils however leads to many issues such as gumming, as well as issues with pumping, injector fouling, atomization, carbon deposits on the piston, wear scars and contamination of the lubricating oil in long engine operations. This may occur due to the high density, viscosity, non-volatility of these oils [54]. Therefore, many researchers have recommended that vegetable oil could be transesterified to decrease its viscosity [54]. Transesterification is the conversion process of vegetable oil to biodiesel to be used in CI engines [55].

Nowadays, a lot of vegetable oil crops (up to 350) can be used and they are considered to be the conventional feedstocks for biodiesel production. They involve sunflower oil in Europe, soybean and canola in Canada, coconut oil in the Philippines, soybean oil in the United States and palm oil in Indonesia and Malaysia [56].

Iinteresting in biofuels have been increased in the last two decades. In Europe, there is a target to fuel 10% of transportation with biofuels by 2020 whereas, the US has a plan to fuel 20% road vehicles with biofuels by 2022 [57]. Biofuels are classified into three classes known as first, second and third generations [57]. First generation involves biofuels from edible feedstocks such as vegetable oil, sugar and starch. While, second generation is based on biofuels from non- edible feedstocks resulted from the residues of food and agricultural processing systems. The use of the first and the second generations contribute to sustainability issues such as use of land and fuel-food competition. In other words, increasing biofuels dependency invested of fossil fuels increases demand for land and food [58]. To overcome these issues, more attention has been paid to the use of algae as biodiesel for its non-edible oil and its higher yields [59]. Therefore, third generation biodiesel is promising approach as compared to the first and the second generations [60]. Aquatic cultivated feedstocks are used to produce third generation. However, high water content is needed to produce algae which considers an issue for many countries.

The study of the properties of biodiesel is important because they affect performance and emissions. Biodiesel fuel is considered to be stable fuel that can be stored for long time. Moreover, its sulfur concentration is low and it does not include aromatic compounds, which results in low PM emissions [61]. The use of biodiesel contributes to an improvement in combustion performance because of its high cetane number [51-53, 62]. In addition,biodiesel results in more complete combustion due to its high oxygen concentration and it is also good lubricant additive due to its high viscosity. However, it has a decreased calorific value and volatility and is thicker in cold weather, thus it requires anti-freeze additives [51-54]. The properties of biodiesel fuels produced from different feedstocks are reviewed in Table 2.1.

2.2.2 Biodiesel Effects on Performance and Emissions

Today, many studies have been concerned with the biodiesel effects on CI engine emissions and performance. Lapuerta et al. [63] published a review paper focusing on the effect of biodiesel on CI engines. They found that there may be no difference in the output power when a CI engine is operated in biodiesel at partial load operation [63]. The possible reason is that the increased fuel consumption of biodiesel compensates for the reduction in its calorific value. However, at full load, the output power resulting from the use of biodiesel is lower than that related to decreased calorific value. Further, the authors reported that the BSFC increase may relate proportionally to a decreasing calorific value. Therefore, replacing diesel fuel by biodiesel fuel (blended or pure) does not influence the thermal efficiency. In contrast, the levels of NO_x levels are increased.

PM levels are reduced because of the absence of aromatics in biodiesel composition. High oxygen concentration in biodiesel fuel composition contributes to more complete combustion and then, low significant levels of UHC and CO emissions.

The EPA [51] reported a summary of the overall results for UHC, CO, PM and NO_x levels as shown in figure 2.2. The level of CO and UHC are reduced when biodiesel concentration increases. The higher biodiesel oxygen concentration can lower the locally fuel rich regions and limits primary particle formation. This contributes to a better combustion efficiency because of the naturally oxygenated state of biodiesel. In other words, a higher oxygen concentration in the biodiesel is available for burning, and this contributes to a more complete and stable combustion and then, decreased emissions.

Table 2.1 Biodiesel properties produced from different feedstocks [54, 64-70]

Feedstock Type	**Cetane Number**	**Density (kg/l)**	**Viscosity (mm2/s)**	**Calorific Value (MJ/kg)**	**Flash Point (°C)**
Rapeseed oil	-	0.882	4.439	-	-
Canola oil	49–52.9	0.837–0.886	4.2–4.5	36.55–40.5	94–183
Honge oil	-	0.870	5.84	36.1	170
Mohr oil based	56	0.870	-	37.5	-
Corn oil	60.9	0.884–0.890	4.17–4.21	37.5	-
Rice bran	51.6	0.872–0.877	4.81–5.6	36–39.6	153
Sunflower	37.1	-	37.1	39.575	274
Castor	-	-	297	39.5	260
Pongamiapinnata	45–67	0.913	27.84	34	205
Cotton	41.2–59.5	0.912	50	39.6	210
Calophylluminophyllum	-	0.896	71.98	39.25	221
Palm oil	61	0.856	4.56	39.8	167.3
Karanja	58	0.890	4.85	34–38	180
Rubber seed oil	37	0.860	5.81	36.5	130
Jatropha	46–55	0.864–0.880	3.7–5.8	38.5–42	163–238
Neem oil	51	0.912–0.965	0.5–48.5	33.7–39.5	34–285
Lard	-	0.877	4.84	36.5	143.5
Beef tallow	-	0.832	4.89	-	152
Mutton fat	59	0.856	8.15	-	-
Chicken fat	48	0.869	2.8	-	74

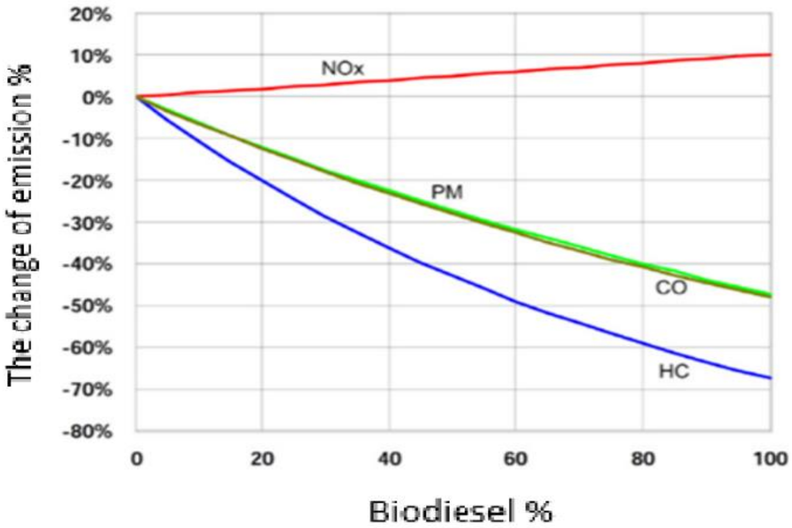


Figure 2.2 Average emissions results produced by biodiesel [51]

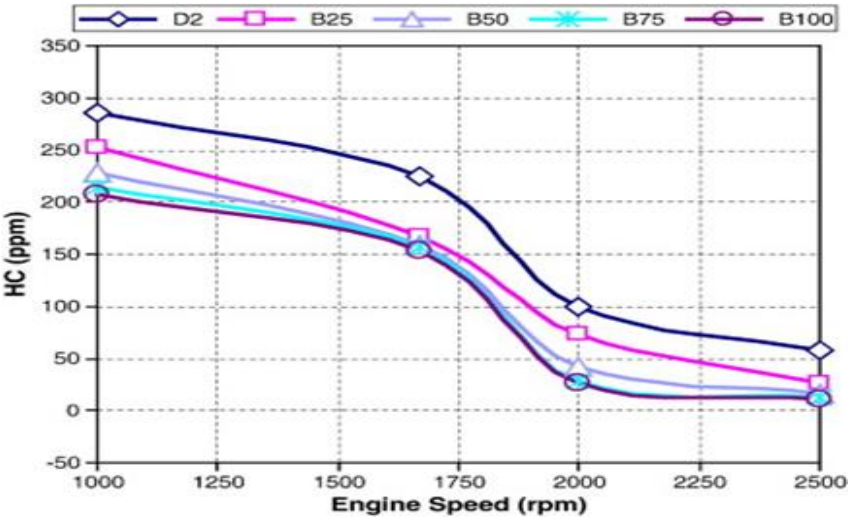
Tomic et al. [71] tested various biodiesel-diesel blends; 15%, 25%, 50%, 75% and 100%. In comparison to diesel fuel, all fuel blends contributed to a higher BSFC by a range of 1.32–13.35%. The possible reason is related to the high density and low calorific value of the blends. The combustion of a biodiesel-diesel mixture is more complete resulting in a decreased CO levels by 1.84–13.15%. However, NO_x emissions at all engine loads are increased, from 1.51–11.38%, with an increasing biodiesel concentration in the blend because of increasing oxygen in exhaust products.

Jatropha oil methyl ester were evaluated by Ong et al. [72] in order to asses emissions and performance characteristics at various engine speeds and high load condition. Overall results of the experiment presented generally a higher torque, lower BSFC and higher power for 10% biodiesel in the blend because of biodiesel effect on blend density and calorific value. However, deteriorating combustion and high heat loses at maximum engine speed increased BSFC. In comparison to diesel fuel, all of the biodiesel blends tested emitted, lower CO, CO_2 and smoke, whereas, a slight increased NO_x levels were recorded. Finally, the authors recommended that 10% jatropha oil methyl ester concentration in the blend performed better than the other blend concentrations.

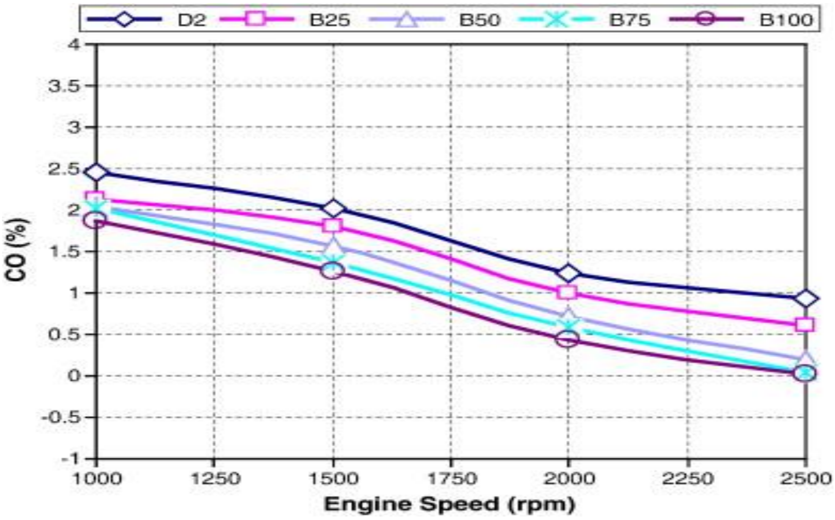
Sureshkumar et al. [73] evaluated pongamiapinnata methyl ester (PPME) influence at 1500 rpm. They found that the BSFC values for 40% PPME and 20% PPME in blends are equal to and lower than that of diesel, respectively. In contrast, further increase of PPME concentration in blends led to high BSFC at all loads because of decreased heating value of blends. In conclusion, they recommended that replacing diesel by PPME at up to 40% by volume was likely to provide better performance and lower emissions, leading to both environmental protection and energy economy.

Altiparmak et al. [74] tested blends of the tall oil methyl ester–diesel at a range of 1800-3200 rpm and high load. It was found that the power output and torque were raised by up to 6.1% and 5.9%, respectively with blending tall oil methyl ester at high engine speed. Moreover, with these blends, CO levels were reduced to 38.9% and NO_x levels were increased to 30% compared to pure diesel and there was no significant effect on smoke opacity at all speeds. The reasons for low CO levels related with high cetane number with blends and nitrogen content in tall oil methyl ester led to more NO_x formation.

Different waste anchovy oil concentration (25% (B25), 50% (B50) and 75% (B75)) blended with diesel fuel were evaluated by Behçet [75]. The experiments were carried out at variable speeds (1000-2500 rpm) and at high load condition**.** Due to the oxygen content of waste anchovy oil, CO and UHC were reduced by 21.3% and 33.42%, respectively at all speeds, as shown in figure 2.3. However, exhaust gas temperature, NO_x and oxygen (O_2) were increased by up to 7.54%, 29.37% and 9.63%, respectively. Short ignition delay, oxygen and nitrogen contents in the fuel led to higher NO_x levels.



a) UHC emissions



b) CO emissions

Figure 2.3 The results of exhaust emissions from No. 2 diesel fuel and waste anchovy oil-diesel blends [75]

Lapuerta [76] dealt with the effect of waste cooking oils-diesel fuel blends at different engine conditions. Waste cooking oils were blended with diesel at three concentrations; 30, 70 and 100% by volume. The overall results showed no significant effect on BTE whereas, low biodiesel calorific value led to higher BSFC. On the other hand, smoke capacity, PM emissions and mean particle size decreased significantly with an increasing content of biodiesel. Particulate distributions were displaced towards small diameter values with increasing biodiesel content.

Panwar et al. [77] tested castor methyl ester (CME) at variable compression ratios at 1500 rpm, and under variable load conditions. They found that high BTE and low BSFC were noted to a certain CME concentration in CME-diesel blends after that a decreased BTE was observed. The possible reason for this related with CME lubricity which reduced frication and then heat loses. When more CME was blended with diesel, lower calorific value resulted. While, a higher exhaust gas temperature was noted when CME content increased. However, NOx levels at low load were not impacted, but slightly increased at full load.

Table 2.2 Summery of some studies of biodiesel effects on characteristics of performance and emissions

Author	**Year**	**Biodiesel Type**	**Test Conditions**	**Performance**			**Emissions**			
				BTE	**Power**	**BSFC**	**UHC**	**CO**	**NOx**	**PM**
Srivastava and Madhumita [78]	2008	Karanja	1500 rpm	−24.87%		+0.3190 kg/kWh	+120 ppm	+ 0.21%	+12%	
Qi et al. [79]	2009	soybean-oil					−27%	−27%	+5%	
Jincheng et al [80]	2010	Jatropha	Two engine speeds; 1500 and 2000 rpm at different loads	+6.7%		+6.8%				
Nabi et al. [81]	2009	Cotton-seed oil (B10, B20, B30)						−24%	+ 10%	+ 24%
Cheng et al. [82]	2008	Waste cooking oil					−37%	−9.2%	+4.1%	
Kegl [83]	2008	Rapeseed oil					−30%	−25%	−25%	
McCormick et al [84]	2004	soybean-oil (B20)					−12%	−17%	+0.6%	−16.4%
Dhar et al. [85]	2012	Neem oil (5,10,20,50and B100)		+12.2%		−14.8%	−33%	−16%	+52%	
Habibullah et al. [86]	2014	Palm oil and coconut oil mixture (B30)		−5.03%	−3.89%	+8.58%	−31.2%	−17.9%	+5.6%	
Parlak et al. [87]	2013	Tobacco oil (B20)		+3%	+2.5%	−1.55		−10%	−9.5%	
Kruczyński [88]	2013	Camelinasativa oil (B100)		+15.5%	+3.3%	+20.8%	+5.26%	+40%	+30%	

*For all studies in the table, the results were compared to reference fuels (diesel fuels) tested

According to most of the studies reviewed in Table 2.2, biodiesel-diesel blends impacts in emissions and performance are summarized below.

Few studies have indicated a lower BTE because of increased viscosity, volatility, decreased calorific value, poor spray characteristics and air fuel mixing [81, 89]. However, others have found that fuelling CI engines with biodiesel resulted in a higher BTE under different engine conditions [77, 80, 85, 87]. The output power of CI engines is reduced and the BSFC is increased with blending biodiesel due to the decreased biodiesel calorific value [63, 71].

Therefore, increasing biodiesel concentration contributes further to output power reduction as well as lower engine torque. However, some studies have shown an increase in output power when biodiesel-diesel blends are used [87, 88]. The reason for this may relate to the better combustion resulting from burning biodiesel-diesel blends. A higher torque is sometimes observed when the blends have a higher cetane number, contributing to better combustion.

There have been many attempts to explain why NO_x levels increase with using biodiesel in CI engines. One study explained that the increase of actual flame temperature with blending biodiesel is caused by a decrease in the heat dissipation through radiation as a result of the lower soot concentration produced [51]. The main source of heat transfer in cylinder is hot PM, which is reduced with biodiesel use. This may result in a higher flame temperature and thus increased NO_x levels [90]. On the other hand, the amount hot PM concentration from diesel fuel are higher, cooling the flame temperature by 25–50 K and thus decreasing NO_x emissions by 12–25% compared to those of biodiesel [51]. Furthermore, the high oxygen concentration of biodiesel may provide further oxygen for

NO_x kinetics. However, some studies have reported lower NO_x emissions when injection timing was adjusted, such as those by Kegl [83] and Gogoi and Baruah [91].

For biodiesel-diesel blends, CO and UHC levels were decreased at different operating conditions [71, 75, 79, 82, 86]. These were due to higher biodiesel oxygen concentration contributing to better combustion compared to pure diesel [51, 89]. Another reason is associated with the high H/C ratio of biodiesel. The absence of aromatics, low sulfur concentration and high H/C ratio in biodiesel are responsible for the lower PM emissions [89, 92].

2.3 Natural Gas-Diesel Dual Fuel

2.3.1 Natural Gas Properties

Natural gas is a promising alternative fuel due to its low cost, generally low emissions and its large reserves, at the same quantities as crude oil [52, 93]. The use of natural gas may contribute to energy crisis reduction [93]. Generally, natural gas consists of a high percentage of methane, ranging from 80-98% by volume, together with ethane (1-8%), propane (2%), pentane and butane (< 1%). Moreover, natural gas includes about 0.2-1.5% carbon dioxide and nitrogen and a small proportion of sulfur compounds. Methane has an octane number of 130 and thus has high knock resistance. Natural gas can be used as a vehicular fuel in liquefied and compressed forms; liquefied natural gas (LNG) and compressed natural gas (CNG). CNG is a natural gas under high pressure (20 MPA) and at ambient temperature whereas the liquid form (LNG) is cooled to low temperature (−161 ^{o}C) at atmospheric pressure.

The properties of natural gas are provided in Table 2.3. High octane number makes natural gas more suitable for SI engines. On the other hand, using natural gas leads to poor ignition characteristics due to its decreased cetane number as well as increased autoignition temperature [93, 94]. Consequently, three different methods which have been developed to feed into the cylinder; hot surface assisted ignition, high pressure DI (HPDI) and the dual fuel system. In the case of HPDI, first, a small pilot diesel amount is induced late in the compression stroke after that natural gas is directly injected into the chamber (see figure 2.4) [94]. At a certain time during the injection of natural gas, or between two injections, the ignition source is provided by the autoignition of pilot diesel [94, 95]. In hot surface assisted ignition mode, natural gas is directly induced into the combustion chamber near to a hot surface which has a high temperature range (1200-1400 K, as shown in figure 2.5. This mode has many benefits; a high thermal efficiency and specific power, but the hot surface durability is the critical issue because of the high temperature needed.

Table 2.3 Alternative fuels and diesel fuel properties

Properties	**Diesel [96]**	**Natural gas**	**Methanol [97]**	**Ethanol [97]**	**Butanol [97]**	**DME [96]**	**Hydrogen**
Chemical Structure	C_{10} to C_{25}	CH_4	CH_3OH	CH_3CH_2OH [98]	C_4H_9OH [98]	$CHOCH_3$	H_2
Molecular Weight	170 [98]	19	32.04	46 [98]	74 [98]	46.069	2.016
Cetane Number	40-55 [99]	-	3.8	5-8	25	55-60 [99]	
Energy Content (MJ/kg)	43	48.6 [94]	20.1	26.9	33.1	28.9	120 [100]
Density at 20 °C (g/ml)	0.82-0.88	0.72 [101]	0.7866	0.7851	0.8098	0.66	0.000838 [100]
Autoignition Temperature (°C)	250	650 [94]	463	423	397	350	500
Flash point (°C)	70	-	12	13	35	−41	-
Boling point (°C)	260		65	78	117-118	−24	20.3
Carbon content	86.57	75 [94]	n/a	52.2 [102]	n/	52.17	0
Oxygen content	0	0	49.93 [52]	34.73 [52]	21.6 [98]	34.57	0
Aromatic Content	20-30	0	-	-	-	0	0

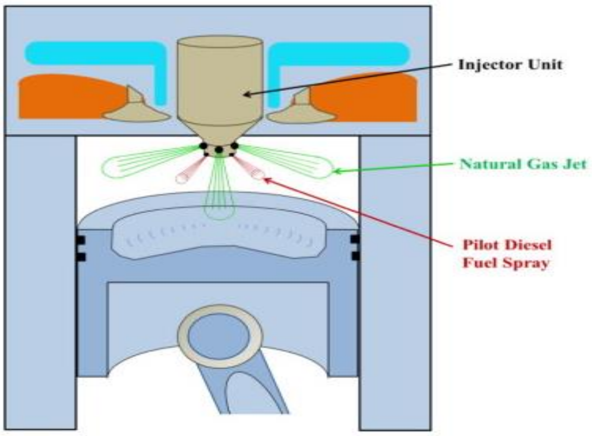


Figure 2.4 Schematic diagram of HPD mode [94]

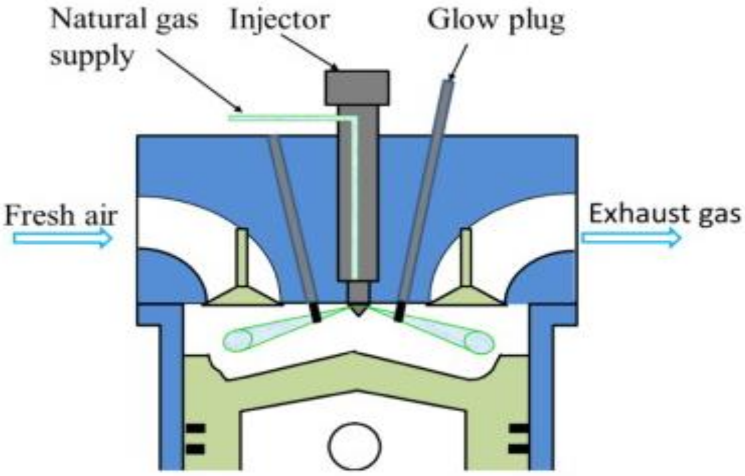


Figure 2.5 Hot surface assisted ignition mode [94]

The dual fuel mode system is the most common system and is designed to run on two types of fuels; conventional fuel and an alternative fuel [52]. Figure 2.6 illustrates a schematic diagram of a dual fuel system [101]. Firstly, the alternative fuel is pressurized and introduced into the intake manifold after that, mixed with air in order to form a homogenous mixture. This is ignited by a spark plug or pilot diesel when the piston is at the TDC [52, 94]. The injected alternative fuel amount changes depending on the engine power output whereas the diesel fuel amount remains constant under different operating conditions.

Dual fuel system is usually designed to run with different fuels such as natural gas, alcohols, DME and hydrogen. These fuels are used as primary and the diesel as a pilot fuel. The dual fuel engine in comparison to the conventional diesel engine usually produces lower PM and NO_x levels. On the other hand, there are some difficulties related to the dual fuel combination. The combustion efficiency is low when it operates at medium and low loads. As a result, CO and UHC emissions are greatly increased with dual fuel combustion [103]. The dual fuel system is more promising method than hot surface assisted ignition and HPDI [94], and therefore, in this section, all studies reviewed were dealt with natural gas influence operating on dual fuel system.

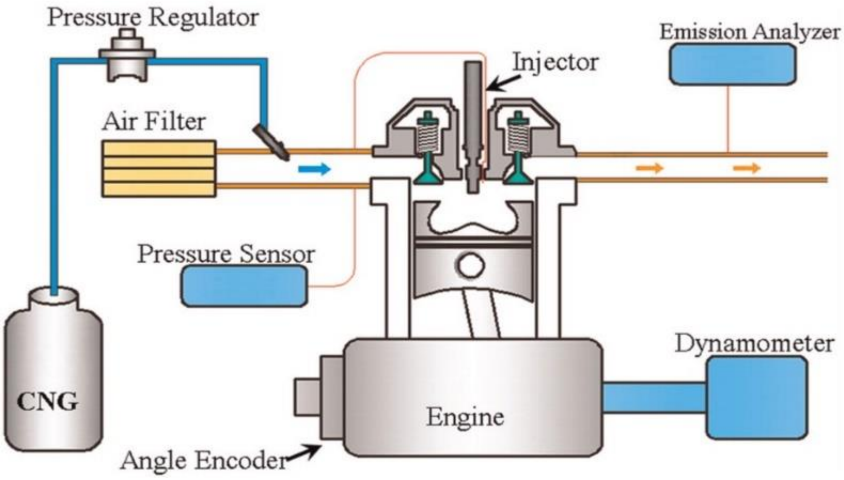


Figure 2.6 Schematic diagram of a dual fuel system [101]

2.3.2 Natural Gas Influence on CI Engine

The air-diesel mixture in the chamber is controlled by diffusion. In contrast, for natural gas, premixed combustion occurs. Adding natural gas to the chamber influences performance and exhaust emissions because of the changes in the process of air-fuel mixture formation. There are many studies that have dealt with natural gas, as provided in Table 2.4.

Diesel-natural gas fuels influences on dual fuel CI engine performance and emissions are summarized below.

The power output is reduced with using dual fuel system in comparison to normal engine for two reasons. First, the calorific value of a diesel-air mixture is higher than that of a natural gas-air mixture [94]. Second, natural gas injection in the intake stroke decreases intake of air hence, volumetric efficiency, which contributes to lower engine power, particularly at high load conditions. Engine power reduction can be recovered by increasing the intake temperature, pressure and pilot diesel amount, but these may lead to knocking [104].

The BTE is slightly lowered in comparison to diesel combustion at both low and medium loads whereas, at high load, the pilot diesel is more likely to be a little higher than or similar to normal diesel combustion [90, 94, 105]. The decrease in the BTE of the dual fuel mode is associated with a too lean mixture of natural gas at low loads. This makes the ignition of the pilot diesel fuel more difficult and provides inadequate combustion, resulting in a poor efficiency of fuel utilization and lower BTE. Furthermore, the heat loss during the combustion at a slow burning rate because the slow speed of flame propagation plays a major role in reducing BTE.

Table 2.4 Studies of the effects of natural gas-diesel dual fuels

Author	**Year**	**CNG or LNG**	**Test Conditions**	**Performance**			**Emissions**			
				BTE	**Power**	**BSFC**	**UHC**	**CO**	**NOx**	**nvPM**
Cheenkachorn et al. [105]	2013	LNG	Full loads, engine speed (1100-1900 rpm)	-3.50% at 1500 rpm and -13.9% at 1900 rpm		-11.6% at 1500 rpm and 13.6% at 1900 rpm		77.% at 1500 rpm	31.25% at 1500 rpm and 68.8% at 1900 rpm	
Papagiannakis et al. [106]	2003		The mass ratio of natural gas ranged from 0 to 80%. by mass Different loads					50% at 30% and 80% natural gas	-33.3% at 80% natural gas and (30-80% natural gas)	
Papagiannakis and Hountalas [107]	2004	CNG	Different loads Two speeds; 1500 and 2500 rpm			20% at 1500 rpm, 5 bar		260% at 1500 rpm and 5 bar 200% at 2500 rpm, 5 bar	-57% at 1500 rpm and 5 bar -22% at 2500 rpm and 5 bar	-88% at 1500 rpm and 5 bar
Lounici et al. [108]	2014		Different loads and speeds		10.3% at 80% load and 2000 rpm	-16.6 at 80% load and 2200 rpm		-28.5% at 80% load and 2000 rpm	20% at 80% load and 2200 rpm	

*For all studies in the table, the results were compared to reference fuels (diesel fuels) tested

Higher CO emissions are detected at the dual fuel mode [90, 94, 105]. The mixture of natural gas-air is ignited by pilot diesel and, at the same time, the flame is propagated. To sustain the propagation of the flame, some mixture areas are very lean, that leads to a reduction of the local temperature as well as the CO oxidation freezes and then, the CO levels increase [94].

The UHC levels are highly increased at dual fuel mode [90, 94, 105]. A small amount of the natural gas-air mixture is exhausted outside of the combustion chamber during the scavenging process because of the valve overlap period. This contributes to the higher UHC emissions. Furthermore, the trapping of the natural gas-air mixture in the quench layer restricts the ignition in the late part of the combustion processes, leading to higher UHC emissions. In addition, too lean mixture and the low temperature in the chamber causes the formation of UHC emissions [94].

Most studies have reported that NO_x levels are lower under the dual fuel mode [90, 105, 106] whilst a few studies found higher NO_x emissions at high loads [94]. It is also noted that increasing the quantity of pilot diesel and the engine load is related to increased NO_x levels although a decrease is observed with rising engine speed [94]. The NO_x reduction may relate to the high specific heat capacity of natural gas compared to that of air [106]. Thus, the injection of more natural gas into the chamber leads to increased mixture heat capacity, attributing to a decreased temperature during the combustion process, especially at the end of the compression stroke. Therefore, NO_x emissions are lowered because of decreased combustion temperature. Further NO_x reduction is clearly observed at low loads because the temperature in the cylinder is already low. The introduction of natural gas into the chamber also reduces the amount of air, which causes a lack of the oxygen required for NO_x formation and therefore results in a decrease of NO_x emissions [94, 106].

Furthermore, at higher engine speeds, NO_x emissions are decreased because there is not enough time in which to form NO_x emissions.

Reduction of PM emissions is one of the main benefits of using natural gas in CI engines [94]. In dual fuel combustion, the amount of diesel fuel used is lower than that used in diesel fuel mode [109]. A large pilot diesel amount is burned during premixed combustion and a little is burned during the diffusion mode. This reduces the formation of soot and results in decreased PM concentrations. The absence of C-C bonds, aromatics and sulphur compounds in natural gas reduces the formation of PM emissions [94].

2.4 Alcohol-Diesel Fuels

2.4.1 Overview

Using alcohol in internal combustion (IC) engines as alternative fuels is not a new approach as alcohols have been used for this purpose from the invention of the IC engine [97]. For CI engines, there are many difficulties associated with the use of pure alcohol such as poor solubility, low calorific value, low cetane number, low flash point and decreased lubricity even though it has a high oxygen content and low cost [53]. The low alcohol cetane number contributes to increased ignition delay [110]. The use of alcohols results in poor autoignition, which is responsible for knocking because of the fast burning of vaporized alcohols. Furthermore, the high latent heat of vaporization causes combustion quenching [111]. Diesel fuel is considered to be a lubricant for CI engines while the lubricating qualities in alcohols are poor. Therefore, the replacement of diesel by alcohols is likely to be difficult [112, 113].

Different dual fuel operations can be used to introduce alcohols into CI engines such as dual injection, alcohol fumigation, alcohol-diesel fuel blend and alcohol-diesel fuel emulsion [112, 114]. The separation of the injection system for each fuel and injection of a high amount of diesel (up to 90%) are known as dual injectors. While, alcohol fumigation refers to adding alcohols to the manifold of intake air and the injection of diesel fuel (up to 50%). Alcohol-diesel blend is the mixture of alcohol-diesel just before the injection period with a concentration of diesel in the mixture of up to 25%. More attention has paid to the use of alcohol-diesel blends for which methanol, ethanol and butanol are commonly used [97]. Finally, alcohol-diesel fuel emulsion is the use of an emulsifier to blend the alcohol with the diesel to prevent separation with a diesel concentration in the blend of up to 25%. In this following section, the more common alcohols, namely methanol, ethanol and butanol are reviewed.

2.4.2 Methanol-Diesel Fuels

2.4.2.1 Methanol Properties

The properties of methanol are provided in Table 2.3. Blending methanol with diesel has many benefits such as approximately high NO_x emissions, low sulfur content and low ozone formation. However, the autoignition of a fuel-air mixture finds difficulty to ignite since methanol cetane number is too low. Methanol is hygroscopic, so it absorbs water from the air and this may then dilute the methanol, resulting in phase separation of the methanol-diesel blend [115]. As result, it was recommended that low methanol concentration be used in the blends [97].

2.4.2.2 Methanol-Diesel Fuels Effects on CI Engine

Methanol-diesel fuel influences have been investigated in many studies available in literature since the use of methanol can reduce air pollution [97, 114]. Some researchers have been concerned about the concentration of methanol to the blend. For instance, the influence of methanol concentration was tested by Huang et al. [116]. The overall results presented a reduction in CO, UHC and smoke, but a large amount of NO_x emissions. Kumar et al. [117] dealt with methanol fumigation effects on CI engine emissions. Decreased NO_x and smoke emissions were noted with methanol fumigation in the intake system. Further, researchers have been concerned with the methanol content in the blend, such as Najafi and Yusuf [118] and Jikar et al. [119], as provided in Table 2.5.

The characteristics of the fuel injection system, namely injection pressure and timing, can influence emissions. Therefore, attention has been paid to recognizing timing and injection pressure influences on CI engines fuelled with methanol-diesel fuel. Sayan et al. [114] were concerned with methanol-diesel fuel. The test used three different methanol percentages (5, 10 and 15%) blended with diesel at three timings (15', 20'and 25') and injection pressures (180, 200 and 220 bar) at 2200 rpm and 20 Nm engine load. The overall results illustrated that BTE, CO, UHC and soot were reduced because of oxygen content of methanol. NOx levels were increased with increasing the ratio of methanol to diesel because of increased combustion temperature. In addition, BTE, CO, UHC and soot emissions were reduced and BSFC and NO_x concentrations were increased with increases in the injection timing and pressure.

In conclusion, most studies presented in this section show that an increase of methanol in methanol-diesel fuel contributes to reductions in BTE, CO, UHC and soot, and results in higher NO_x and BSFC. The possible reason for low CO and UHC emissions is the natural oxygen state of methanol improving methanol-diesel combustion. The low calorific value is more likely to be responsible for the higher BSFC. Increasing engine load, injection pressure and timing reduce UHC, CO and smoke with slight increased NO_x.

Table 2.5 Studies about the effects of methanol-diesel fuels on CI engines

Author	**Year**	**Engine Type**	**Test parameters**	**Performance**	**Emissions**
Najafi and Yusuf [118]	2009	Four-stroke CI engine	Different methanol content:10, 20 and 30%	Higher torque and BTE Lower BSFC	
Jikar et al. [119]	2011	Four stroke CI engines	Different methanol content:10, 20 and 30%	Higher torque and BTE Lower BSFC	
Sayin and Canakci [120]	2009	Single cylinder CI engine	Different methanol content: 5, 10 and 15%. Two different engine loads; 15 and 30 Nm. Different injection timings	Higher BSFC Lower BTE	Higher NO_x, CO_2 emissions Lower CO, UHC emissions
Chao et al. [121]	2001	Heavy-duty CI engine	Different engine load. Different methanol content:5, 8, 10 and 15%		Higher CO, UHC emissions Lower NO_x, PAHs, PM emissions
Zhang et al. [122]	2012	Turbocharged CI engine	10% methanol		Higher NO_x, UHC emissions Lower CO, soot emissions
Canakci et al. [123]	2009	Single cylinder, Four strokes, CI engine	Injection pressure	Higher BSEC Lower BTE	Higher NO_x, CO_2 emissions Lower CO, UHC, soot emissions
Song et al. [124]	2008	Four-stroke DI engine	10 and 80% methanol contents Injection pressure, timing Different engine loads and speed engine	Higher BSFC	Higher CO, UHC emissions Lower NO_x, smoke emissions
Qi et al. [125]	2010	Four-stroke DI engine	5 and 10% methanol contents Reference fuel; 50% diesel and 50% biodiesel. Different engine loads	Lower power, torque output	Lower CO, smoke emissions

*For all studies in the table, the results were compared to reference fuels (diesel fuels) tested

2.4.3 Ethanol-Diesel Fuels

2.4.3.1 Ethanol Properties

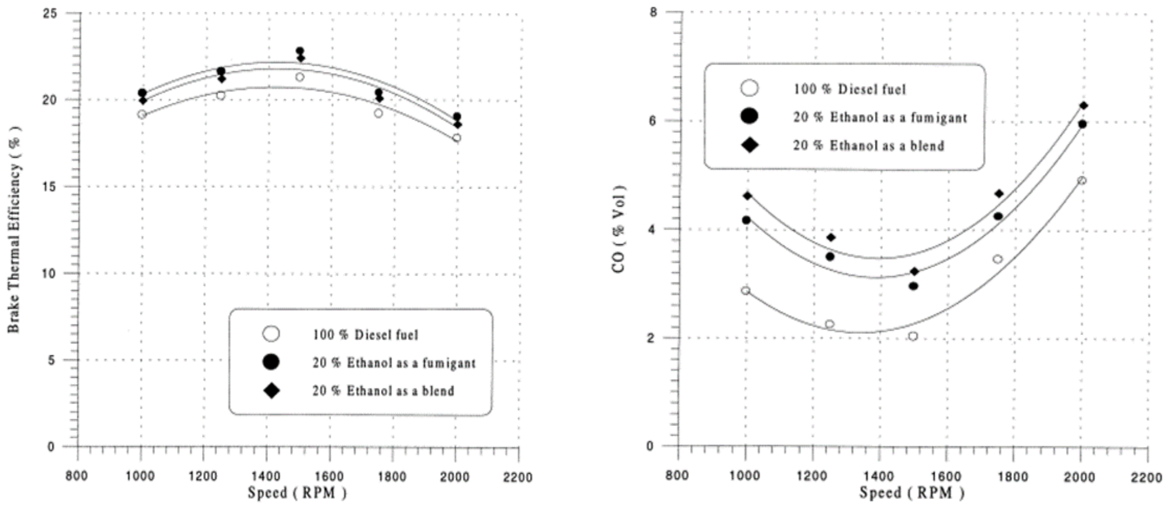
Ethanol is now the most common of the alcohol-based fuels. Ethanol is miscible with water and is a flammable polar solvent. In the 1980s, it was demonstrated that an ethanol-diesel blend was acceptable as a fuel for CI engines. On the other hand, producing ethanol was costly at that time, this blend was considered as storage fuel. Nowadays, the production process of ethanol is more competitive with that of diesel, so more attention has been paid to this fuel [126]. There are many methods that can be used to adapt ethanol such as ethanol emulsions, ethanol-diesel blends, ethanol fumigation and dual fuel injection [127].

The main benefit of using ethanol is associated with its oxygen concentration. Ethanol is considered to be one of oxygenated blends which leads to low PM emissions [127]. However, there are many issues that should be considered when CI engines are fuelled by an ethanol-diesel blend. To ensure the formed blends solubility, an additive is often employed. Increasing ethanol concentration in diesel leads to poor fuel lubricity which impacts the fuel pumps and injectors. Furthermore, ethanol has a low cetane number resulting in a decreased blend cetane number meaning increased delay of ignition. According to ASTM D 975-02 for No. 2 diesel, the minimum cetane number is 40, whereas blending ethanol with diesel may reduce the cetane number to below 40 [126]. Therefore, an ignition improver such as 2-ethylhexylnitrate is required to raise the cetane number [97]. The energy content is reduced by 2% for each 5% of ethanol in the blend by volume [128]. This is directly related to the output power of a CI engine. In addition, because of decreased ethanol flash point, ethanol-diesel formed fuel may suffer from accidental ignition. Consequently, ethanol-diesel blends should be handled with greater care [97]. The properties of ethanol are given in Table 2.3.

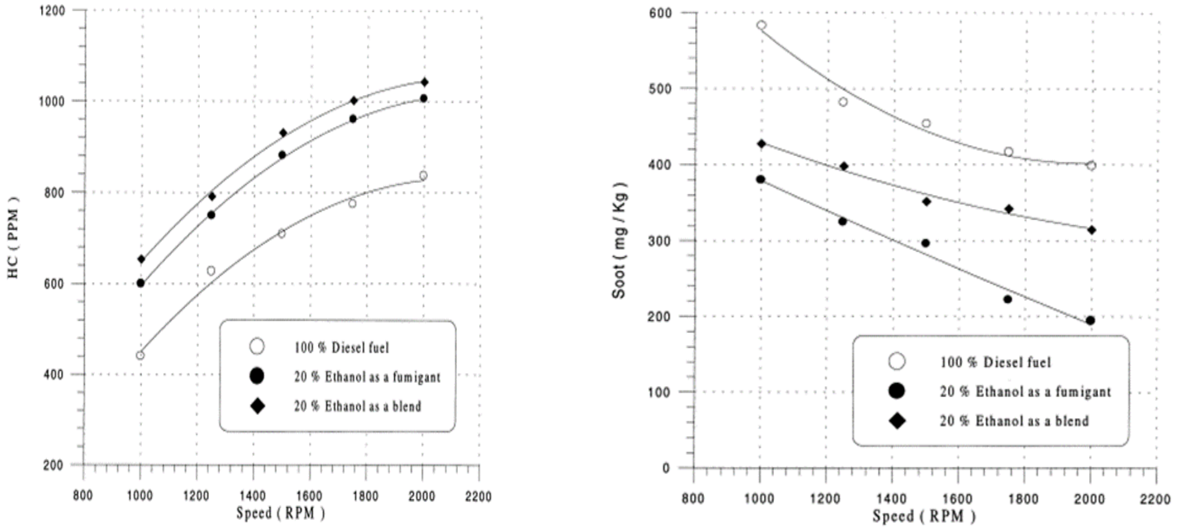
2.4.3.2 Ethanol-Diesel Fuels Influences on CI Engine

Many researches have been concerned with blends of ethanol-diesel. Rakopoulos et al. [129] provided a study comparing ethanol-diesel to neat diesel at different ethanol percentages (5%, 10% and 15%), at 2000 rpm and four variable load conditions. CO and smoke levels were reduced while UHC levels increased with using ethanol-diesel blends. An associated long spray penetration resulted in more fuel in boundary layer resulting in high UHC formation. Furthermore, lower NO_x levels were observed with blending ethanol. In terms of performance, there was a proportional relation between ethanol percentage and BSFC and BTE because of low ethanol calorific value.

Some studies have used more than one method, such as the research done by Abu-Qudais et al. [112]. These authors evaluated ethanol-diesel blends and ethanol fumigation influence. Different ethanol percentages were used to determine the best performance with lower emissions. The results showed that both methods may have the same effect on performance and emissions. For ethanol fumigation, the optimum ethanol percentage was 20% with an increase in BTE (7.5%), CO emissions (55%) and UHC emissions (36%) and reduction in soot mass concentration (51%). For ethanol-diesel blends, 15% methanol was found to be the optimum percentage. This percentage contributed to decreased soot mass concentration (32%) but increased BTE (3.6%), UHC emissions (34%) and CO emissions (43.3%), as illustrate in figure 2.7.



(a) BTE % (b) CO emissions



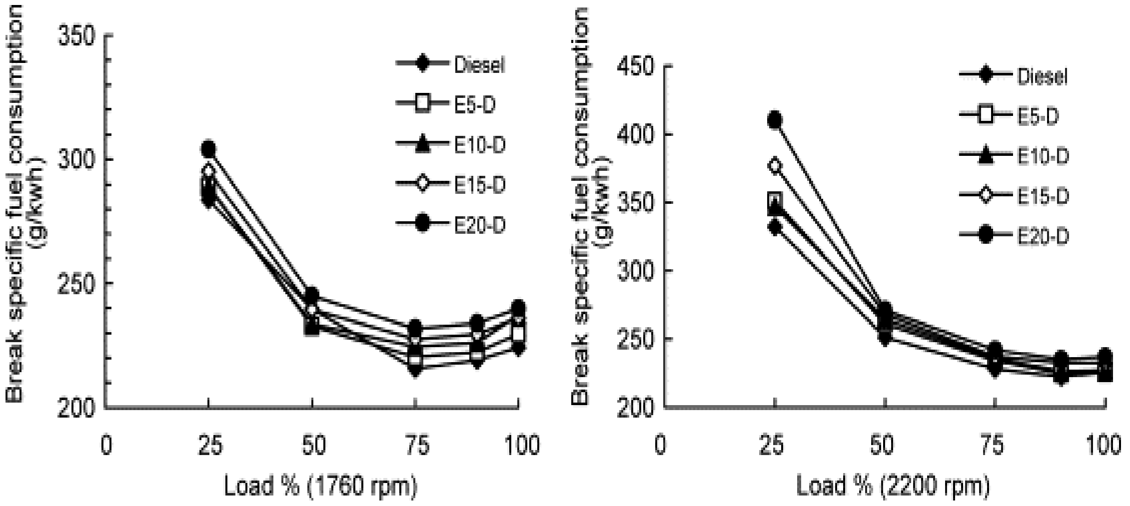
(b) HC emissions (d) Soot emissions

Figure 2.7 The exhaust emissions and BTE of ethanol fumigation, ethanol-diesel blends and diesel fuel [112]

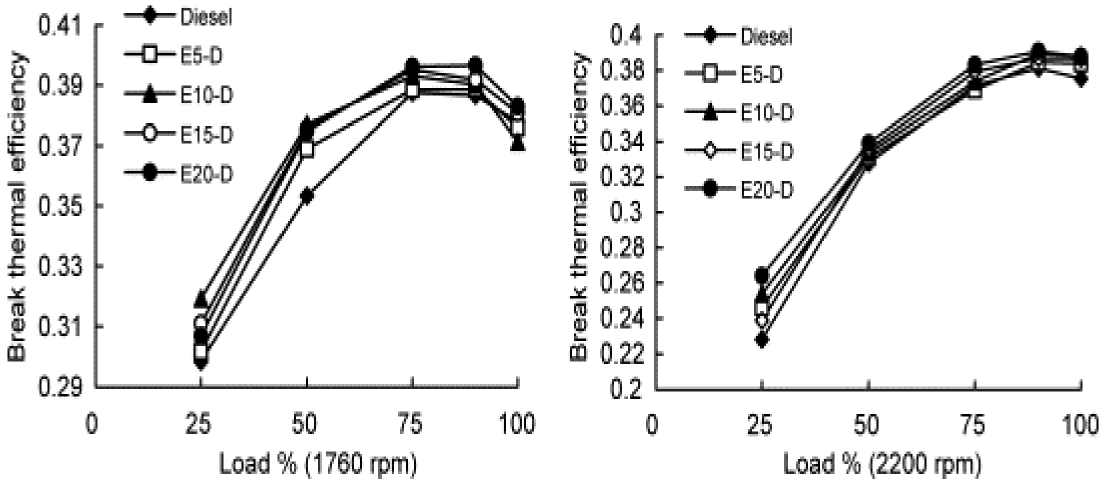
Lapuerta [130] dealt with the effect of 10% ethanol-90% diesel blends volume at different engine conditions. There was insignificant effect on gaseous emissions, but a reduction in PM emissions were observed. Particulate size distributions in number were moved towards small particle diameter values when ethanol-diesel blend used. Furthermore, particulate distributions in mass reduced because of a reduction in large particles instead of increased mass of small particles.

Bilgin et al. [131] investigated different ratios of ethanol to diesel (2%, 4% and 6%) at constant speed and at different compression ratios (19, 21 and 23, respectively). They found that the blend with 4% ethanol increased the efficiency and the output power whereas the BSFC was reduced over the various compression ratios. At a compression ratio of 21, the highest efficiency was obtained. Furthermore, Li et al. [132] investigated various ethanol percentages (5%, 10%, 15% and 20%). It was noted that CO, NO_x and smoke levels were decreased. In contrast, BSFC, BTE and UHC levels were slightly increased, as illustrated in figure 2.8.

Further works have paid attention to the additives used in ethanol-diesel blends. Can et al. [133] conducted a study employing blends with a range of ethanol ratios (10-30% by volume) including an additive (unsaturated fatty acid) and ignition improver (isooctyl nitrate). They concluded that the levels of emissions were varied according to ethanol content, operating conditions, ignition improver and additives. Vegetable methyl ester-ethanol-diesel influence was reported by Chen et al. [134]. Overall, adding methyl ester up to 30% by volume restricts the separation. The time of ignition was delayed when the combustion duration and ethanol content increased and flame luminosity was reduced. PM and smoke emissions reduced with increasing ethanol content as incomplete combustion was achieved as a result of oxygen concentration of ethanol at different loads.



a) BSFC results at 1760 rpm b) BSFC at 2200 rpm



c) BTE results at 1760 rpm d) BTE results at 2200 rpm

Figure 2.8 BTE and BSFC results of various ethanol-diesel blends [132]

Banugopan et al. [135] evaluated different concentrations of ethanol. In this study, 1% isopropanol was added to enhance the homogeneity of the blends and to avoid their separation. The temperature of the inlet air was increased to 40, 50 and 60 °C. There was a proportional relationship between specific fuel consumption and ethanol content. Furthermore, increasing the temperature of the inlet air contributed to higher UHC levels at different loads. Di et al. [136] reported on DI CI engine emissions of diesel blended with different ethanol and biodiesel contents (2%, 4%, 6% and 8% in volume). For both ethanol-diesel and biodiesel-diesel blends, UHC and CO levels decreased at high load due to better air-fuel mixture and NO_x decreased at low load. While, high NO_x levels were increased with load because of high combustion temperature. Further studies regarding ethanol-diesel fuels are illustrated in Table 2.6.

In summary, most publications reviewed in this section show that using ethanol-diesel blends contributes to lower power output and higher fuel consumption because of a decrease in the heating value of ethanol. A reduction in PM, NO_x and CO levels were mostly observed but high UHC levels were found. On the other hand, in some studies, lower UHC and higher other emissions were related to the increase in ethanol concentration. Cetane or ignition improvers, stabilizing and lubricating additives could be added to improve the properties of ethanol-diesel fuel blends.

Table 2.6 Studies of ethanol-diesel fuels effects on CI engine

Author	**Year**	**Engine Type**	**Test parameters**	**Performance**	**Emissions**
Caro et.al.[137]	2001	Four-cylinder IDI engines and single cylinder DI engine	10%, 15% and 20% methanol 2% stability additive	Lower power output, cetane number	Decreased CO and smoke levels Increased UHC levels
Likos et al. [138]	1982	Six-cylinder TDI Cl engine	10%, 25% and 50% methanol 10%, 25% and 50% stability additive Ignition improver Different engine loads		Lower CO, UHC emissions higher CO, UHC emissions at high loads Higher NOx emissions
Cole et al. [139]	2001	TDI CI engines	10% and 15% ethanol Different torques and speeds		Lower PM, CO, UHC, NO$_x$ emissions
Koganti et al. [140]	2004	Three-cylinder DI CI engine	5% ethanol CN improver Different engine speeds	Lower power output Higher thermal efficiency, BSFC, ignition delay	Lower CO, PM emissions Higher NO$_x$ emissions
Bhattacharya et al. [141]	2004	DI CI engine	11%, 17% ethanol 27.8%, 33.3% stability additive 1-butanol- ethanol–diesel 17 micro-emulsions		Higher NO$_x$, UHC emissions Lower CO emissions
Ren et al. [102]	2008	DI CI engine	5%, 10% and15% ethanol 0.2% stability additive	Ignition delay, heat release and combustion duration	Decreased NO$_x$, smoke levels
Xingcai et al. [142]	2004	Single cylinder, DI CI engine	5%, 10%, 15% and 20% ethanol 1.5% stability additive, CN improver Different engine loads	Increased BSFC, BTE	Decreased CO, NO$_x$ and smoke levels Increased UHC emissions
Labeckas et al. [143]	2011	Four-cylinder, DI CI engine-	15% ethanol 5% stability additive Various engine speeds and loads	Increased BSFC Decreased BTE	Lower CO, NO$_x$, smoke emissions Higher UHC, CO$_2$ emissions

*For all studies in the table, the results were compared to reference fuels (diesel fuels) teste

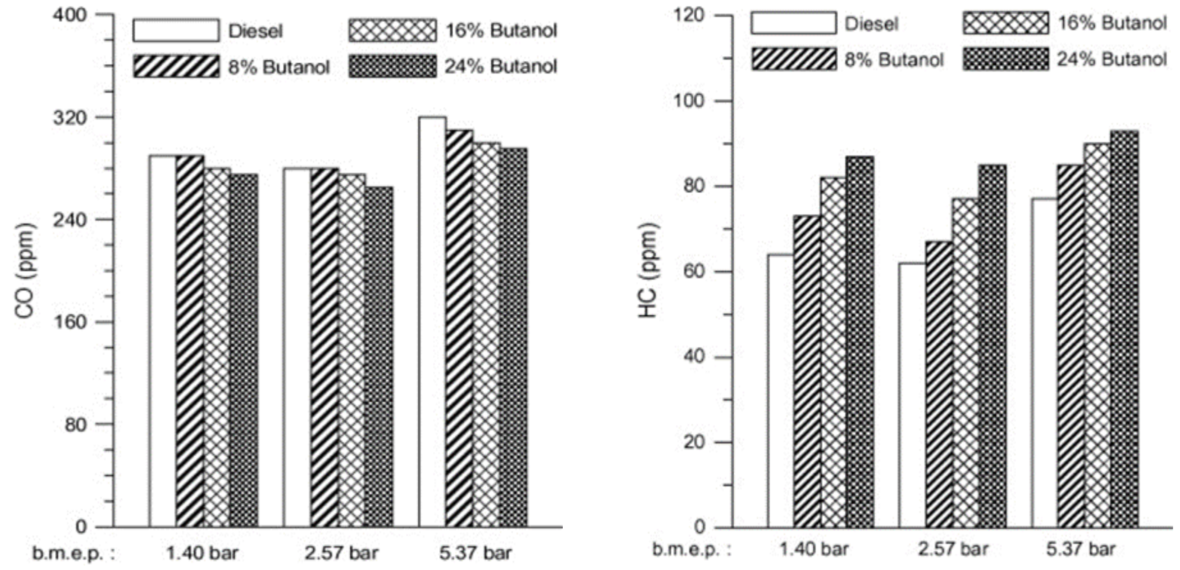
2.4.4 Butanol-Diesel Fuels

2.4.4.1 Butanol Properties

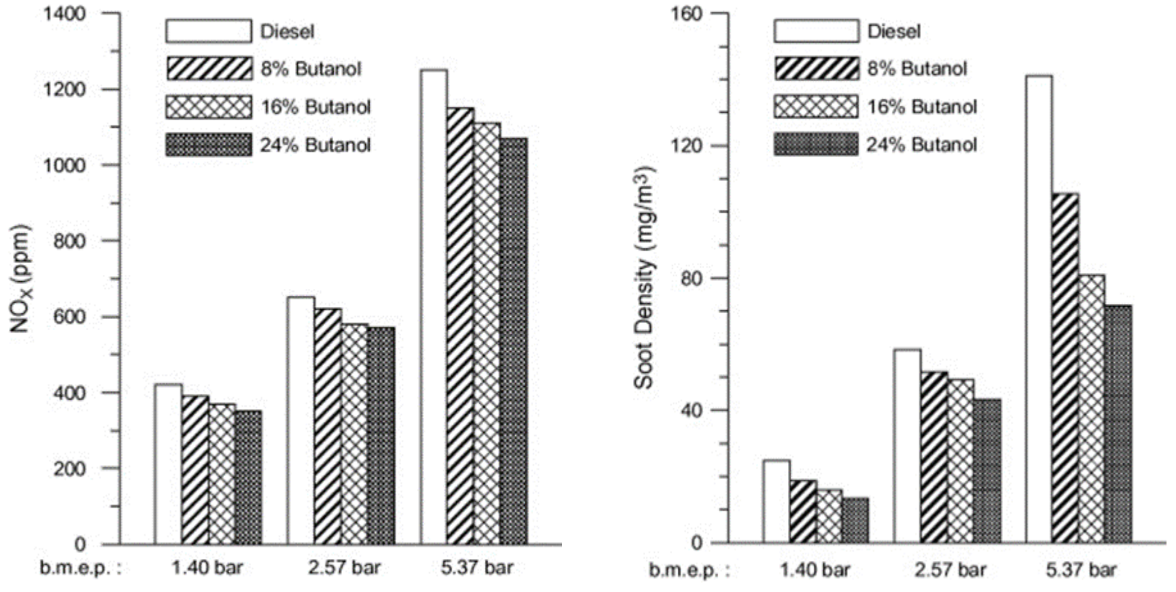
Butanol is a desirable alcohol for use in CI engines. It consists of four carbon atoms existing as four isomers such as n-butanol, s butanol, i-butanol and tert-butanol. These approximately have the same calorific value and molecular weights. In comparison to methanol and ethanol, butanol is less influenced by changes in the weather due to its lower hygroscopicity, and it is safer due to its higher flash point and has a 25% higher calorific value [97]. The use of butanol as a blend with diesel fuel is a strong competitor for the very common alcohols (methanol and ethanol). Szwaja and Naber [144] believed that butanol is favourable because butanol properties as CI engine fuel are better than those of methanol and ethanol. Butanol's cetane number is in the medium range allowing for the blend of a significant butanol concentration in butanol-diesel blends without a considerable impact on the total blend cetane number. Furthermore, the butanol carbon chain is longer than those of ethanol and methanol, which makes its viscosity higher than those of ethanol and methanol [97], with butanol properties are provided in Table 2.3.

2.4.4.2 Butanol-Diesel Fuels Effects on CI Engine

Few studies have dealt with the use of butanol in a CI engine. Rakopoulos et al. [98] evaluated three different butanol concentrations in diesel blends at 2000 rpm and at different engine load conditions. Overall, smoke and CO were reduced at different load conditions due to the oxygen content of butanol. Blending butanol with diesel lowered the blend calorific value contributing to low combustion temperature as well as low NO_x emission. However, high UHCs emitted because of high heat of evaporation of butanol as shown in figure 2.9. However, the increase in BSFC was lower than the corresponding low blend calorific value. A slight increase in BTE at different loads because of low heat loses of blends**.** Further, Rakopoulos et al. [145] studied two different butanol concentrations in diesel blends at two engine speeds (1200 and 1500 rpm) and under three load conditions. The overall results of the tests were similar to the previous study by Rakopoulos et a [98].



(a) CO emissions (b) UHC emissions



(b) NO_x emissions (d) Soot density

Figure 2.9 The exhaust emissions of three different n-butanol concentrations blended with diesel at different load conditions [98]

Dogan [146] evaluated different n-butanol contents (5%, 10%, 15% and 20%) in n-butanol-diesel blends. The tests were carried out under different loads and at 2600 rpm. They reported that a slight increased BTE, BSFC and UHC emissions were noted with increased n-butanol concentration while the exhaust gas temperature, smoke capacity and CO levels and NO_x levels were decreased under all loads. The oxygen content of butanol enhanced oxidization process resulting in better BTE, lower CO emissions, while the low calorific value led to high BSFC.

Zhang [147] studied butanol-ultra low sulfur diesel blends impacts on PM at variable output powers and constant speed. The results showed that a decreased particulate mass and increased organic carbon in PM emissions when the butanol concentration was increased in the blends. The total number of particles reduced with butanol-diesel blends, whereas, the number of small particles (less 15 nm in diameter) increased up to 20% at low load.

Hasan et al. [148] evaluated iso-butanol-diesel blends. The blends were tested with different iso-butanol contents (10, 20, 30 and 40% by volume) and under many different operating conditions; different engine speeds ranged 375-625 rpm at different loads. As the engine speed increased, BSFC, lower brake power, exhaust gas temperature and higher BTE were indicated while the air-fuel ratio increased. The reduction in exhaust temperature and brake power were related with the increased heat evaporation of butanol-diesel blends. While, low calorific value of butanol-diesel blends led to higher BSFC. High BSFC and low combustion temperature were responsible for low BTE. They recommended that increasing iso-butanol content in diesel fuel (up to 30%) can lead to desirable engine performance.

Furthermore, Karabektas and Hosoz [149] also evaluated the emissions and the performance of CI engines with different contents of iso-butanol (5%, 10%, 15% and 20%) in iso-butanol-diesel blends at variable speeds ranged from 1200 to 2800 rpm (at intervals of 200 rpm) and at high load. As the iso-butanol content increased, a reduced brake power and increased BSFC at low speed were observed because of low calorific value of butanol. Another observation related to, low butanol viscosity and density led to leakage in the fuel system and produced low brake power. A slight increased BTE was noted at high speed due to butanol oxygen concentration. Using the blends of butanol-diesel led to decreased NO_x and CO levels because of increased H/C ratio and decreased calorific value. Low cetane number, density and viscosity of butanol contributed to high UHCs.

Ozsezen et al. [150] studied different iso-butanol contents (5%, 10% and 15%) at three different load conditions (150, 300 and 450 Nm, respectively) and constant speed (1400 rpm). BSFC was increased with 5% and 10% iso-butanol while BSFC was highly increased with the 15% blend. There was an inverse relationship between the iso-butanol content and BTE. In contrast, the smoke capacity, NO_x and CO levels were decreased and UHC levels slightly increased in comparison to diesel fuel. High H/C ratio and sufficient oxygen concentration of blends associated with low CO emissions and smoke capacity. High evaporation heat of blends contributed to low combustion temperature as well as low NO_x levels. However, high evaporation and low cetane number of blends led to slower and poor air-fuel mixing process and hence, high UHC levels. Further studies concerning the effects of butanol-diesel fuels on CI engines are shown in Table 2.7.

The studies that have been reviewed in this section indicate that CO, NO_x and smoke were decreased at variable engine speeds and loads. Low oxygen content and high H/C ratio of blends lowered CO and smoke emissions. The blend combustion temperature was low associated with low calorific value, high H/C ratio and high evaporation heat as well as low NO_x emissions. Some studies indicated that UHC emissions were increased with blending butanol at different speeds and loads because high evaporation heat of blends led to slower and poor air-fuel mixture, long spray penetration and more fuel remaining in boundary layer. However, some studies reported lower UHC emissions, as shown in Table 2.7. Blending butanol with diesel led to a lower calorific value which increased BSFC. However, in some studies, slightly increased BTE was observed due to butanol's oxygen concentration. While, others indicated that significant increase in BSFC was responsible for low BTE.

Table 2.7 Studies regarding butanol-diesel fuels effects on CI engines

Author	**Year**	**Engine Type**	**Testing parameters**	**Performance**	**Emissions**
Asfar et al. [151]	2003	Single cylinder, four-strokes diesel engine	5%, 10% iso-butanol 10% stability additive	Higher BSFC	Lower CO, NO_x, UHC and soot emissions
Biao et al. [62]	2011	High-speed CI engine	20%, 30% n-butanol Different engine speeds and loads	Higher BSFC	Lower soot emissions
Lujaji et al. [152]	2011	4-cylinder TDI CI engine	5%, 10% n-butanol 10%, 15% stability additive	Lower BSFC	Lower CO_2 and smoke
Altun et al. [153]	2011	Single cylinder four-strokes, CI engine	10%, 20% n-butanol 20% stability additive	Increased BSFC and BTE	Decreased CO, NO_x and UHC levels
Yao et al. [154]	2010	TDI heavy duty CI engine	5%, 10%, 15% n-butanol EGR, multi-injection timing		Lower CO, UHC and soot emissions

*For all studies in the table, the results were compared to reference fuels (diesel fuels) tested

2.5 Dimethyl Ether (DME)

2.5.1 DME Properties

DME is defined as a liquefied gas produced from feedstocks [155]. It is difficult to use pure DME in CI engines because of its low viscosity and low density [52, 155]. However, DME can be blended with liquefied petroleum gas (LPG), methyl ester and biodiesel and is a favourable alternative fuel with only minor modifications. This is because there are no C-C bonds in the DME molecular structure, it also has a low autoignition temperature and high oxygen concentration, at 35% by mass. The properties of DME are provided in Table 2.3 and its advantages and disadvantages as an alternative fuel for CI engines are detailed below [155-157].

The advantages of DME

- The high oxygen concentration and no C-C bonds of DME are responsible for low PM and smoke emissions.
- Low autoignition temperature and high cetane number of DME contribute to better combustion, low ignition delay and less noise.
- Low boiling temperature of DME contributes to rapid evaporation when DME is injected.

The disadvantages of DME;

- The viscosity of DME is low that may cause a leak of the fuel system. This relies on sealing clearances.
- Its low lubricity causes wear scars on moving parts of the fuel system.

- Low modulus of elasticity of DME is less than that of diesel as a consequence of DME compressibility being up to six times in a closed system.

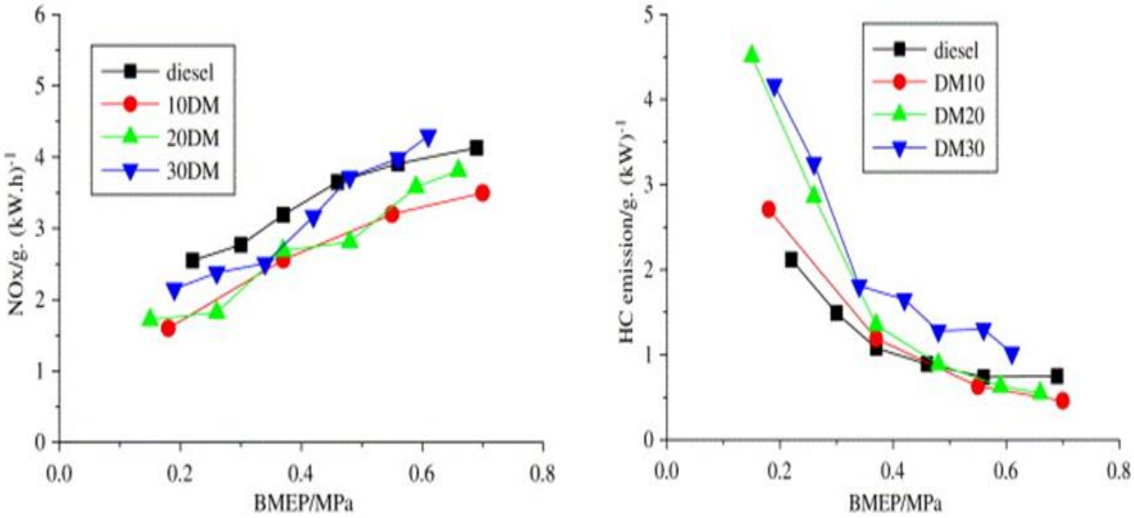
- Combustion enthalpy of DME is less than that of diesel because of its oxygen concentration that requires a large injected volume and long period of DME injection to deliver the same energy amount to that of diesel.

2.5.2 The Effects of DME-Diesel Fuels on CI Engine

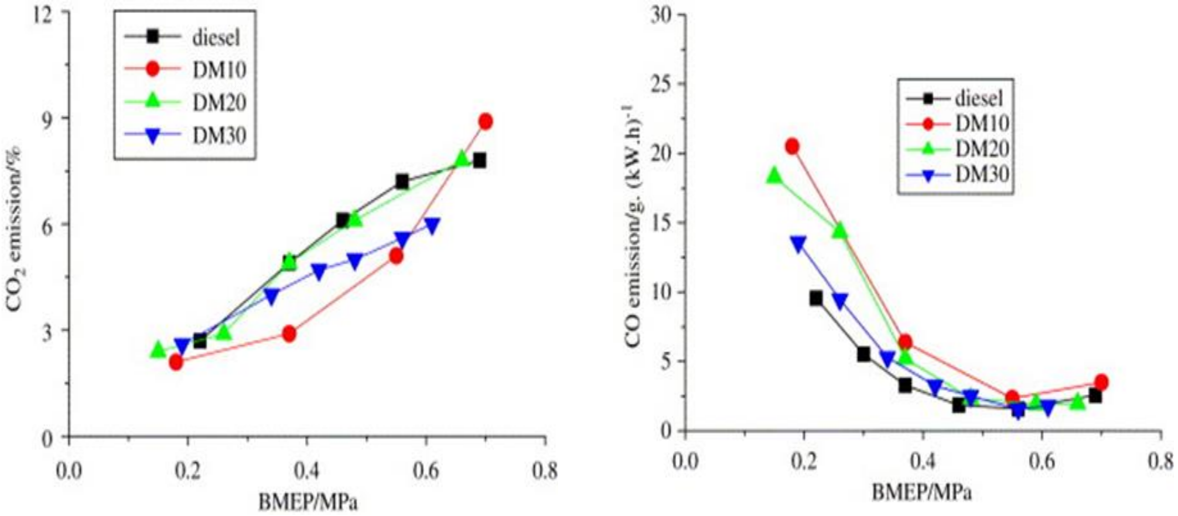
Since 1995, studies regarding DME performance and emissions have been underway. Many researchers have paid attention to DME as a future CI engine fuel with the Japan DME Forum and the emergence of the International DME Association (IDA) in 1990. Some of the studies about the influence of DME on performance and emissions are reviewed below.

Ying et al. [99] tested different DME concentrations (10%, 20%, 30% by mass) in diesel. The overall results of the study showed slight decreased UHC and CO levels, but significant increased smoke, CO_2 and NO_x concentrations were observed compared to neat diesel at high loads (see figure 2.10). However, at low loads, DME-diesel blends produced lower smoke because of the lean mixture.

Youn et al. [158] dealt with DME fuel influences on the emissions and performance of a four-cylinder CI engine. ULSD was used as a reference fuel in the experiments. Overall, the ignition delay and combustion pressure of the USLD were less and slower than those of DME, respectively. Furthermore, NO_x emissions resulting from DME combustion were slightly higher whereas the soot emissions were approximately zero compared to ULSD. CO and UHC emissions of DME were lower than those of USLD due to the volatility and oxygenated components of DME.



(a) NO_x emissions (b) UHC emissions



(c) CO_2 emissions (d) CO emissions

Figure 2.10 The emissions results of different DME concentrations (10%, 20%, 30% by mass) in diesel and pure diesel [99]

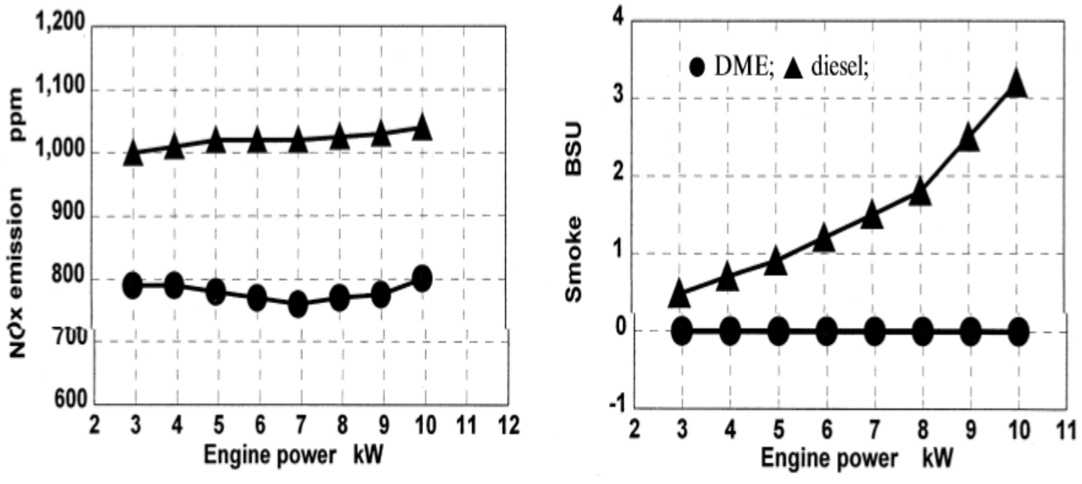
Arcoumanis et al. [155] reviewed DME as a fuel for CI engines. They obsereved lower PM levels. NO_x levels produced by DME can meet the regulations with high EGR in combination with a NOx trap. Hewu and Longbao [159] tested DME-diesel blend (10%-

90%). Overall, fuel consumption and power output are not impact by a DME-diesel blend. Smoke, UHC and NO_x levels were decreased significantly.

Teng et al. [96] studied DME impact on engines with different EGR rates. They indicated that no soot results from DME combustion and they recommended that a particulate filter is not needed in the after-treatment system. At high EGR rate, NO_x levels resulting from the use of DME can meet the US 2007 standards.

Kajitani et al. [160] dealt with the effects of neat DME on CI engine emissions and performance. The main findings of this study are that it is necessary to add lubricity improvers to DME to avoid wear scars and to maintain fuel injector performance when a conventional fuel injector is used. The soot and UHC emissions produced by DME were negligible. However, NO_x levels of DME and diesel fuel are the same.

Study by Wang et al. [156] presented that the higher effective thermal efficiency (up to 3%) and power output of DME were achieved by adjusting many parameters such as using a larger plunger diameter and larger flow area of the nozzle. Furthermore, the combustion of DME was more likely to be smokeless and resulted in low NO_x levels, noise and pressure rise rate in comparison to diesel, as shown in figure 2.11. They recommended that the use of DME plays a major role in reducing CI engine emissions.



a) NO$_x$ emissions b) Smoke emissions

Figure 2.11 NO$_x$ and smoke emissions of DME and diesel fuels [156]

Blends of n-Butane-DME were tested experimentally by Lee et al. [161]. The concentration of n-Butane ranged 0-40% by mass and all blends were tested at 1500 rpm and different loads. A slight increase in power output and lower fuel consumption were observed in the case of n-Butane-DME blends in comparison to diesel. The improvement of output power and fuel consumption were attributed to the higher n-butane energy content. Furthermore, CO and UHC levels resulting from the blends were high at low engine loads. Finally, the authors concluded that the concentration of n-butane can be increased up to 30% by mass in blends to be used in CI engines. This was demonstrated according to the output power and the exhaust emissions of the tested blends.

Kajitani et al. [162] evaluated the propane-DME blends influences on CI engine. They noted that the content of propane in the blends could be less than 40% by mass to gain better propane-DME combustion. Within this blending limit, the increase in propane content led to lower CO and UHC emissions under high loads. However, these emissions were increased under low loads. The levels of NO$_x$ were reduced as the propane concentration increased. Furthermore, the soot emissions resulting from propane-DME combustion were very low.

In conclusion, according to most of the studies reviewed above, the effect of pure DME fuel and DME blends are summarized below.

In comparison to diesel fuel, lower brake power output and higher BSFC are observed with using DME due to low DME calorific value [157]. However, the BTE of DME is similar to or slightly increased because of its better combustion characteristics, including its high cetane number [157]. The improvement of BTE and slight decrease in BSFC can be gained by an increase of DME injected to the combustion chamber [155, 157].

In comparison to diesel fuel, some studies found that the levels of NO_x produced were higher [96, 99, 155, 158] while others indicated that they were lower [156, 162]. The reason for the lower NO_x levels may be associated with the high DME cetane number and low DME calorific value. Another reason is that the short ignition delay results in a low peak temperature of the combustion and a smaller amount of premixed DME [155]. However, high NO_x emissions result from DME combustion. The high cetane number, excellent evaporation and atomization of DME may result in a fast reaction of DME combustion.

The levels of UHC are usually equal to or less than those of pure diesel combustion [155]. The high cetane number, better evaporation and atomization of DME are compared to diesel and lead to shorter ignition delay of DME. This makes it difficult for much richer or much leaner mixture regions to occur because of the lower mixing period. Moreover, the DME oxygen concentration contributes to the occurrence of fewer fuel-rich regions and hence, UHC emissions are lower [96, 155]. In addition, quenching can cause UHC emissions when the injected fuel is sprayed onto the cold walls. However, in the case of

DME combustion, UHC emissions are decreased because of chamber wall wetting. This is attributed to the short spray tip penetration and the faster evaporation of DME in comparison to diesel.

CO levels are usually low because DME has a high H/C ratio and high oxygen content [155, 163]. These contribute to better mixing and rapid intermediate oxidation. On the other hand, higher CO levels sometimes result from DME combustion according to the characteristics of the operating conditions or engine operating system [155]. For example, a large spray hole and a long duration of injection are needed when DME is used as to provide the same diesel energy. The injection pressure is also lower than that of diesel due to the compression characteristics of DME. Consequently, high CO emissions are produced. PM emissions from the combustion of DME are difficult to increase because soot formation requires a low or free oxygen content and direct C-C bonds [155, 163]. However, the oxygen content in DME is approximately 34.8% and there are no C-C bonds.

2.6 Hydrogen-Diesel Dual Fuel

2.6.1 Hydrogen Properties

Hydrogen is odourless, colourless and does not produce harmful emissions when it is burned with oxygen [164]. Hydrogen is used in fuel cells where the fuel is converted to clean energy by an electrochemical reaction converting the chemical energy of hydrogen and an oxidizing agent into electricity [164]. On the other hand, this method is a very costly process and needs development. However, the latest method is reviewed in this section.

Hydrogen can be produced from oil and water. Recently, a high proportion of hydrogen (95%) has been produced from fossil fuel-based methods [164]. The properties of hydrogen are provided in table 2.3. Low hydrogen gas density is a major issue relating to the storage space needed to power a car with a reasonable driving distance. Moreover, the low density contributes to a reduction in the energy density in the cylinder and this results in low power output. A reduction in fuel consumption can be gained with a lean mixture since the flammability range of hydrogen provides a range of air-fuel mixtures) [164].

2.6.2 The Effects of Hydrogen on CI Engine

A few studies have dealt with hydrogen influence only in CI engines. Homan et al. [165] found that the operation of a CI engine with hydrogen only was limited because of the high hydrogens resistance to autoignition. This was not resolved even at high compression ratios. Some authors recommended the use of a glow plug and multiple-strike spark plugs can be used to assist hydrogen combustion. However, most studies indicate that using hydrogen as is a more attractive method for the use of hydrogen in CI engines. This is because the low autoignition temperature of diesel can overcome the autoignition resistance of hydrogen [164].

Varde and Frame [166] studied experimentally the possibility of particulate reduction resulting from aspirating small hydrogen quantities. Overall, smoke concentrations were lowered at part load whereas they were slightly decreased at high load. It was found that the optimum percentage of hydrogen for smoke reduction was between 10% and 15% on an energy basis. It was also observed that UHC emissions were not influenced by the fumigation of hydrogen. However, NO_x levels increased with the increase in hydrogen quantity.

The behaviour of NO_x emissions from hydrogen-diesel combustion was studied by Lilik et al. [167]. The quantity of hydrogen injected into the intake air was up to 15% on an energy basis. They observed that diesel resulted in higher NO_x levels. In particular, a decrease in NO emissions and an increase in NO_2 emissions, which NO_2 emissions becomes the dominant component of NO_x in some combustion modes, as shown in figure 2.12.

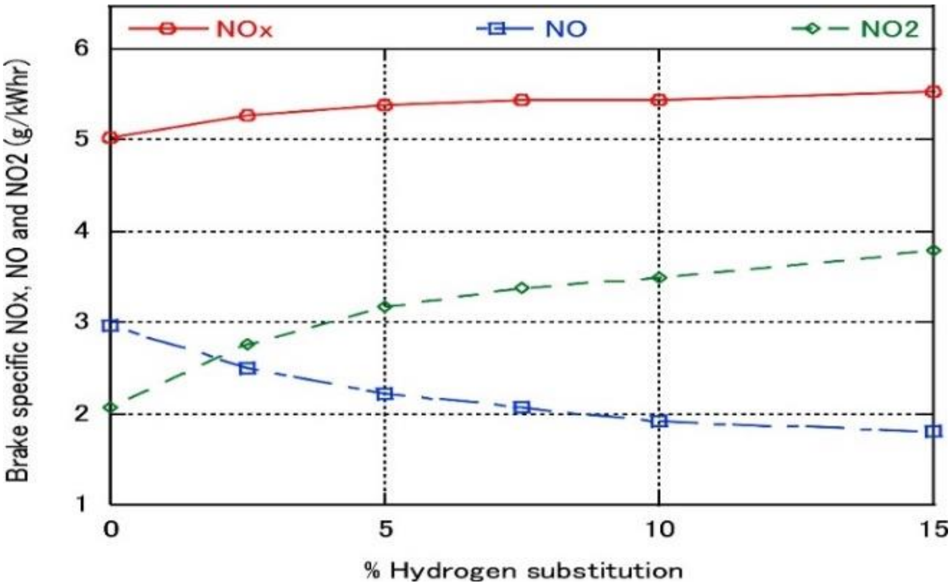
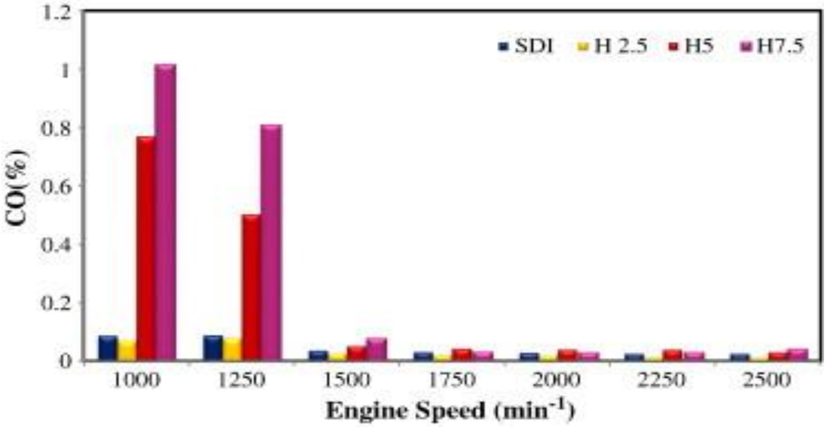
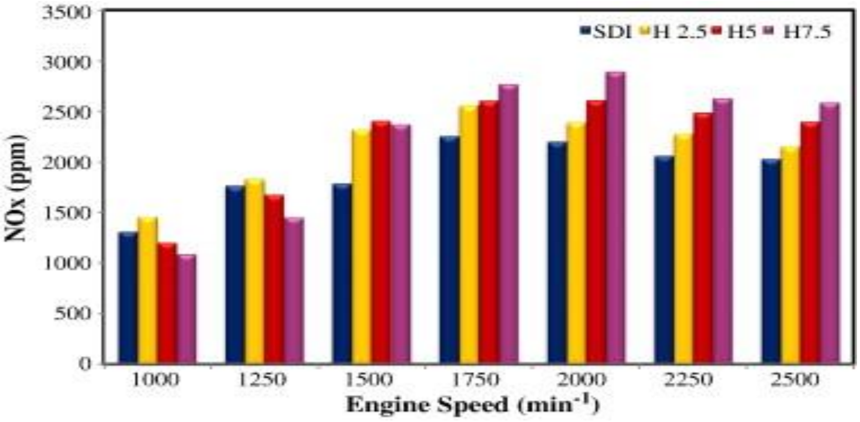


Figure 2.12 NO_x, NO, NO_2 vs. the percentage of hydrogen on energy basis [164, 167]

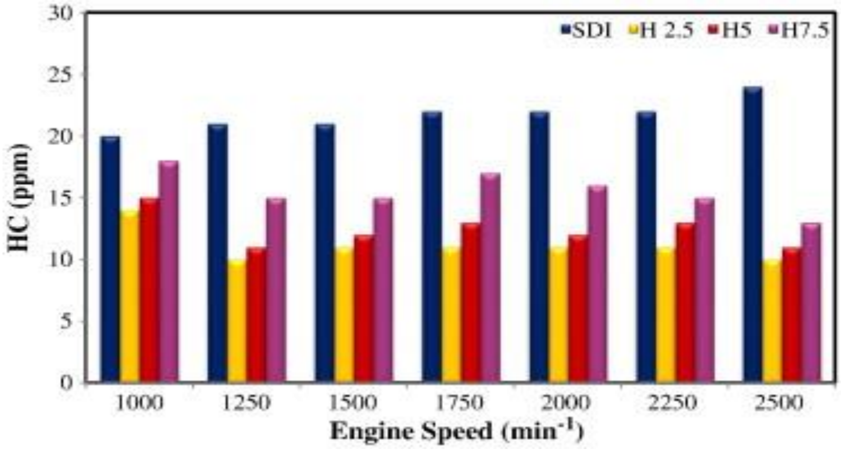
Köse and Ciniviz [168] evaluated hydrogen-diesel dual fuel effects at variable speeds at full load. The percentages of hydrogen by volume added to the combustion chamber were 2.5, 5 and 7.5%. The overall results of the experiment indicated higher power output, torque output, thermal efficiency and NOx levels with adding hydrogen, whereas, lower UHC, CO and O2 emissions were observed. At 7.5% hydrogen addition, an increase in power output and torque by up to 17% at 2250 rpm and 8.3% at 1250 rpm, respectively, was observed in comparison to diesel mode, as illustrated in figure 2.13.At low engine speeds (i.e. 1000 and 12500 rpm), the addition of 5% and 7.5% hydrogen by volume reduced oxygen concentration in the combustion chamber as compared to diesel mode and 2.5% hydrogen. As a result, low oxygen led to poor oxidization resulting in high CO emissions. Further studies regarding with hydrogen-diesel dual fuels are reviewed in Table 2.8.



a) CO emissions



b) NO_x emissions



c) UHC emissions

Figure 2.13 The exhaust emissions of hydrogen-diesel fuels and standard diesel fuel (SDI) [168]

Table 2.8 A summary of hydrogen-diesel dual fuel influence on CI engine

Author	**Year**	**Engine type**	**Test conditions**	**Performance**	**Emissions**
Saravanan and Nagarajan [169]	2008	Four- stroke single cylinder DI CI engine	1500 rpm engine speed, 3.78 kW power output. Under different loads	with 30% hydrogen addition, an increase of BTE from 22.78% to 27.9%	With 90% hydrogen, decreased NO_x levels from 2762 to 515 ppm at 70% load Lower PM and smoke emissions by 50% at full load
Zhou et al [170]	2014	Four-stroke 4 cylinder DI CI engine	1800 rpm engine speed, Under different loads		Lower NO_x levels at low loads, while higher NO_x levels at high loads Lower UHC levels with more than 30% of hydrogen at low and medium loads Lower PM, CO and CO_2 with adding hydrogen
Karagöz et al [171]	2016	Four-stroke single cylinder DI CI engine	1100 rpm engine speed, Under full load		Lower CO levels by 67.3% and 69.2%, for 22% and 53% hydrogen addition, respectively Significant higher NO_x levels for 53% hydrogen addition Slight higher UHC levels with adding hydrogen
Jhang [172]	2016	Four-stroke 6-cylinder DI CI engine	Idle engine speed Under a range of engine loads	Increased BTE and decreased BSFC with increasing hydrogen content	Higher NOx and UHC levels at high load Lower CO, CO_2 levels at high load
Karagöz et al [173]	2015	Four-stroke single cylinder DI CI engine	1100 rpm engine speed Under 40%, 60%, 75% and 100% loads		Increased NO_x levels at full load Lower NO_x and smoke levels at low loads Lower CO, CO_2at full loads

*For all studies in the table, the results were compared to reference fuels (diesel fuels) tested

In conclusion, some studies found that BTE increased, particularly with an increase in hydrogen content [168, 169, 172]. The use of hydrogen-diesel dual fuel rather than diesel leads to improvement in the fuel-air mixture homogeneity, contributing to better combustion [168]. Moreover, using hydrogen-diesel can result in low fuel consumption because the flammability range of hydrogen allows the CI engine to operate over a varied range of air-fuel mixtures that leads to decreased the fuel consumption gained by the lean mixture [172].

Increasing hydrogen content leads to decreased NOx levels at low loads and increased at high loads [170, 172, 173]. Diesel calorific value is lower than that of hydrogen so the increase of hydrogen content contributes to higher peak combustion pressure and temperature [164, 172]. In particular, a high peak combustion temperature contributes to increased NO_x levels. Under high load, an increase of NO_x levels is obtained because the faster combustion is enhanced by the high diffusivity and speed of the flame.

The smoke or PM levels are decreased with increasing hydrogen content because of the improvement in homogeneity, decreased diffusion combustion phase and hydrocarbons. This reduction in smoke or PM emissions may be associated with a reduction in the carbon content and enhancement in the rate of soot oxidation because of high temperature in cylinder [169, 171].

Most studies indicated that CO_2 and CO emissions were reduced with increasing hydrogen concentration under different loads [170, 172, 173]. The main reason for these reductions may be related to the high H/C ratio due to the hydrogen addition [172]. Hydrogen enrichment also contributes to improvement in the combustion efficiency and shortens the combustion duration, resulting in low CO and CO_2 emissions. In addition, hydrogen has a diffusion parameter which helps in forming a more uniform premixed combustible mixture so that accessibility to oxygen increases [173]. Some studies showed lower UHC levels produced using hydrogen-diesel dual fuel [168, 170]. However, a few studies found higher UHC emissions resulted, although these still met the emissions regulations [171, 172]. The addition of hydrogen to the combustion chamber contributes to a reduction of carbon content of the air-fuel mixture resulting in decreased UHC emissions compared to neat diesel combustion.

2.7 Hydrocarbon Fuel Blends

2.7.1 Aromatics-Hydrocarbon Fuel Blends

The effects of sulfur compounds on CI engine emissions and performance has been resourced. It was found that they are responsible for higher PM and SO_2 emissions. Therefore, the sulfur concentration in the diesel composition was lowered to 10-15% ppm in many countries [6]. Attention also has been paid to aromatics because they represent 20-30% of diesel fuel composition [174]. Aromatics are defined as chemical compounds that contain six carbon atoms or heteroatoms structured in benzenoid ring [38]. Aromatics in diesel fuel have a range of carbon atom from ten to twenty atoms. They can be divided into three types based on their structure: single-, double- and multi-ring aromatics [38]. An increase in aromatic concentration contributes to a lower cetane number, high fuel density and poor lubricity [45]. Further, it contributes to higher CI engine exhaust emissions, especially for PM and NO_x [175].

2.7.1.1 The Effects of Aromatics on Emissions

Many studies have been concerned about blends of aromatics and hydrocarbon fuels (diesel fuel or heptane etc.) and their effects on CI engine emissions. Therefore, in this section, previous studies investigating the influence of hydrocarbon fuels blended with various aromatic contents or species are reviewed.

Qian et al. [176] evaluated different aromatics effects on the combustion characteristics and emissions. Aromatics, namely toluene, tetralin, 1-methylnaphthalene and n-butylbenzene, were blended with commercial diesel at 70-30% by volume. The results showed that aromatics-diesel blends contributed to a lower viscosity and higher density. Toluene-diesel blend influenced the distillation temperature of the fuel in the mixture. Also observed were an increase in the ignition delay and the peak value of heat release rate. For multi-ring aromatics, the ignition delay and the peak heat release rate were higher than those of single aromatics. The duration of combustion was shortened, particularly for multi-ring aromatics. In addition, the maximum rise rate of pressure was increased at medium and high loads.

For emissions from aromatics-diesel blends, CO levels were increased. Particularly, the CO levels of blends including multi-aromatics were higher compared to blends with single ring aromatics. UHC emissions of blends with single ring aromatics and diesel fuel were approximately the same, however, they were higher when blends with multi-ring aromatics were burned. At medium and higher loads, for aromatics-diesel blends, higher NO_x levels were detected compared to diesel fuel. Because of a long ignition delay, smoke levels were improved. Blending aromatics with diesel resulted in shifting of the peak value of the particle number to the small size side range, as shown in the distribution curve of figure 2.14. Finally, PM emissions resulting from blends with single ring aromatics were higher than those of multi-ring aromatics.

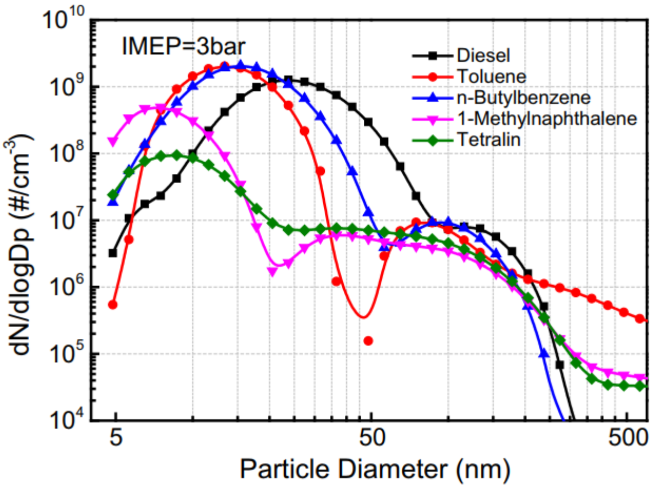


Figure 2.14 Effects of 30% aromatics/diesel on PM emissions [176]

Kidoguchi et al. [177] tested cetane number and aromatic concentration impact at variable loads, timings and injection pressures. The changes in cetane number and aromatic concentration were controlled independently. Overall, decreasing cetane number with the same aromatic concentration contributed to an initial higher heat release, increased ignition delay, increased NO_x and decreased PM levels at high load. On the other hand, for the fuel with a high cetane number, high PM levels were produced because of the long duration of combustion. High UHC levels at low load were produced as incomplete combustion was enhanced by increased delay of ignition.

Changing in the aromatic concentration at constant cetane number had no significant effect on the characteristics of combustion. Higher PM and NO_x levels were recorded when the aromatic concentration was increased. The authors assumed that the higher PM and NO_x levels were associated with the high temperature and locally rich regions formed by reason of the high adiabatic flame temperature and the difficult pyrolysis of hydrocarbons that contain aromatics. At the same time, slow physical processes such as turbulent mixing and evaporation also play major roles.

The effects of Tri-methyl benzene were reported by Khabbaz and Mobasheri [178]. Three different Tri-methyl benzene percentages by volume (10, 15 and 20%) were blended with diesel fuel that has a higher cetane number, at 57. The results presented that the increase in Tri-methyl benzene content led to a reduction of cetane number and kinematic viscosity while, the energy content and density increased. When the content of Tri-methyl benzene was increased from 0% to 20% by volume, PM emissions reduced by about 10%, whereas and NO_x emission increased by about 5%, as shown in figure 2.15. The authors found that the Tri-aromatic influence was similar to the other aromatics influence in the composition of diesel fuel in regard to cetane number.

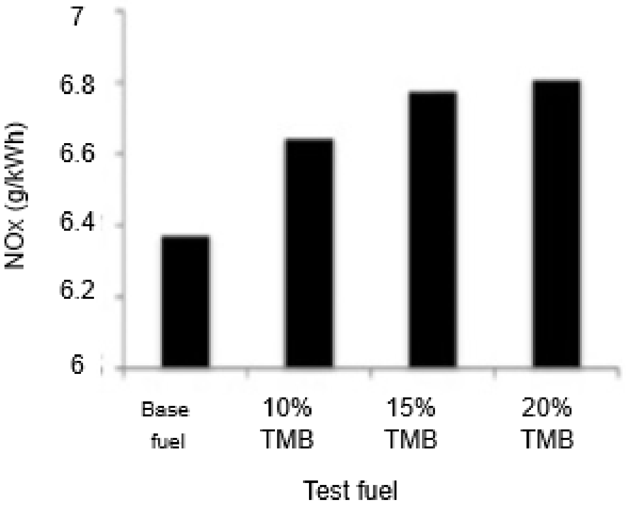


Figure 2.15 NO_x emissions for Tri-methyl benzene and base fuel [178]

Kidoguchi et al. [43] evaluated cetane number and aromatic concentration influences at variable loads, injection pressures and timings. Aromatic concentration and cetane number of fuels tested were changed independently with an almost constant sulfur concentration of less than 1 ppm by mass and the same 90% distillation temperature (T90). The base fuel used had an aromatic concentration of 24 wt% and cetane number of 55. The five fuels tested were divided into two test groups. First test group consisted of three fuels with three different cetane numbers (43, 55 and 62, respectively) and no aromatic content. The second group had two fuels with 38 wt% aromatic content and two different cetane numbers; 43 and 55. It is significant to note that the fuels with 38 wt% aromatic content were composed of diaromatic content of 11.1 wt% and monoaromatic content of 27.6 wt%.

The overall results indicated that increasing the content of aromatics for high cetane number fuel contributed to increased PM and NO_x levels while with fuels with a decreased cetane number, increased aromatic content contributed to high UHC emissions at retarded injection timing. Reducing the cetane number whilst maintaining aromatic content produced low NO_x and PM emissions at high engine load, but higher UHC levels were emitted because of longer ignition delay.

Xiao et al. [179] tested toluene and methylnaphthalene impacts. In this study, Heptane was used as a base fuel and different aromatic contents (from 0% to 20% by mass) were added to the base fuel without an ignition improver. Heptane was used because it can ignite easily due to its high cetane number of 56. Toluene and methylnaphthalene were selected to represent monoaromatics and diaromatics, respectively. The experimental data indicated that the increase in aromatic content led to higher NO_x, smoke and UHC emissions compared to the base fuel. When toluene content was increased from 0% to 20% by mass, smoke, NO_x and UHC levels increased by 55%, 12% and 35%, respectively compared to those of 100% heptane while, smoke and NO_x levels rose by 63% and 30%, respectively with increasing methylnaphthalene content from 0% to 20% by mass. The authors concluded that a proportional correlation was found between smoke emissions and carbon-air ratio. This increase in the flow rate of carbon to the CI engine occurred because the H/C ratios of both aromatic species were less than that of 100% heptane, as shown in figure 2.16. They also reported that methylnaphthalene effect on smoke concentrations were not significantly greater than toluene.

Aromatic content and structure effect on particulates were evaluated by Fukuda et al. [180]. The first fuel used as base fuel was a low sulfur Chevron diesel fuel. The second fuel consisted of the base fuel blended with a single-ring aromatic specious 10% by volume (1-2-3-4 tetrahydronaphthalene) while, the base fuel and a double-ring aromatic at 10% by volume (naphthalene) were blended to form the third fuel. The cetane number and boiling points were decreased. The overall results presented that the soot emissions of 1-2-3-4 tetrahydronaphthalene increased by 9% in comparison of both naphthalene and the base fuel, which were similar. However, insignificant naphthalene impact on soot provided by this study is not agreed with most studies in literature.

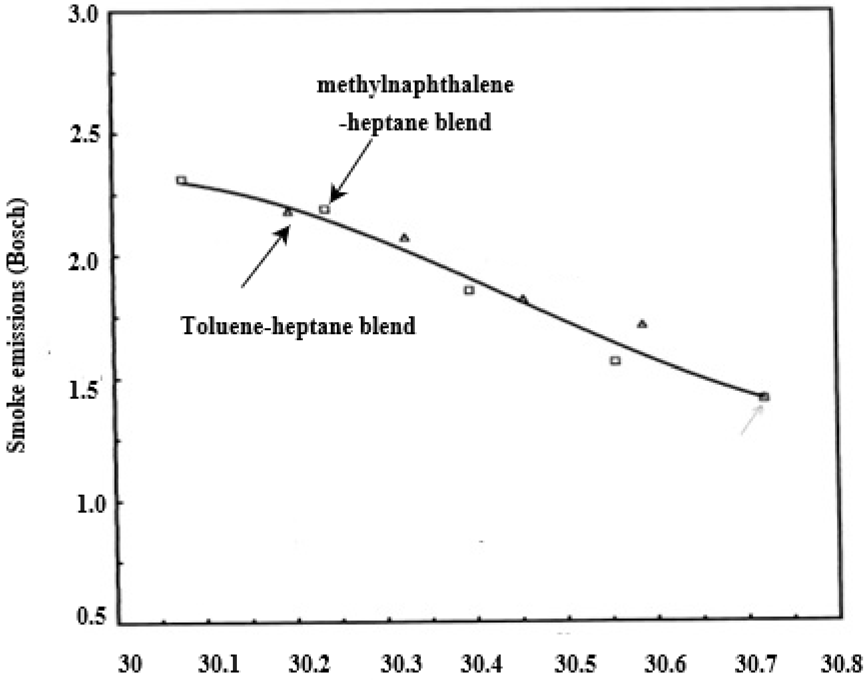


Figure 2.16 Air to carbon ration by mass effects on smoke for fuels tested [179]

Neill et al. [181] carried out experiments in order to investigate different poly-aromatic levels effects on NO_x and nvPM levels . Eight fuels were formed by blending eight fuels from sands crude oil and conventional oil sources. These fuels were divided to three groups based on density level. Each group had different poly-aromatic content and similar density. Cetane improver was added to the test fuels to adjust the cetane number to 46 ± 3 using 2-ethyl hexyl nitrate. The reference fuel was a commercial diesel fuel with a cetane number of 46.6. The results showed no significant differences in NO_x and nvPM levels among fuels in each group. However, NO_x emissions were influenced as ploy-aromatic or density level increased. NO_x emissions were increased with density because of the physical density influence on the fuel injection system. While the chemical impact of ploy-aromatic content on the flame temperature was due to the lower hydrogen content, as shown in figure 2.17.

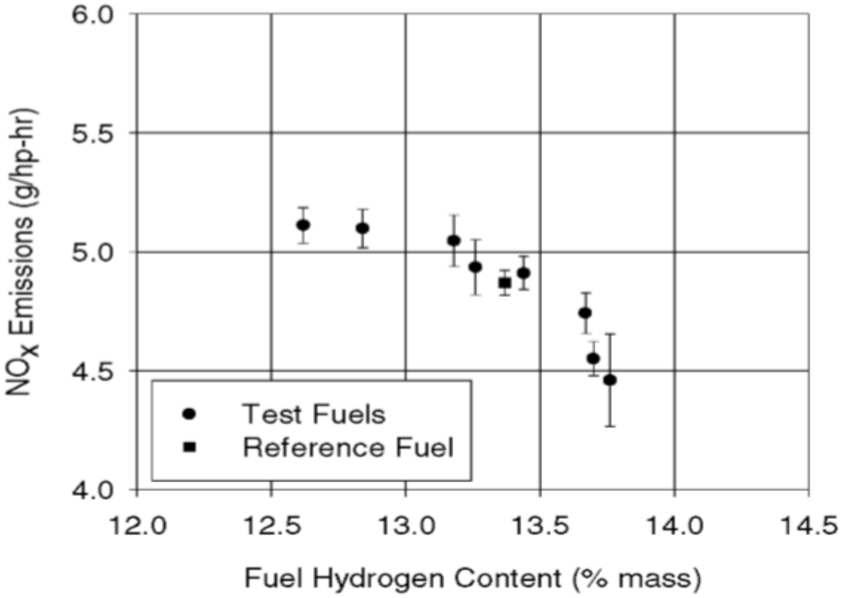


Figure 2.17 NO_x level vs. content of fuel hydrogen [181]

In conclusion, most studies reviewed indicated that increasing aromatic concentration in a fuel resulted in increased NO_x, PM and sometimes UHC emissions [43, 179, 181]. Kidoguchi et al. [177] concluded that higher PM and NO_x emissions may be related with the high temperature and locally rich regions formed because of the high adiabatic flame temperature and difficultly of pyrolysis of aromatics. In addition, aromatics have low H/C ratios resulting in higher flame temperatures and thus high NO_x emissions [181]. Multiaromatic rings influence on smoke emissions were not significantly greater than that of mono-aromatic rings [179].

2.7.1.2 State of the Art

Many diesel properties influence emissions and performance, such as cetane number, oxygen content, aromatic content, and sulfur content. Cetane number is an important factor for the diesel combustion quality. Many studies such as Kidoguchi et al. [43] and Reijnders et al. [41] recommended typically high cetane number. Moreover, oxygen content influence is evaluated by many studies, such as Zhou et al. [182]. Blending sufficient content of oxygenated species with diesel fuel is recommended to enhance the combustion process and then, positively influence emissions, whilst sulfur content is a contributor to high SO_2 and PM emissions. Therefore, the sulfur content in diesel fuel has been lowered to between 10 and 15 ppm in many countries [6]. These implementations (together with the cetane number, oxygen, and sulfur concentration) have led some authors to address aromatic content.

Most studies reviewed in chapter indicated that increasing aromatic content in a fuel result in increased NO_x, PM and sometimes UHC emissions [43, 179, 181]. Kidoguchi et al. [177] reported that higher NO_x and PM levels are associated with the high temperature and locally rich regions formed due to the difficultly of pyrolysis of aromatics and high adiabatic flame temperature. Moreover, increasing aromatic content contributes to low H/C ratio leading to higher flame temperatures and hence, high NO_x emissions [181]. However, there are knowledge gaps in how different aromatic concentrations can impact engine performance. Therefore, studying the influence of different aromatic concentrations in a fuel on CI engine performance is the major contribution to knowledge from this work.

Few studies have focused on different aromatic species influences on exhaust emissions, for example Qian et al. [176], Khabbaz and Mobasheri [178], Xiao et al. [179], and Fukuda et al. [180]. A study conducted by Qian et al. [176] focused on different aromatics, such as toluene, tetralin, 1-methylnaphthalene, and n-butylbenzene. The effect of tri-methylbenzene was investigated by Khabbaz and Mobasheri [178] and a study by Xiao et al. [179] considered toluene and methylnaphthalene. Finally, tetralin and naphthalene were tested experimentally by Fukuda et al. [180]. However, many aromatic species have been not investigated in literature, in terms of their impacts on emissions. Moreover, different aromatic species effects on engine performance are need to be investigated. Therefore, studying the influence of different aromatic species on CI engine performance is another contribution to knowledge from this study.

2.7.2 Alkanes Hydrocarbon Fuel Blends

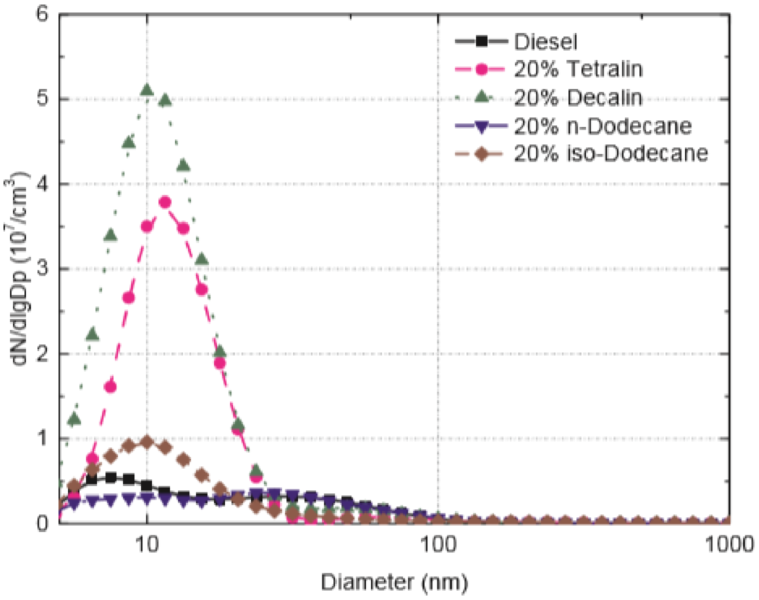
Alkanes are saturated hydrocarbons i.e. carbon atoms are saturated with hydrogen atoms. Alkanes are an important diesel component, which affects PM emissions. Diesel usually contains different types of alkanes; iso-alkanes, n-alkanes, and cycloalkanes, forming 60-80% of total diesel composition [183]. Therefore, some studies were dealt with alkane’s role on PM emissions in CI engines.

Li et al. [183] evaluated different alkanes influences on emissions at variable load conditions. For PM emissions, the study evaluated only the impact of alkanes in particulate size distribution. Iso-dodecane, n-dodecane, and decalin were selected to represent iso-alkanes, n-alkanes, and cycloalkanes, respectively and tetralin was chosen to represent aromatics. These species were blended with diesel at 10% and 20%, respectively. The results showed that decalin and tetralin produced high levels of particulate number at low load as shown in figure 2.18. It was because of their lower H/C ratios in comparison to other test species. At high load, the impact of alkane classes on particulate numbers presented as n-alkanes > cycloalkanes > iso-alkanes > aromatics. Moreover, the peak value of particle size distribution moved towards to the right side because of prolonged combustion duration which resulted in more time to polymerize [183]. However, this result contradicts other findings as aromatics impact significantly particulate number compared to alkanes.

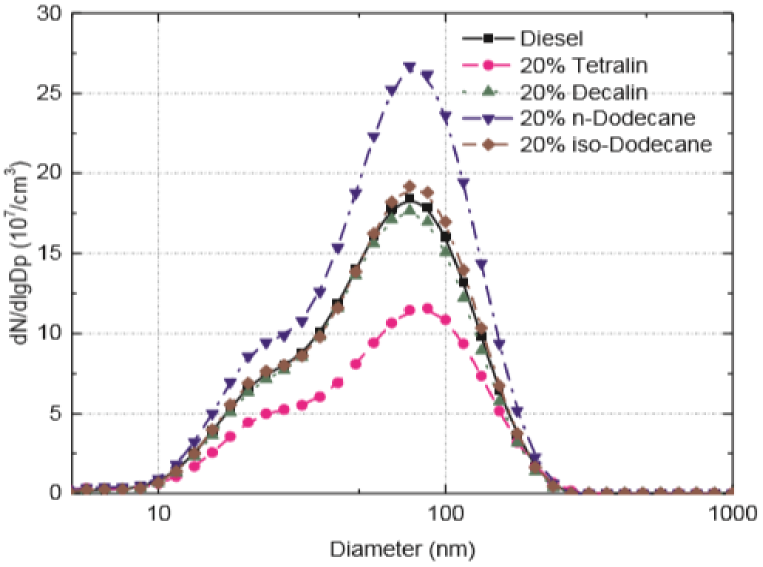
Nakakita et al. [184] investigated different alkanes effects on CI engine emissions at different load conditions. At low load, it was observed that cycloalkanes had more tendency to particulate formation compared to other alkanes. The variation in the emissions due to the impact of alkanes was related to their molecular structures. However, the impact of alkanes was insignificant at high load.

Qian et al. [185] tested the impact of iso-alkanes on the PM size distribution. Iso-dodecane, iso-octane, and 2,2,4,4,6,8,8-heptamethylnonane were selected to represent iso-alkanes. The injection timing and pressure were maintained at 7 °CA BTDC and 120 MPa, respectively. Overall, the distribution of PM peak values of iso-alkanes-diesel blends decreased compared to diesel at high load [185]. It might be because of better volatility and lower viscosity of iso-alkanes. Iso-alkanes-diesel blends have low volatility, leading to easier gasification during the injection process. Further, the low viscosity of the blends made the fuel spray easier to break and improved air-fuel mixing. The better fuel-air mixture attributed to low PM formation.

Song and Lee [186] experimentally investigated the role of different fuel components (e.g. sulfur, aromatics, alkanes) in turbocharged engine PM emissions. Cycloalkane fuels attributed to the highest PMs among fuel enriched alkanes. Fuels with high iso-alkane concentration produced the lowest PMs compared to other fuels. These results are an agreement with the previous study [184]. Particulate distribution size of fuel enriched iso-alkanes showed that nucleation mode particles were dominant whereas, accumulation mode particles were significant in the case of aromatic fuels [186].



(a) At IMEP = 2 bar



(b) At IMEP = 8 bar

Figure 2.18 Distribution of particulate size of diesel-alkanes and diesel-aromatics blends [183]

In conclusion, Takatori et al. [187] suggested that the structure of alkanes should be considered as one of the properties of diesel which is closely associated with the particulate formation. PM emissions were increased with the increase in ring and branch number of alkanes [21]. In addition, alkane components have a role in PM production because they influence other fuel properties such as cetane number, H/C ratio, and density. Although alkanes contribute to PM production, their tendency is less than aromatics [21, 187].

2.8 Conclusion from Literature Review

The impact of different alternative fuels on performance and emissions of CI engines has been reviewed. Promising alternative diesel fuels namely biodiesel, three types of alcohols (e.g. methanol, ethanol and butanol), compressed and liquefied natural gas, DME, hydrogen and aromatics-and alkanes-hydrocarbon fuel blends have been critically reviewed.

Biodiesel as a pure fuel or blend in CI engines contributes to low CO and UHC levels because complete combustion is achieved as a result of oxygen concentration present in the fuel and high H/C ratio of biodiesel. Higher oxygen concentration, no aromatic concentration and low sulfur concentration in biodiesel contribute to lower PM emissions. However, NO_x levels increase due to increased in-cylinder combustion temperature particularly at high load. Biodiesel also impacts the performance of a CI engine by lowering output power and increasing BSFC at different conditions due to low calorific value of biodiesel.

The use of natural gas in CI engines using a dual fuel mode system leads to lower output power, because natural gas-air mixture has low calorific value. Lower BTE at low load is caused by the lean mixture of natural gas-diesel fuel. The lean mixture also contributes to incomplete combustion as CO oxidization freezes rather than converting to CO_2. Furthermore, trapping of the natural gas-air mixture in the boundary layer restricts the ignition in the late part of the combustion process, leading to higher UHC emissions at different engine conditions. PM concentrations decrease significantly because there are no C-C bonds, aromatics, sulfur compounds in natural gas composition.

Use of pure alcohol in CI engines is difficult because of its lower calorific value, cetane number, flash point and lubricity even though its oxygen content. However, butanol is a more promising alcohol because of its higher cetane number and miscibility, therefore it a more suitable blend with diesel fuel than other alcohols. Generally, at different engine conditions, blending alcohols with diesel contributes to low CO, PM and smoke emissions because of oxygen concentration, lower aromatic concentration and high H/C ratio of blends that enhances oxidization process. High evaporation heat of blends is likely to reduce combustion temperature and hence, low NO_x emissions especially at low load. However, UHC is increased with increasing alcohol content because the high evaporation heat of alcohols which lengthens penetration spray and then, more fuel in the crevices and the boundary layer. Low calorific value and density of blends lead to higher BSFC and lower brake power as compared to diesel. In some studies, a slight increased BTE are gained due to the oxygen content of alcohols, whereas, others indicated low BTE because of high BSFC according to power produced.

DME is a more promising alternative CI engine fuel because of its high cetane number, its oxygen concentration and no C-C bonds. However, the low lubricity and calorific value of DME are main challenges facing its use. Using DME in CI engines results in low CO, UHC, soot and PM levels due to high cetane number, no C-C bonds and DME oxygen content at different loads. However, high cetane number and oxygen concentration of DME result in high combustion temperature as well as high NO_x levels. DME combustion impacts power output and fuel consumption due to its lower calorific value at different loads and speeds.

Hydrogen-diesel dual fuel results in lower BSFC because flammability range of hydrogen allows the CI engine to operate over a wide range of lean mixtures even with higher engine loads. CO, UHC, PM and soot emissions are reduced due to decreased carbon content of the fuel.

Aromatic content in hydrocarbon fuels could be lowered due to its impact on PM, NO_x and UHC emissions. The reason for this may relate to the high adiabatic flame temperature, low H/C ratio, high density and difficult pyrolysis of aromatics. However, reducing the aromatic content leads to low fuel lubricity, which may damage fuel system components. Alkanes also contribute to PM emissions but, their tendency is less than aromatics. Comparison between different types of alkanes, provided that cycloalkanes produce the highest concentrations of PMs.

2.9 Knowledge Gaps

There are knowledge gaps in how different aromatic concentrations can impact engine performance. Therefore, studying the influence of different aromatic concentrations in a fuel on CI engine performance is the major contribution to knowledge from this work.

As per the literature, different aromatic species effects on engine performance are need to be investigated. Therefore, studying the influence of different aromatic species on CI engine performance is another contribution to knowledge from this study. The effect of most aromatic species on emissions investigated in this study have been not assessed in the literature as provided in table 2.9. Moreover, it can be concluded that most of the previous studies discussed the effects of polycyclic and monocyclic aromatics on emission. On the other hand, there is no particular study in the area of same type of aromatics that discuss their effect on CI engine emissions and hence, more detailed analysis needs to be done for particular type of aromatics. Therefore, this knowledge gap is also covered in the study.

Models and correlations between emissions and properties of aromatic fuel blends need to be developed as there is a lack of details in literature. Therefore, in the present study, PM and NO_x correlations are developed as function of significant impacted fuel properties such as H/C ratio, density and aromatic content.

To address these knowledge gaps, sixteen different aromatic species were investigated experimentally using a CI engine rig. Each aromatic was blended with a base fuel at three different contents: 5%, 10%, and 15% by mass. Low aromatic base fuel was used in the present study, whereas most studies in the literature used diesel fuel or alkanes blends as a base fuel. The criteria for selection of the tested aromatic species and base fuel are discussed in Sections 3.1 and 3.2.

Table 2.9 Summary of aromatic species investigated in literature and knowledge gaps

Aromatic	**Reference**	**Emissions**					**Performance**	
		CO	**UHC**	**Smoke**	**NO_x**	**PM**	**BSFC**	BTE
Toluene	[176, 179]	√	√	√	√	√	×	×
Styrene		×	×	×	×	×	×	×
o-Xylene		×	×	×	×	×	×	×
Ethylbenzene		×	×	×	×	×	×	×
α-Methylstyrene		×	×	×	×	×	×	×
Pseudocumene	[178]	×	×	×	√	√	√	×
Cumene		×	×	×	×	×	×	×
5-Tert-Butyl-m-Xylene		×	×	×	×	×	×	×
Diethylbenzene		×	×	×	×	×	×	×
p-Cymene		×	×	×	×	×	×	×
Tertbutylbenzene		×	×	×	×	×	×	×
3-Isopropylcumene		×	×	×	×	×	×	×
Indene		×	×	×	×	×	×	×
Indane		×	×	×	×	×	×	×
Tetralin	[176, 180]	√	√	√	√	√	×	×
Methylnaphthalene	[176, 179, 180]	√	√	√	√	√	×	×

√ Available in literature × Data gap

2.10 Aims and Objectives

Study of effects of fuel components is an important approach that can help in reducing CI engine emissions and improving performance. As discussed in previous section, there are knowledge gaps in how different aromatic species and their properties can affect exhaust emissions and performance. Therefore, the aim of this study is to investigate experimentally the role of different alkylbenzenes and polycyclic aromatics in surrogate fuels on emissions and engine performance. Then, aromatics in diesel surrogate fuel are reformed with optimum selection of aromatics that produce low exhaust emissions and better engine performance. In addition, one of the aims is to develop correlations between aromatic surrogate fuel properties and harmful CI engine emissions; PM and NOx emissions. In order to archive these aims, many objectives need to be done as below.

- Ensuring repeatability and durability of the CI engine rig as there has not been PhD study on the performance and emissions of CI engines in the Low Carbon Combustion Centre (LCCC), at the University of Sheffield.
- Providing fundamental data that can help students in future research.
- Selecting test alkylbenzenes and polycyclic aromatics and preparing fuel blends.
- Analysing and reporting the impact of different aromatics on emissions and performance of the CI engine.

3. BLEND SELECTION AND PROPERTY ANALYSIS

3.1 Overview

This chapter explains how fuel blends are prepared. The criteria for the selection of base fuel and tested aromatics is also discussed. Tested aromatics are chosen according to their dominant concentrations in diesel fuel composition and different physical and chemical properties. Low aromatic surrogate diesel fuel is used as a base fuel. Each aromatic was blended with base fuel at three concentrations: 5%, 10%, and 15% by mass. This provides an opportunity to evaluated both total aromatic content and different aromatic species effects at the same time. Finally, property analysis is used to establish how each fuel property can affect the other.

3.1 Base Fuel Selection

Related studies on aromatics available in the literature used two different aromatic-hydrocarbon fuel blends. Diesel fuel was selected as a base fuel in most studies, whereas one study used binary aromatic-alkane blends, as shown in Table 3.1. Each type of surrogate fuel has both advantages and disadvantages. Aromatic-diesel fuel blends can be operated in CI engines without modifications when the aromatic content in blends is ≤20%. This is illustrated by the studies of Khabbaz and Mobasheri [178] and Fukuda et al. [180]. The possible reason for this relates to an insignificant corresponding change in global blend properties compared to diesel fuel, as CI engines are designed to operate in diesel fuel mode. However, blending a large quantity of aromatics (>20%) changes global fuel blends (i.e. excessive increase of ignition delay time and too low cetane number); hence, this impacts on engine operability. Moreover, aromatic species are costly compared to diesel fuel. To test high aromatic content in aromatic-diesel fuel blends, Qian et al. [176]

carried out major engine modifications. The intake and exhaust of engine cylinders were rebuilt with the aim of reducing fuel consumption. Moreover, fuel injectors were equipped with extra control to make the injection more precise in both timing and quantity.

Table 3.1 Different base fuels used in aromatics related studies

Author	Year	Engine Type	Surrogate Fuel	Aromatic Content in fuel blends	Tested aromatics
Qian et al. [176]	2017	Modified Single-cylinder DI CI engine	Aromatics-diesel fuel blends	30% by volume	Toluene Tetralin 1-methylnaphthalene n-butylbenzene
Khabbaz and Mobasheri [178]	2014	TDI CI engine	Aromatics-diesel fuel blends	10%, 15% and 20% by volume	Tri-methyl benzene
Xiao et al. [179]	2000	Single-cylinder Cooperative Fuel Research (CFR) engine	Aromatics-heptane blends	From 0% to 20% by mass	Toluene Methylnaphthalene
Fukuda et al. [180]	1992	Single-cylinder DI and ID CI engine	Aromatic-diesel fuel	10% by volume	-2-3-4 tetrahydronaphthalene Naphthalene

Conversely, alkane species can be used as a base fuel instead of diesel fuel as shown in table 3.1. Fueling regular CI engines with this type of surrogate fuel can be difficult because their properties are unlike those of diesel fuel. A flexible CI engine is needed that can run with a varied range of surrogate fuels unlike diesel fuel properties. For example, Xiao et al. [179] used a Cooperative Fuel Research (CFR) engine to test aromatic-heptane blends. Heptane has a low density (684 kg/m^3) and boiling point (44 °C) compared to diesel fuel (at 835 kg/m^3 and 390 °C).

In the present study, each tested aromatic was blended with low aromatic base fuel at three concentrations: 5%, 10%, and 15% by mass as shown in Figure 3.1. A blend of diesel fuel and straight chain alkanes (70%:30% by mass) was used as a base fuel. The aim in using this blend as a base fuel was to reduce the aromatic concentration in the base fuel, as it is an inexpensive blend. Furthermore, it can be operated in a CI engine without any alterations such as injection timing and pressure.

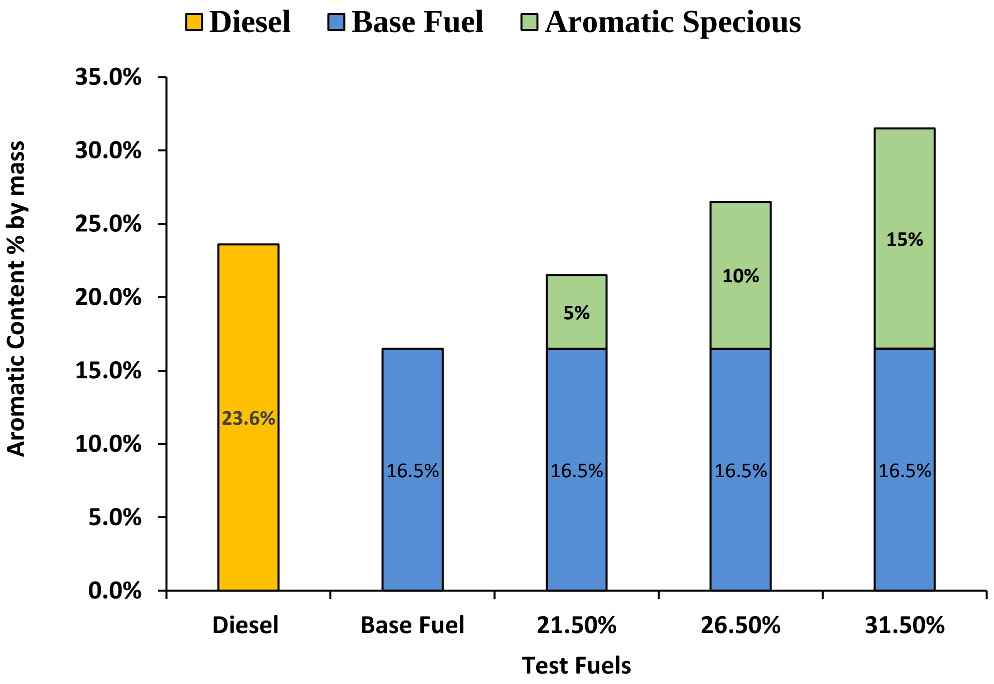


Figure 3.1 Aromatic content % in fuel blends

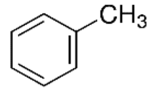
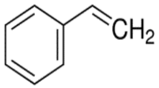
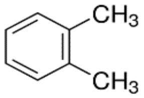
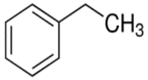
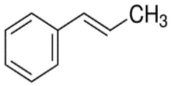
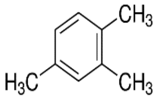
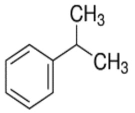
3.2 Aromatics Selection

In this PhD study, the fuel blends tested consisted of the base fuel and different concentrations of aromatic species. Each aromatic was blended with the base fuel at three concentrations: 5%, 10%, and 15% by mass. This provided an opportunity to evaluate the effect of both total aromatic content and different aromatic species at the same time. Sixteen aromatic species were selected according to their presence in diesel fuel and their properties are discussed below.

Aromatic species are very widely commercially diesel fuel available. However, dominant aromatics in most diesel fuels are monocyclic-aromatic ring (alkylbenzenes) and polycyclic-aromatic rings [188]. Moreover, diesel samples were tested based on IP 391, by Intertek Cleb Brett, in London, UK. The results showed that alkylbenzenes and polycyclic aromatics represented 86.8.% and 13.14% of total aromatic content in diesel fuel, respectively. Therefore, 4 polycyclic aromatics and 12 different alkylbenzenes were selected, as presented in Table 3.2 and 3.3.

Aromatics with different chemical and physical properties were also selected with the aim of covering the effect of these properties on both emissions and performance. The H/C ratio of an aromatic compound is an important property that has an effect on PM emissions [179, 181]. However, the effect of aromatics with different H/C ratios on other exhaust emissions and performance needs to be investigated. Therefore, selected aromatics have a range of H/C ratios (0.88 to 1.5). In addition, density and calorific value may play a significant role in BSFC, NO_x and PM levels [48, 181]. Densities and calorific values of the species range from 838–1000.1 kg/m^3 and 28.09–43.016 MJ/kg, respectively.

Table 3.2 Properties of alkylbenzenes, base fuel, and diesel fuel

Representative Name	Fuel/ aromatic Name	Chemical Structure	Density (kg/m^3)	Calorific Value (MJ/kg)	Boiling Point (°C)	H/C ratio	Aromatic Content % by mass			Cetane Number
							Low Content	Medium Content	High Content	
1	Toluene		865	42.439	111	1.143	21.5	26.5	31.5	3
2	Styrene		906	42.205	145.2	1.000	21.5	26.5	31.5	-
3	o-Xylene		879	42.875	144	1.250	21.5	26.5	31.5	8.3
4	Ethylbenzene		867	43.016	136	1.250	21.5	26.5	31.5	6.2
5	α-Methylstyrene		909	31.667	164	1.111	21.5	26.5	31.5	-
6	Pseudocumene		876	42.383	169	1.333	21.5	26.5	31.5	8.9
7	Cumene		864	38.488	152	1.333	21.5	26.5	31.5	7

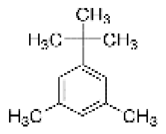
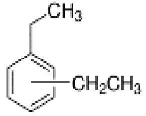
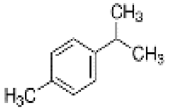
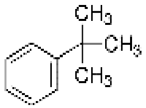
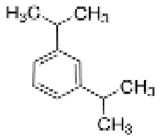
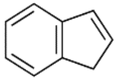
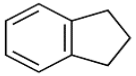
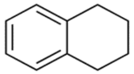
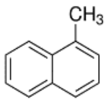
8	5-Tert-Butyl-m-Xylene		838	39.157	204	1.5	21.5	26.5	31.5	-
9	Diethylbenzene		870	40.255	183.7	1.400	21.5	26.5	31.5	-
10	p-Cymene		860	38.422	177	1.400	21.5	26.5	31.5	-
11	Tertbutylbenzene		867	35.762	167.8	1.400	21.5	26.5	31.5	-
12	3-Isopropylcumene		856	32.773	203.2	1.500	21.5	26.5	31.5	-3
Base fuel	Low aromatic diesel	-	809.8	43.6	390	1.910	16.5			60
Reference fuel	Diesel Fuel	-	835	41.7	355	1.860	23.6			51.6

Table 3.3 Properties of polycyclic aromatics, base fuel, and diesel fuel

Representative Name	**Fuel/ aromatic Name**	**Chemical Structure**	**Density (kg/m^3)**	**Calorific Value (MJ/kg)**	**Boiling Point (℃)**	**H/C ratio**	**Cetane Number**	**Aromatic Content % by mass**		
								Low Content	**Medium Content**	**High Content**
1	Indene		996	28.09	181	0.889	-	21.5	26.5	31.5
2	Indane		965	42.16	175	1.111	8.60	21.5	26.5	31.5
3	Tetralin		973	38.20	206	1.200	8.9	21.5	26.5	31.5
4	Methylnaphthalene		1000.1	36.70	240	0.909	0.00	21.5	26.5	31.5
Base fuel	Low aromatic diesel	-	809.8	43.6	390	1.910	60	16.5		
Reference fuel	Diesel Fuel	-	835	41.7	355	1.860	51.6	23.6		

3.3 Property Analysis

The performance and emissions of CI engines are significantly affected by the properties of fuel used. However, it can be difficult to predict the effect of particular properties on engine performance and emission formation. The properties of fuel are highly dependent on each other [39]. Therefore, correlations have been developed between important fuel properties and are provided in Table 3.4. In particular, the correlations aid in determining the effect of aromatic content on the other fuel properties because the present study concentrates on aromatic impact.

Table 3.4 Matrix of correlations between fuel properties

Property	**Density**	**H/C ratio**	**MW**	**Calorific value**	**CN**	**AC %**	**T_b**	**T_f**	**T_A**
Density (kg/m^3)	1.00								
H/C ratio	-0.71	1.00							
Molecular weight (MW) (g/mole)	-0.40	0.58	1.00						
Calorific value (MJ/kg)	0.02	-0.15	-0.42	1.00					
Cetane Number (CN)	-0.58	0.84	0.50	0.05	1.00				
Aromatic Content % by mass (AC %)	0.62	-0.68	-0.66	0.12	-0.98	1.00			
Final Boiling Point, T_b (°C)	-0.49	0.64	0.75	-0.23	0.89	-0.94	1.00		
Flash Point T_f (°C)	0.23	0.06	0.74	-0.38	0.12	-0.21	0.40	1.00	
Autoignition Point T_A (°C)	0.74	-0.73	-0.66	0.03	-0.86	0.86	-0.79	-0.15	1.00

It can be seen that aromatic content influences many properties such as density, cetane number, H/C ratio, calorific value, boiling point and autoignition point. For example, there is a strong correlation between aromatic content and H/C ratio with a -0.68 coefficient. This means increasing aromatic content in fuel leads to lower global H/C ratios because aromatics have low H/C values compared to other fuel components such as alkanes [50]. Cetane number also is highly impacted by aromatic content with -0.98 coefficient so, increasing aromatic content of fuel leads to low global cetane number and hence, increased ignition delay time [43]. As aromatics are heavy hydrocarbons and have high densities, increased aromatic content in fuel leads to large droplets formation during injection and then, poor oxidization. The corresponding change in fuel properties due to blending aromatics can help in understanding resultant emissions and performance as discussed in chapters' five to seven.

3.4 Data Analysis

3.4.1 Emissions Analysis

The present study covered 300 test points by using 48 fuel blends, diesel fuel and optimum blend at low (1.1 kW) and high (4.5 kW) loads, respectively. Each test fuel was tested three times to ensure the repeatability of experimental data. Raw data was obtained by averaging the results of each fuel. Uncertainties and measurement ranges of exhaust emissions are provided in Table 3.5.

Table 3.5 The uncertainties and ranges of exhaust emissions

Instrument	**Emission**	**Range**	**Uncertainty**			
			Linearity	**Drift**	**Noise**	**Total**
9000MGA multi-gas	CO	0-400 ppm	1%	2.38%	0.22%	3.6%
3000HM HC	UHC	0-1000 ppm	2%	2%	1.73%	5.73%
4000VM	NOx	0-4000 ppm	1%	3.80%	1%	5.8%
LII 300 particulate	PM	Up to 20 g/m3	-	-	-	17.2%

After that, the results of gaseous emissions were converted from the concentration of gaseous emission (ppm) to BSFC (g/kWh) using the following equations [189].

$$\mathrm{NO_x}\left(\frac{\mathrm{g}}{\mathrm{kWh}}\right) = 6.636 \times 10^{-3}\mathrm{NO_x}(\mathrm{ppm}) \qquad \mathrm{Eq}(3.1)$$

$$\mathrm{CO}\left(\frac{\mathrm{g}}{\mathrm{kWh}}\right) = 3.591 \times 10^{-3}\mathrm{CO}\ (\mathrm{ppm}) \qquad \mathrm{Eq}(3.2)$$

$$\mathrm{UHC}\left(\frac{\mathrm{g}}{\mathrm{kWh}}\right) = 2.002 \times 10^{-3}\mathrm{UHC}\ (\mathrm{ppm}) \qquad \mathrm{Eq}(3.3)$$

3.4.2 Performance Analysis

Performance analysis used agrees with study done by Singh et al. [190]. If the performance parameter is calculated using certain measured quantities, then uncertainty in measurement of “y” is given follows:

$$\frac{\delta\, \mathrm{y}}{\mathrm{y}} = \left[\left(\frac{\delta\, \mathrm{y}}{\partial \mathrm{x}_1}\,\delta\, \mathrm{x}_1\right)^2 + \left(\frac{\delta\, \mathrm{y}}{\partial \mathrm{x}_2}\,\delta\, \mathrm{x}_2\right)^2 + \left(\frac{\delta\, \mathrm{y}}{\partial \mathrm{x}_3}\,\delta\, \mathrm{x}_3\right)^2 + \cdots\cdots\cdots + \left(\frac{\delta\, \mathrm{y}}{\partial \mathrm{x}_n}\,\delta\, \mathrm{x}_n\right)^2\right]^{0.5}$$

$$Eq(3.4)$$

i. Engine Condition (Brake Power)

Engine condition is controlled by brake power using an electrical heater. The brake power is determined as a function of electric current (I), voltage (V) at constant speed (N). While, $\delta\mathrm{N}, \delta\mathrm{V}$ and $\delta\mathrm{I}$ are the change in measurements of speed, voltage and current during sampling. The uncertainty of brake power is calculated using Eq (3.6).

$$BP = \frac{2\pi NT}{60} = \frac{2\pi NVI}{60} \qquad Eq(3.5)$$

BP = f(N,V,I)

$$\frac{\delta\mathrm{BP}}{\mathrm{BP}} = \sqrt{\left(\frac{\delta\mathrm{N}}{\mathrm{N}}\right)^2 + \left(\frac{\delta\mathrm{V}}{\mathrm{V}}\right)^2 + \left(\frac{\delta\mathrm{I}}{\mathrm{I}}\right)^2} \qquad Eq\ (3.6)$$

Where; N is equal to 1500 rpm, I is equal to 16 A and V is equal to 280 V

$$\frac{\delta \mathrm{BP}}{\mathrm{BP}} = \sqrt{\left(\frac{1}{1500}\right)^2 + \left(\frac{1}{280}\right)^2 + \left(\frac{0.1}{16}\right)^2}$$

$$\frac{\delta \mathrm{BP}}{\mathrm{BP}} = 0.0072 = 0.72\%$$

ii. BSFC

BSFC uncertainty is calculated using Eq (3.8). Where m is fuel mass consumed (kg) and t is time (s) required for each test point. The change in measurements of mass, time and brake power are represented as $\delta\mathrm{m}, \delta\mathrm{t}$ and $\delta\mathrm{BP}$, respectively.

$$\mathrm{BSFC} = \frac{\text{mass of fuel consumed/ unit time}}{\text{power}} \qquad \mathrm{Eq(3.7)}$$

$$\mathrm{BSFC} = \frac{\mathrm{m}}{\mathrm{t} \times \mathrm{BP}}$$

$\mathrm{BSFC} = \mathrm{f(m, t, BP)}$

$$\frac{\delta \mathrm{BSFC}}{\mathrm{BSFC}} = \sqrt{\left(\frac{\delta \mathrm{m}}{\mathrm{m}}\right)^2 + \left(\frac{\delta \mathrm{t}}{\mathrm{t}}\right)^2 + \left(\frac{\delta \mathrm{BP}}{\mathrm{BP}}\right)^2} \qquad \mathrm{Eq(3.8)}$$

Where; m is equal to 0.66 kg and t is equal to 120 s for each test point.

$$\frac{\delta \mathrm{BSFC}}{\mathrm{BSFC}} = \sqrt{\left(\frac{0.001}{0.66}\right)^2 + \left(\frac{1}{120}\right)^2 + (0.0072)^2}$$

$$\frac{\delta \mathrm{BSFC}}{\mathrm{BSFC}} = 0.011 = 1.11\%$$

iii. BTE

BTE uncertainty is calculated using Eq (3.10).

$$\mathrm{BTE} = \frac{\mathrm{BP}}{\mathrm{CV} \times \text{mass of fuel consume per unit time}} \qquad \mathrm{Eq(3.9)}$$

$$\mathrm{BTE} = \frac{\mathrm{BP}}{\mathrm{Q} \times \mathrm{m/t}}$$

$$\mathrm{BTE} = \mathrm{f(m, t, BP)}$$

$$\frac{\delta \mathrm{BTE}}{\mathrm{BTE}} = \sqrt{\left(\frac{\delta \mathrm{m}}{\mathrm{m}}\right)^2 + \left(\frac{\delta \mathrm{t}}{\mathrm{t}}\right)^2 + \left(\frac{\delta \mathrm{BP}}{\mathrm{BP}}\right)^2} \qquad Eq\ (3.10)$$

$$\frac{\delta \mathrm{BTE}}{\mathrm{BTE}} = \sqrt{\left(\frac{0.001}{0.66}\right)^2 + \left(\frac{1}{120}\right)^2 + (0.0072)^2}$$

$$\frac{\delta \mathrm{BTE}}{\mathrm{BTE}} = 0.0111 = 1.111\%$$

3.5 Conclusion

Tested aromatics are selected optimally according to their contents in diesel fuel composition and the verity of physicochemical properties such as density. H/C ratio and calorific value. Also, low aromatic base fuel used, differs from those in literature. Each aromatic is blended with the base fuel in three contents; 5, 10 and 15% by mass respectively. Correlations among fuel properties are analysed in order to find each property influence on another. Finally, the uncertainties of experimental measurements of emissions and performance are calculated.

4 EXPERIMENTAL SET-UP

4.1 Overview

This chapter provides a detailed description of CI engine and instruments used in this PhD study. The first part of this chapter involves the specifications of the CI engine and its supplementary parts namely fuel consumption unit, dynamometer, electrical heaters, and control panel. While, operating principle and specifications of gaseous analysers are provided in the second part of this chapter. Finally, the functions of Laser-Induced Incandescence (LII) and Richard Oliver smoke meter are discussed.

4.2 Experimental Set-up

In the present study, the fuel blends were tested by using an experimental rig consisting of a CI engine block, a mobile emissions laboratory (MEL) unit, and particulate and smoke instruments as shown in Figure 4.1 and 4.2. The rig is installed at the LCCC. The durability and repeatability of the CI engine rig were ensured to achieve one of objectives of the present study (as mentioned in Section 1.7). The operating principle and set-up procedure for each part of the rig is discussed in detail in the following sections.

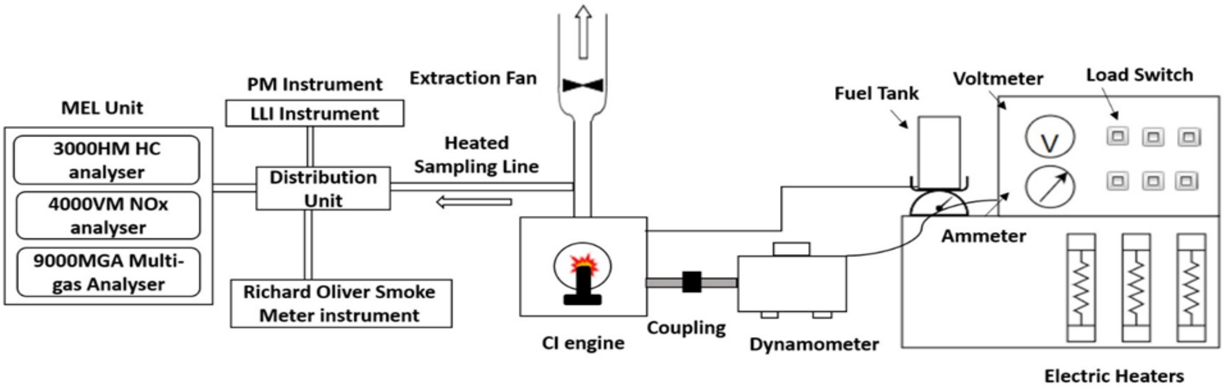


Figure 4.1 Schematic diagram of experimental setup

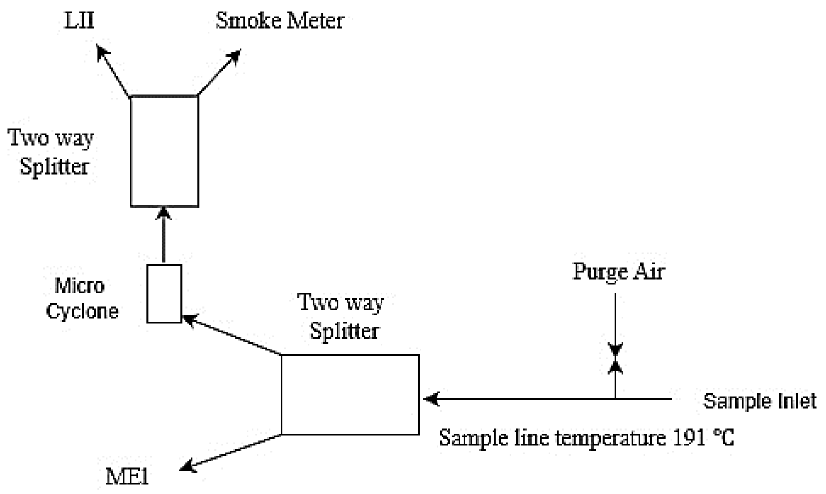


Figure 4.2 Schematic diagram of distribution unit

4.2.1 Engine Set-up

The engine block consists of five parts: a CI engine, a fuel consumption unit, a dynamometer, electrical heaters, and a control panel (as shown in Figure 4.3). The experiments in the present study were carried out using a natural aspirated single-cylinder four-stroke DI CI engine without any modifications (such as injection timing and pressure). Engine specifications are provided in Table 4.1. The CI engine was operated at a constant speed (1500 rpm) and two load conditions (1.1 kW and 4.5 kW), together with a water-cooled system, where the inlet cooling water and air temperatures were kept at 25 ºC and 28°C. To set electrical loading, the output shaft of the engine was coupled with a dynamometer that generates electric power and was controlled using a control panel.

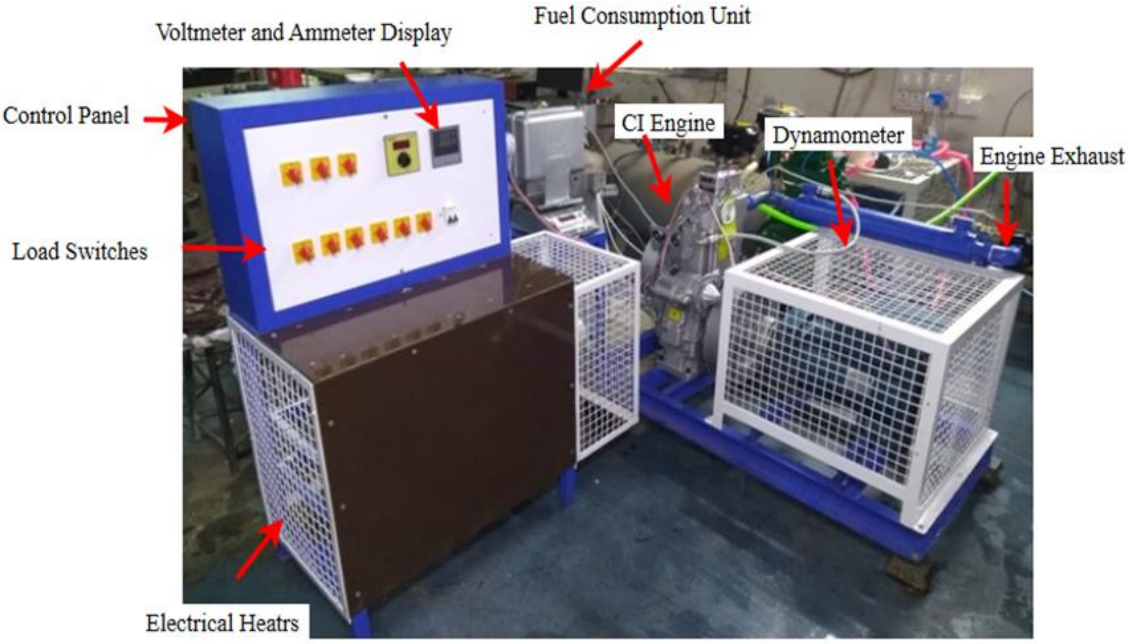


Figure 4.3 Direct injection CI engine parts

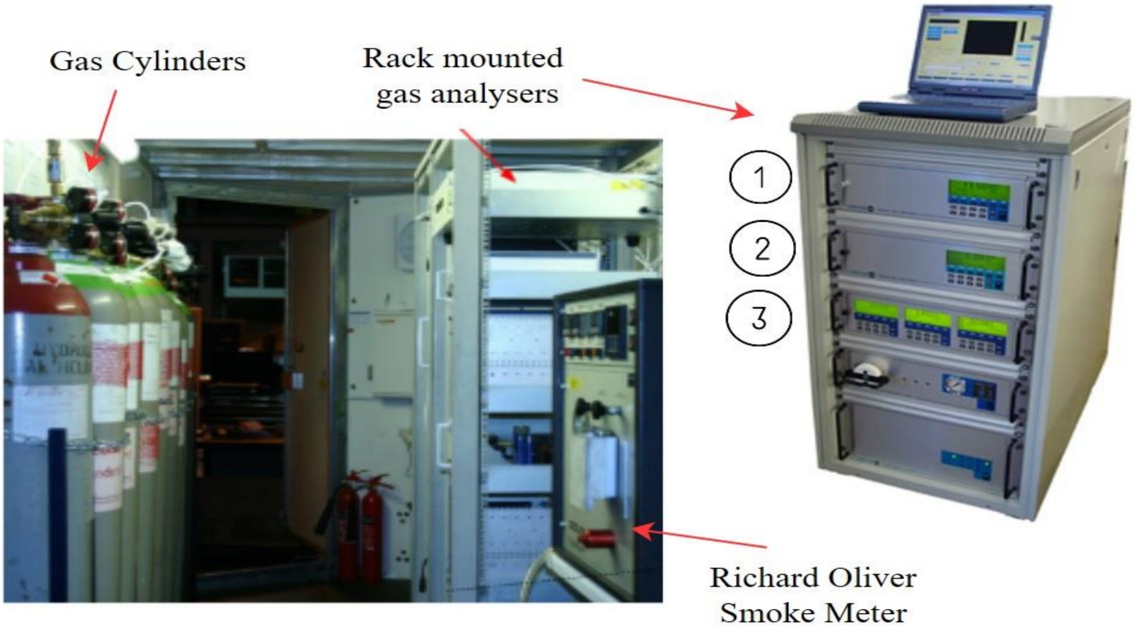
The fuel mass flow rate (kg/s) was measured using an electronic weighing scale which was turned on during testing to avoid any drift. Furthermore, this work is comparative that's why absolute datum does not impact the trends and correlations developed. Two fuel pipes were lined with the mechanical fuel pump in the intake system. The first pipe was used to feed the engine and the second was used for the return fuel. Both pipes could use either fuel tank; one tank was used during testing and the other was used to test another fuel. Hence, the fuel tank could be exchanged for another one without shutting down the engine. The heated sample line (at 191 °C) was fitted to the engine exhaust directly to draw emissions into the measuring instruments without any condensation. The sample line was then connected to an isolated distribution unit as shown in Figure 4.1. Then, the sample emissions were passed through three sub-heated lines into the MEL unit, the laser-induced incandescence (LII) instrument, and the smoke meter instruments. The rig was first operated using diesel fuel until it reached steady conditions. The operating procedure for the test campaign is provided in Appendix B1 and B2.

Table 4.1 CI engine Specifications

Engine Type	Single cylinder four stroke water cooled
Bore	87.5 mm
Stroke	80.0 mm
Speed	1500 rpm
BHP	10 HP
Compression ratio	16.7 : 1
Injection	Direct Injection
Swept Volume (CC)	481 cm^3
Method of Start	Cold Start
Engine Rotation	Standard Rotation Clockwise facing Flywheel
Governor Type / Class	Centrifugal / B1 Class
Fuel Injection Timing by Spill Cut Off Method	24° BTDC
Fuel Injection Equipment	Bosch Nozzle Bosch Pump Injection Release Pressure 190/210 kg/cm^2
Valve Tappet Clearance Inlet (mm)	0.20
Valve Tappet Clearance Exhaust (mm)	0.25
Lubrication System	Plunger Pump
Crank Shaft Height (mm)	170
Operating Conditions	
Load/ Brake mean effective pressure	1.1 kW, 0.173 MPa (Low load) 4.5 kW, 0.754 MPa (High Load)
Cooling water temperature	25°C
Intake air temperature	28°C

4.2.2 Mobile Emission laboratory

The MEL was used to characterise the concentrations of gaseous exhaust emissions. The MEL can be used in different combustion systems such as internal combustion (IC) engines, gas turbines, and airfields. The MEL contains gaseous analysers, gas cylinders, and gas filters, as shown in Figure 4.4. The exhaust emissions were drawn from the CI engine into the MEL through a heated sample line. In the MEL, the emissions sample was first passed through the gas filter and then distributed into four different gas analysers for each type of gaseous emission. Necessarily, zero and span gas cylinders are equipped with gaseous analysers for calibration purposes and computers are mounted to record the measurements. The standard procedure of the MEL unit is provided in Appendix B2. An overview of the analysers and gas cylinders is provided in the following subsections.



No	**Instrument**	**Gaseous Emissions**
1	3000HM analyser	UHC
2	4000VM analyser	NO_x
3	9000MGA analyser	CO, CO_2 and O_2

Figure 4.4 Mobile Emission Laboratory (MEL) Unit

4.2.2.1 Span and Zero Gas Cylinders

To ensure the analyser response matched the concentration of the sample, certain span and zero gas cylinders were used to calibrate the analysers as shown in Table 4.2. First, a zero gas was passed through each analyser; then, a span gas from the gas cylinder was drawn into the analyser. A measurement point for known concentrations was obtained from both zero and span readings as shown in Figure 4.5.

Table 4.2 Calibration span and zero gas cylinders

Instrument	**Span gas**	**Zero gas**	**Linearity prior to the test campaign**
4000VM analyser	487 ppm NOx	N_2	2%
9000MGA analyser	10% CO_2, 1000 ppm CO	N_2	2%
3000HM analyser	101 ppm Propane	Air	1.5%

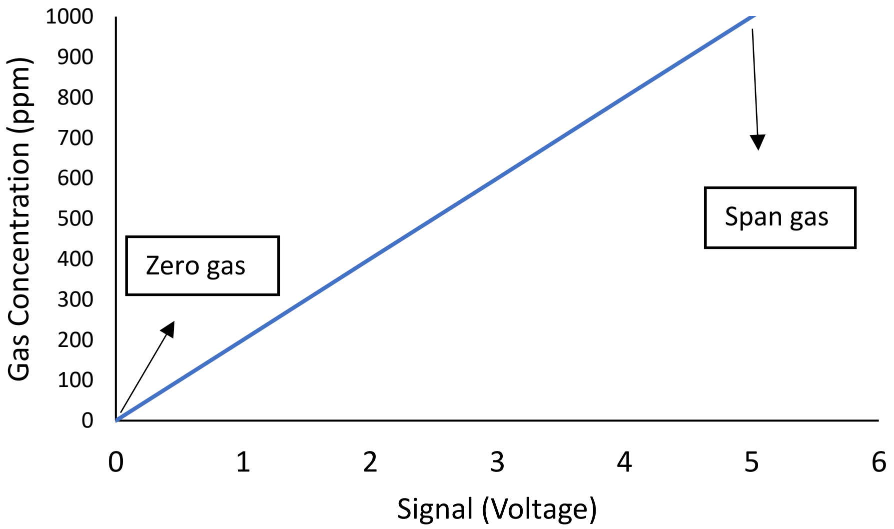


Figure 4.5 Zero and span calibration line

A zero nitrogen cylinder (with 99.9% purity) was selected for the gaseous analysers except for the 3000HM analyser, because using nitrogen gas changes the ionisation fuel-air ratio of the ionisation flame resulting in inaccurate calibration. Accordingly, the 3000HM analyser was zeroed by supplying synthetic air instead of nitrogen gas to deliver the required oxygen content into the FID flame zone, while the FID was fuelled by a hydrogen-helium gas mixture of 40%:60%.

In FID method, the type of span gas (i.e. methane or propane) used is proportional to carbon concentration in sample. In this study, propane is used as a span gas. The response to one mole of propane is equivalent to three moles of carbon. As FID method is based on volume/volume fraction, ppm of propane is equivalent to three ppm of carbon. Therefore, it is important to note that ppm of propane measured is equivalent to ppm of carbon multiplying by factor of 3.

4.2.2.2 Gaseous Analysers

The 4000VM heated vacuum analyser offers a reference technique for measuring NO_x emissions. It can be used for automobile emissions research laboratories and has automatic operation, which includes start-up, measurement range, and calibration [191]. The main advantage of this technique comes from its ability to measure hot wet sample gas with high sensitivity and accuracy. The technique relies on a heated vacuum chemiluminescence. Thus, NO_x can be measured using a photomultiplier tube that can detect the light from the gas-phase titration of NO_x and ozone as shown in Figure 4.6 [191]. If the volume of excess ozone and sample gas are controlled accurately, the level of light in the reaction chamber is proportional to NO_x concentrations in the sample gas.

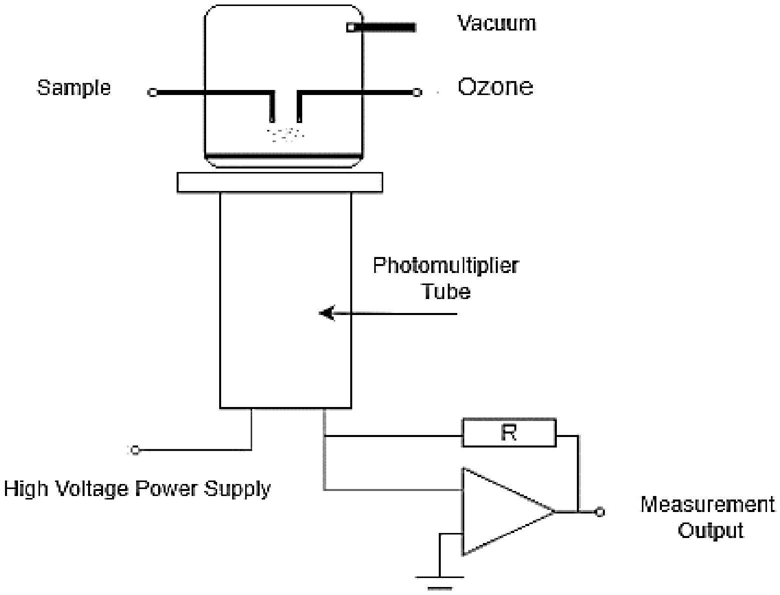


Figure 4.6 Heated vacuum chemiluminescence technique [191]

The 9000MGA analyser is microprocessor-based gas analyser, which is able to measure three types of exhaust gases, namely O_2, CO, and CO_2. A dumb-bell paramagnetic is used in the analyser for measuring O_2. Here, the paramagnetic sensor featured two nitrogen glass spheres, which were mounted on rotating suspension. This assembly provided a strong magnetic field for attracting oxygen molecules. This resulted in a force on both nitrogen spheres, and the effect of torque strength on the suspension was relative to the content of oxygen. Meanwhile, an non dispersive infra-red (NDIR) gas technique was used to measure CO and CO_2 [192]. This technique relied on the energy absorption of particular gas in the IR region, where IR energy draws through two parallel tubes and recombines in a detector as shown in Figure 4.7 [192]. One tube (known as the measurement cell) contained the sample to be analysed, while another tube (the reference cell) contained the non-absorbing gas nitrogen. The sample absorbed energy in the IR region and then reduced the amount of energy passing through the measurement cell into the detector. The reduced energy (due to sample absorption was compared to that passing through the reference cell. The difference is relative to the number of relevant carbon molecules in the optical path.

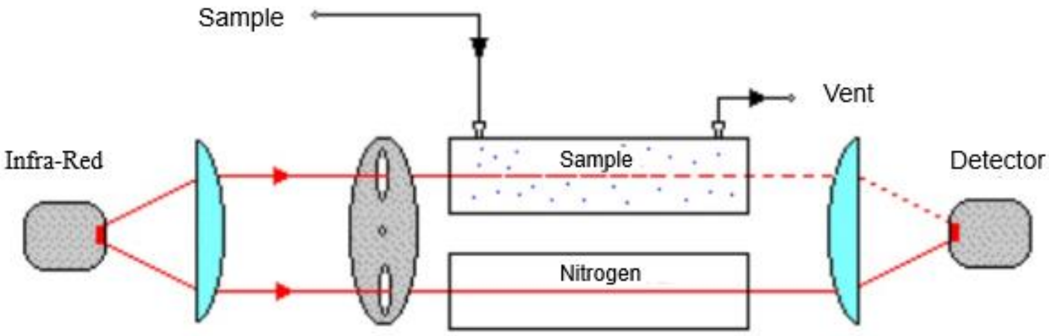


Figure 4.7 Principle of IR technique [192]

The 3000HM is a hydrocarbon analyser that has an automatic operation including auto-calibration, auto-ignition, auto-range, and auto-purge on shutdown. The principle of flame ionization detection (FID) is used in the 3000HM analyser to detect volatile organic compounds in a gas stream. The principle of this instrument relies on the production of ion current from burning of the sample in hydrogen flame. Hydrogen atoms from hydrocarbon molecules in sample gas are stripped to form electrons and carbon radicals [193]. This is a short-lived condition with charged components that recombine quickly. However, in the case of an electrostatic field, hydrogen atoms can be driven towards electrodes as shown in figure 4.8 [193]. This creates sufficient current with a flame that is proportional to the number of hydrocarbon molecules. The ion current is amplified and is then presented as ppm readings.

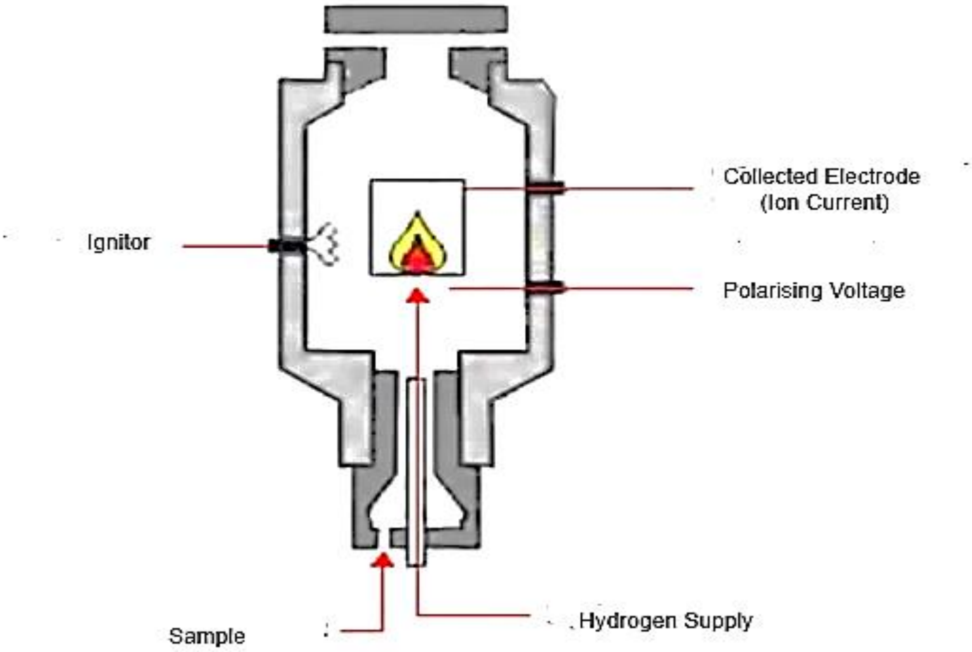


Figure 4.8 Principle of Flame Ionisation Detector [193]

4.2.3 Laser-Induced Incandescence (LII) instrument

The LII300 particulate instrument is a tool for time measurements of primary particle size and soot particulate concentration [194]. However, in this study, primary particle size is not measured. The LII instrument can measure soot emissions directly from the engine exhaust or sampling over a varied range of operating conditions and concentrations.

The LII300 system (Figure 4.9) consists mainly of a pulsed neodymium-doped yttrium aluminium garnet (Nd:YAG) laser, a measurement cell , and two detectors. The Nd:YAG laser operates with 60 mJ/pulse at 1064 nm and 20 Hz [195]. The light laser with short pulse duration (below 20 ns) is used to increase soot temperature from ambient temperature to just below the temperature of particle vaporisation (4000 K) so that soot interacts with the laser path that absorbs light [194]. Photodetectors and collection optics are used to account for the thermal radiation of soot particles. Appropriate calibration and analysis of incandescence signals is conducted to measure particle concentration. The temperature of particles is then reduced using a complex cooling process, which includes nanoscale heat transfer and light absorption. The LII is insensitive to liquid particles (compared to carbon particles) because liquid particles absorb an insignificant amount of laser energy. Although low concentrations of metallic ash might be present in the sample, it has low absorption of light and is less likely to survive at high temperatures. Therefore, the LII instrument is totally suitable for measuring elemental carbon in the exhaust.

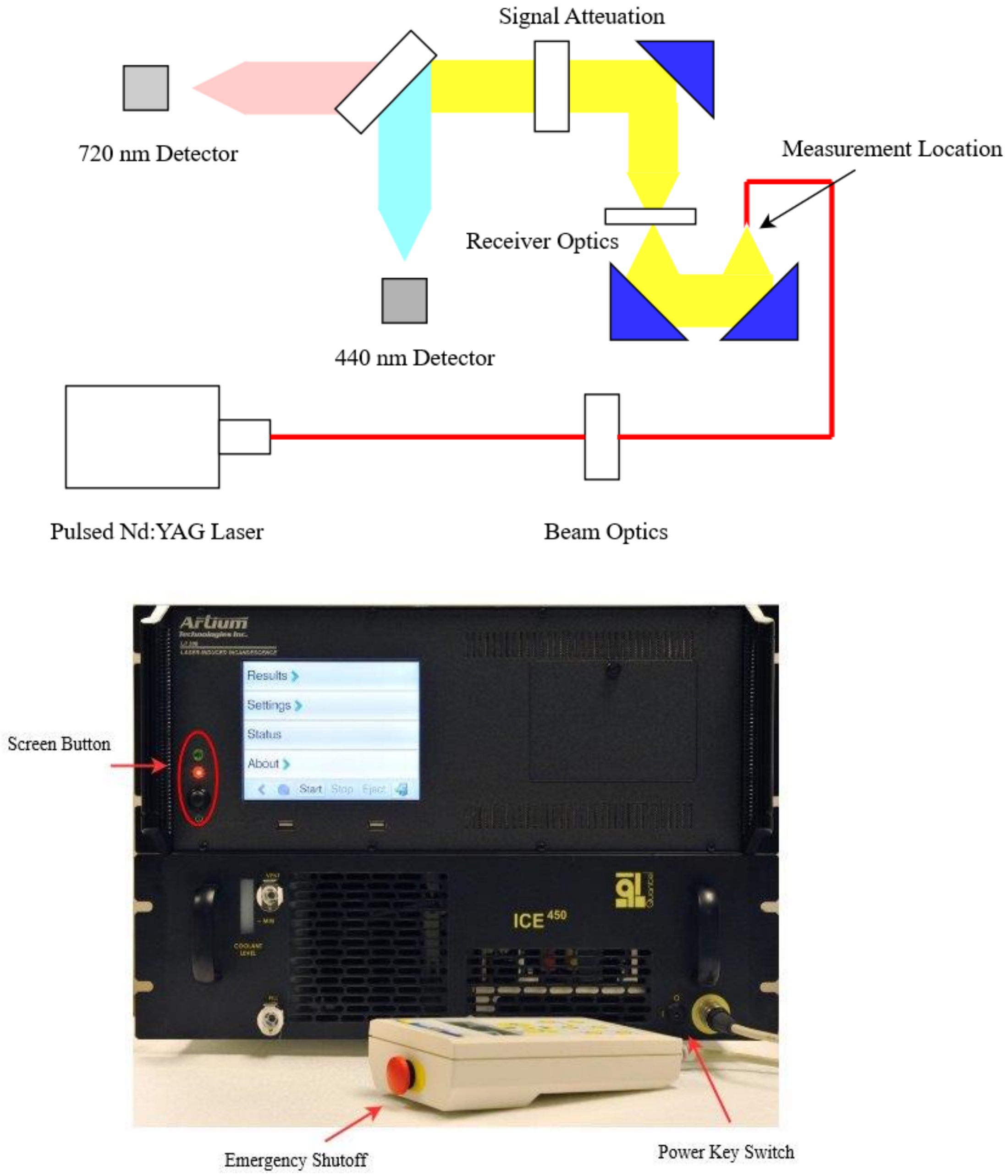


Figure 4.9 Schematic layout of the LII system [193]

Two photomultipliers are used in order to certify the reliability of luminescence signal. Accordingly, photomultipliers are employed to detect precise wavelength at exactly 720 nm and 440 nm. The soot luminescence is focused on the photomultiplier and then, is beamed on a narrow band interference filter. The signal detected, is converted to voltage in order to measure soot temperature, whereas, at certain temperature, the intensity of the absolute signal is used to measure the volume or mass of soot fraction. Standard procedure of LII instrument is provided in Appendix B2.

4.2.4 Richard Oliver Smoke Meter

A Richard Oliver smoke meter is an instrument that is used for the measurement of smoke emissions. The instrument is designed to run automatically (as per SAE ARP1179). In this study, aero smoke meter is used rather automotive. This is not an issue as the aim of this study is to compare between smoke results of different fuel blends rather than actual values. The instrument principle depends on drawing a certain sample volume through a Whatman no. 4 filter paper at constant operating conditions (volume flow rate, pressure, and temperature) [196]. The volume flow rate of the sample was maintained at 9.2 L/min for all tested blends. The sample handling module (including pipework, flowmeter, and valves) were heated and maintained at 60 ºC using a pump drive motor installed externally. The holder block of the filter was aluminium alloy with a diameter of 5.5 cm as shown in Figure 4.10. To measure the smoke number, the filter paper reflectance was recorded before and after sampling using the EEL043M Smokestain Reflectometer manufactured by Diffusion Systems. Then, the smoke numbers of tested fuel blends were obtained using the following equation: The instrument procedure is available in Appendix B2.

$$\mathrm{Smoke\ Number} = 100\left[1 - \frac{\mathrm{R_s}}{\mathrm{R_w}}\right] \qquad \mathrm{Eq(4.1)}$$

where, R_s: absolute reflectance of the stained filter, and R_w: absolute reflectance of clean filter.

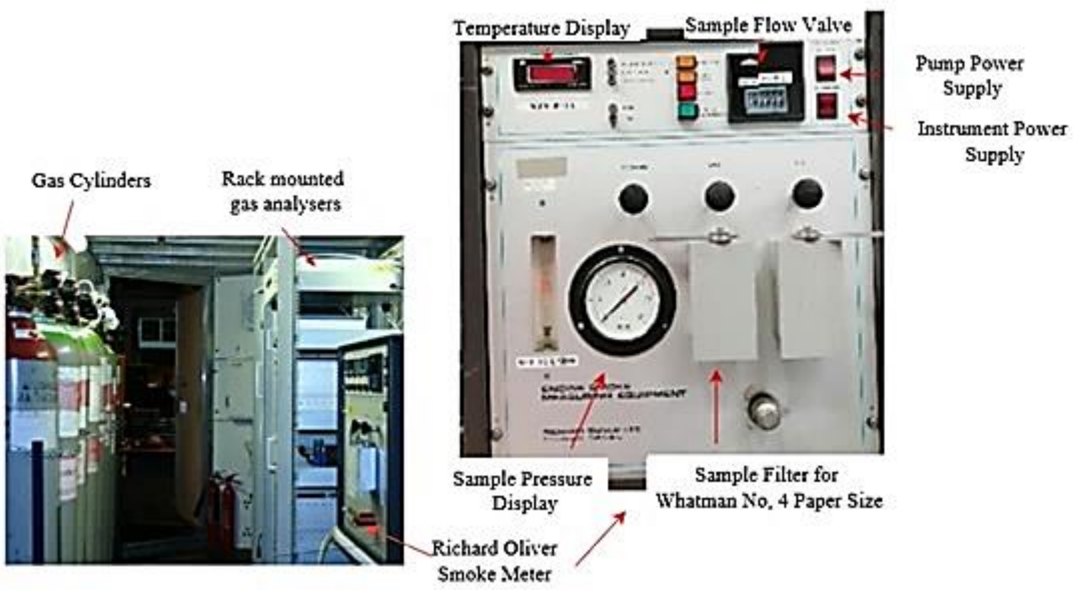


Figure 4.10 Richard Oliver smoke meter

4.3 Conclusion

The configuration of experimental rig consists mainly of CI engine, the MEL unit, particulate and smoke instruments. The engine type is DI four-stroke engine which is coupled with a dynamometer in order to control electrical load. The engine also is fitted with fuel consumption unit consisting of weighing scale, fuel tank and inlet and return pipes. In the MEL unit, gaseous analysers (i.e 4000VM, 9000MGA and 3000HM analysers) are fitted with span and zero cylinders and then, calibrated precisely. LII and smoke instruments are set-up and used in agreement with each instrument standard procedure. The specifications and operating principle of each part of the rig are briefly explained.

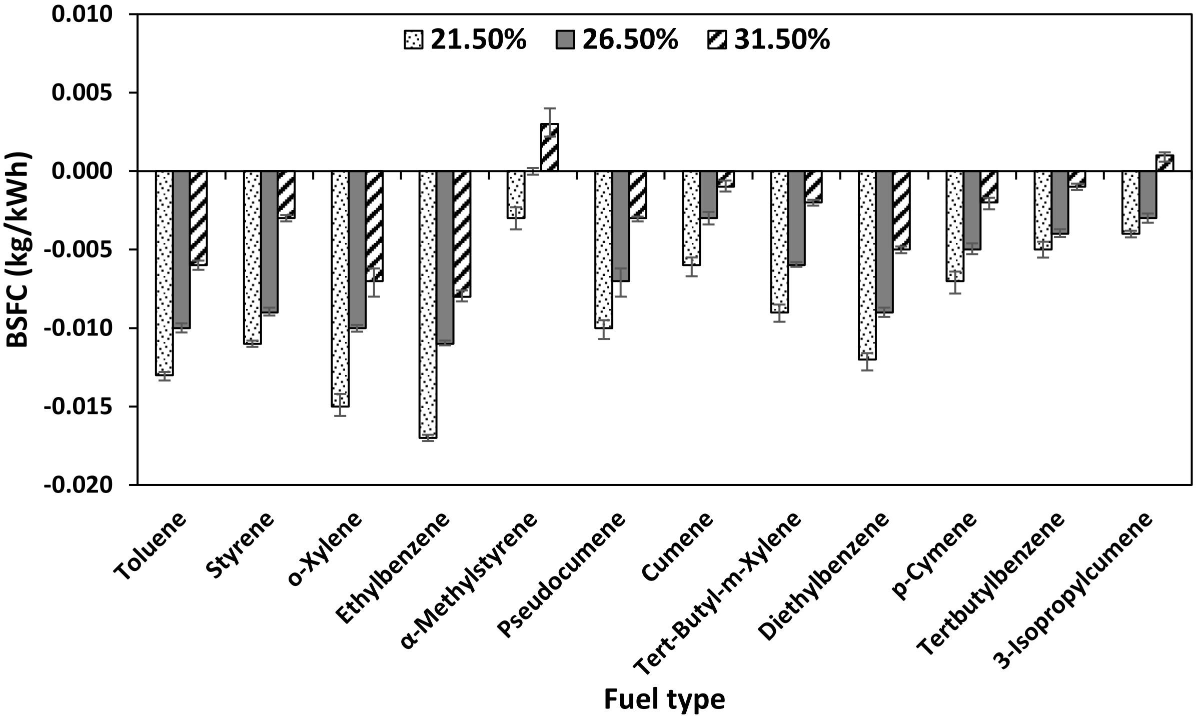
5 EFFECT OF ALKYLBENZENES ON CI ENGINE

5.1 Overview

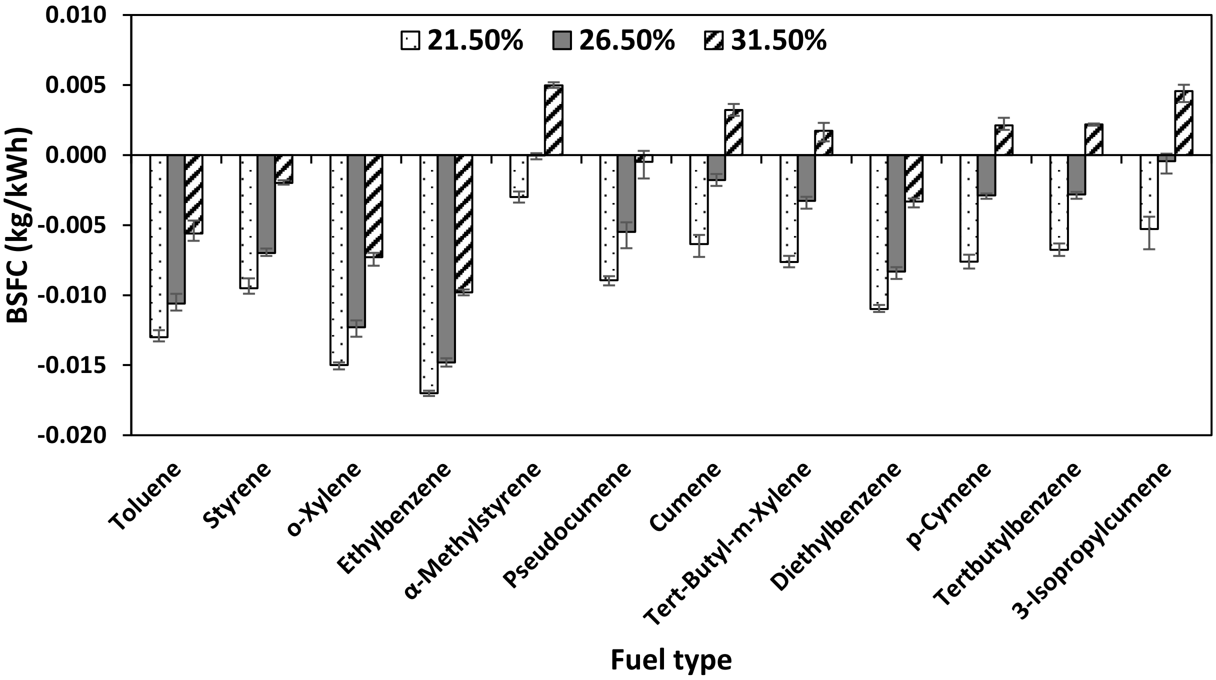
In this chapter, different alkylbenzenes were experimentally investigated using the single-cylinder direct-injection CI engine at two different loads (i.e. 1.1 kW and 4.5 kW, respectively) and constant speed (1500 rpm). Different Alkylbenzenes were blended with low aromatic base fuel in three percentages i.e. 21.5%, 26.5% and 31.5% by mass. This chapter presents the results from the investigation of alkylbenzenes. A brief discussion is provided about the effect of different alkylbenzenes on emissions and performance of CI engine. Correlations are developed for PM and NO_x emissions as function of fuel properties.

5.2 Performance

In this section, the effects of aromatic content and its structure on the performance of a diesel engine, such as engine brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) are discussed. When engine load increased, more fuel was injected into the combustion chamber with constant induced air. This led to a richer air-fuel mixture and then, high BTE compared to too lean mixture at low load. BTE improves at high load condition as losses due to friction and water pump correspond to a small fraction of the indicated power. At no load condition (idle), the BTE is minimal as friction and water pump losses are significant. Both BSFC and BTE of test fuels were compared to the base fuel and commercial diesel fuel. The effect of structure and alkylbenzene contents on BSFC and BTE at low and high load is shown in Figure 5.1 and 5.2 respectively. The overall results showed slightly higher BSFC and lower BTE with increasing aromatic content in test fuels compared to the base fuel. This is due to lower calorific value and cetane number of the fuel blends with aromatic blending. A higher concentration of aromatics increases the ignition delay and adversely affects the engine performance [197].



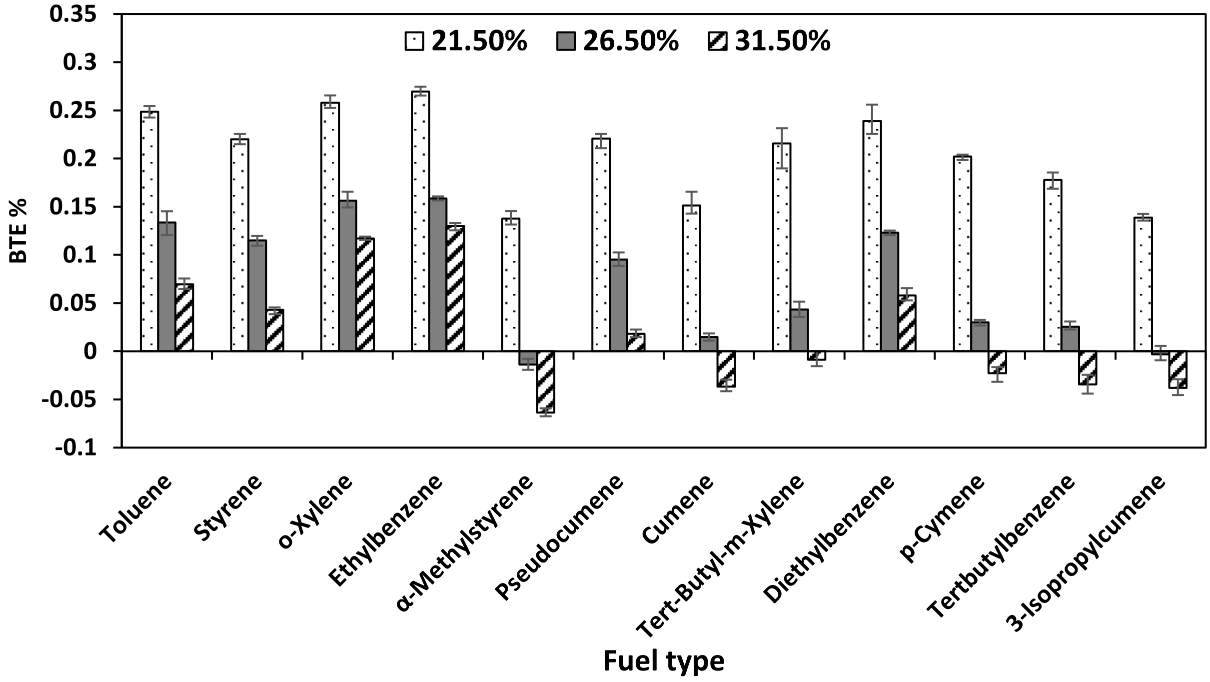
(a) Low load



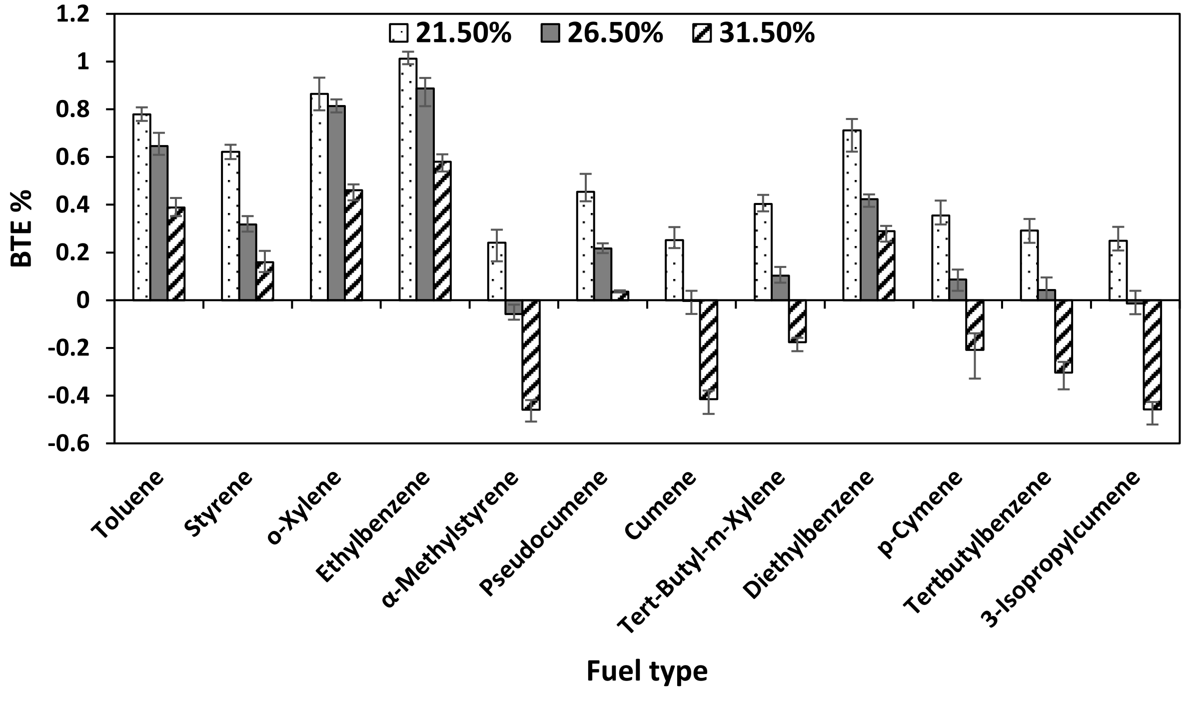
(b) High load

Figure 5.1 BSFC results of alkylbenzene blended fuels compared to diesel fuel

BSFC depends upon the effectiveness of an engine to convert the available chemical energy of the fuel into useful work output. BSFC is affected by many fuel properties such as calorific value, cetane number, density, viscosity etc. [198]. BSFC is lower for all the tested fuel blends at high load condition compared to low load condition. This is clarified with relatively high heat losses from the walls of the combustion chamber at low load condition, which adversely affects the efficiency. Therefore, more fuel is required for the same output power at low load condition [32]. BSFC increases with the higher aromatic contents in the blend. Due to the low calorific values of fuel blends with 31.5% aromatic content by mass, more fuel was required to attain the same power output. Although alkylbenzenes are heavy hydrocarbons, global density of test fuel was still less than that of diesel due to low density of base fuel. Low global density improved spray characteristics, reduced fuel droplets size and thereby, improves the combustion efficiency. Due to lower overall cetane number and calorific value of fuel blends, BSFC increases with aromatic content. Moreover, it shortens the ignition delay for fuels with 21.5% aromatic content by mass and increases the in-cylinder pressure [199]. Due to this, the fuel vaporization and air-fuel mixing is improved that leads to better combustion and reduced fuel consumption. Furthermore, higher boiling point of aromatics along with their higher degree of unsaturation restricts the pyrolysis of the fuel and consequently adversely affects the combustion resulting in higher BSFC for fuel blends with 31.5% aromatic content by mass. H/C ratio also contributes to increasing the BSFC of fuel blends with higher aromatic contents. The highest improvement was observed with ethylbenzene in which BSFC was reduced by 2.54% and 5.66% at low and high load conditions, respectively with 5% blending in the base fuel. Moreover, BTE is increased by 2.07% and 3.6% at low and high load conditions respectively for the same blend. The performance of ethylbenzene is followed by o-Xylene, toluene, diethylbenzene, styrene, pseudocumene, 5-tert-butyl-m-Xylene, p-Cymene, tertbutylbenzene, cumene, 3-isopropylcumene, α-methylstyrene.



(a) Low load



(b) High load

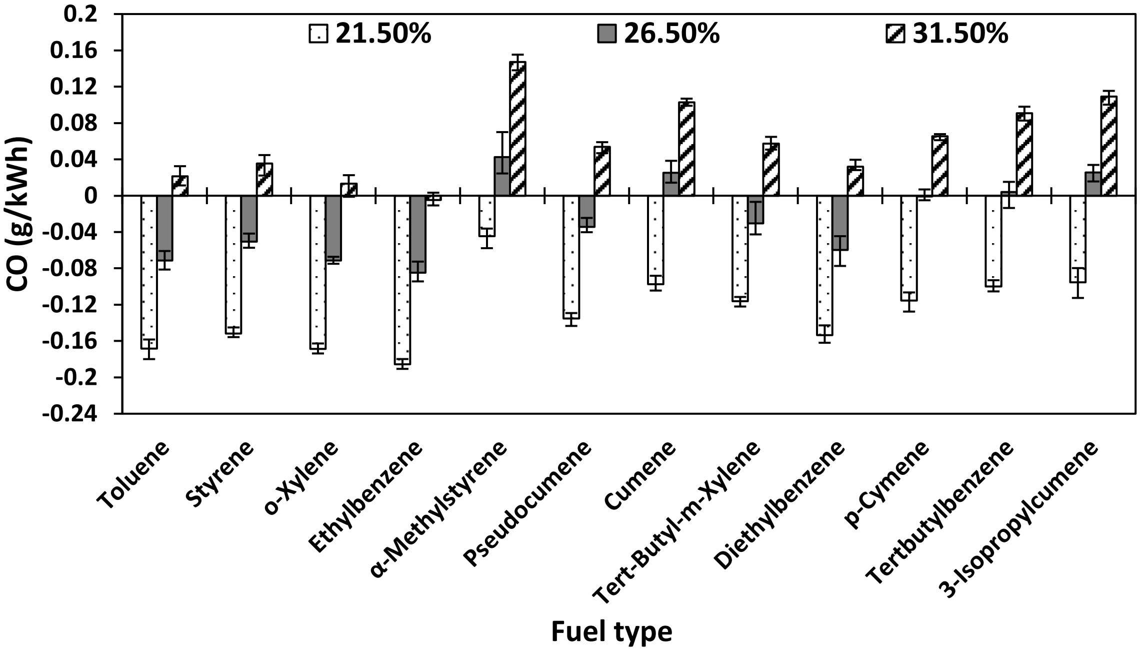
Figure 5.2 BTE results of alkylbenzene blended fuels compared to diesel fuel

5.3 Pollutant Emissions

5.3.1 CO and UHC Emissions

Aromatic contents and their structure affect the emission formation. The effect of different compositions of fuel blends on CO and UHC emissions at low and high load conditions is shown in Figure 5.3 and 5.4 respectively. CO and UHC are produced in diesel engine due to incomplete combustion of fuel used [190]. CO and UHC emissions are higher at low load condition compared to high load due to the lean air-fuel mixture which led to incomplete combustion. CO concentrations were increased with aromatic content, which is similar to studies by Qian et al. [176] and Hochhauser [175]. The higher CO emissions were produced because alkylbenzenes have dominant C-C bonds, low H/C ratio and no oxygen content. This made the homogeneity of air-fuel mixture more difficult leading to incomplete combustion. At high load, more CO emissions are converted to CO_2 due to better air-fuel mixture and oxidization process.

However, fuels with a lower calorific value produced high CO emissions at both engine loads. In particular, at low load condition, 15% α-methylstyrene- 85% base fuel produced the highest CO levels as compared to other tested alkylbenzenes. This is because of the inferior combustion characteristics of this fuel blend due to its low calorific value and cetane number compared to the other alkylbenzenes. UHC formation depends mainly on the formation of rich fuel pockets in the boundary layer region. All the tested alkylbenzenes have lower boiling point that shorten the penetration distance and enhances the fuel atomization. This results in reduced UHC emissions [200]. An increase in the aromatic content in the fuel result in increased global density of the fuel and leads to a long penetration distance and increased UHC emissions. The UHC emissions are higher for heavier aromatics. This is mainly contributed by the higher degree of unsaturation of these aromatics that leads to the higher concentration of unburnt hydrocarbon compounds and deteriorates the combustion performance of the ternary mixtures in the engine cylinder.



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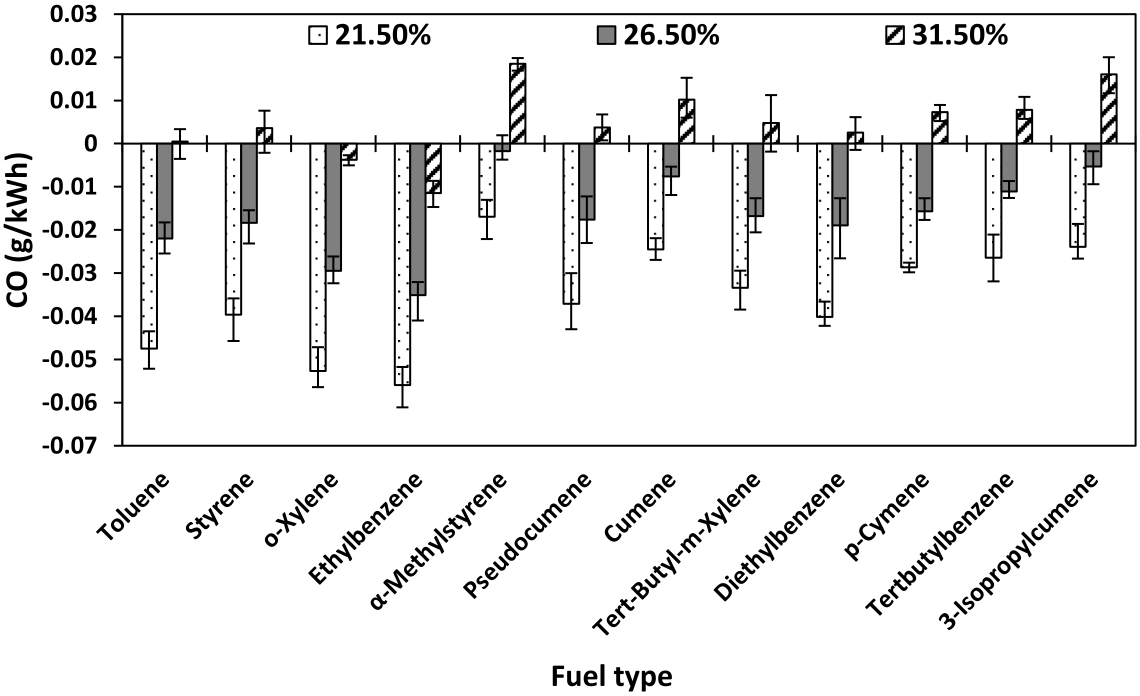

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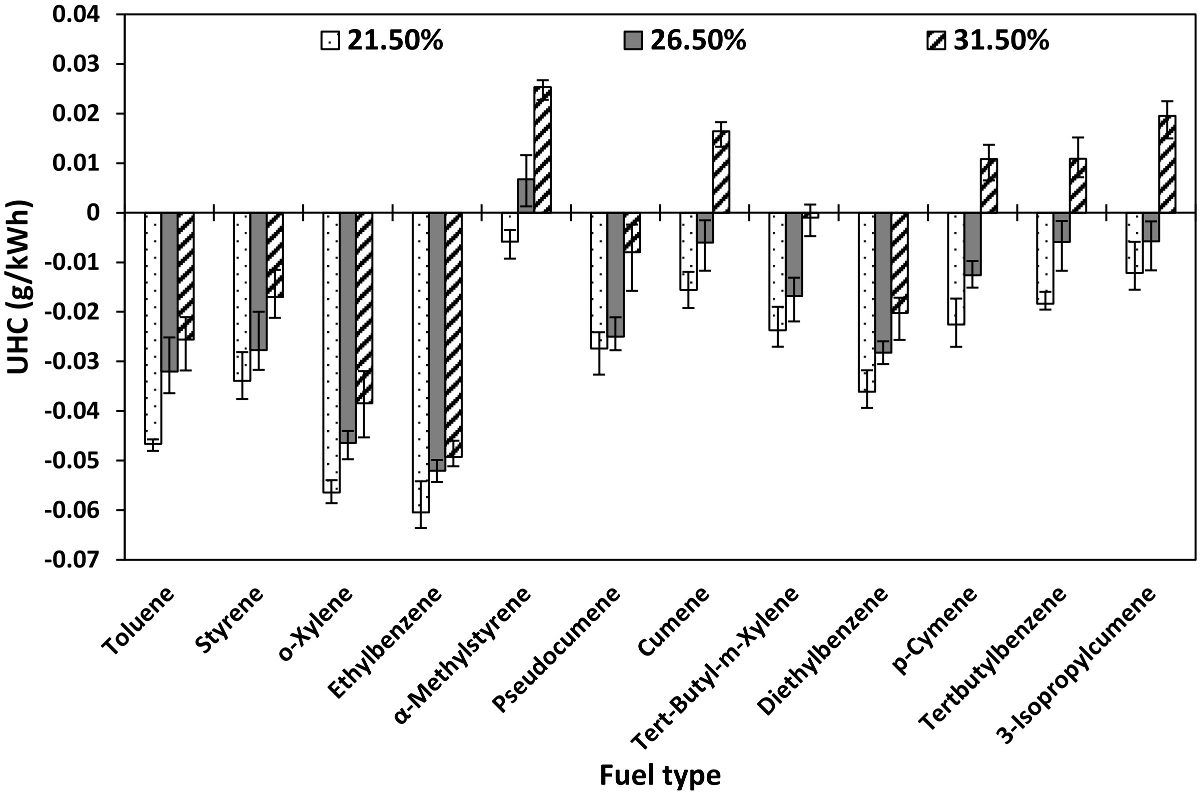
Figure 5.3 CO results of alkylbenzenes blended fuels compared to diesel fuel



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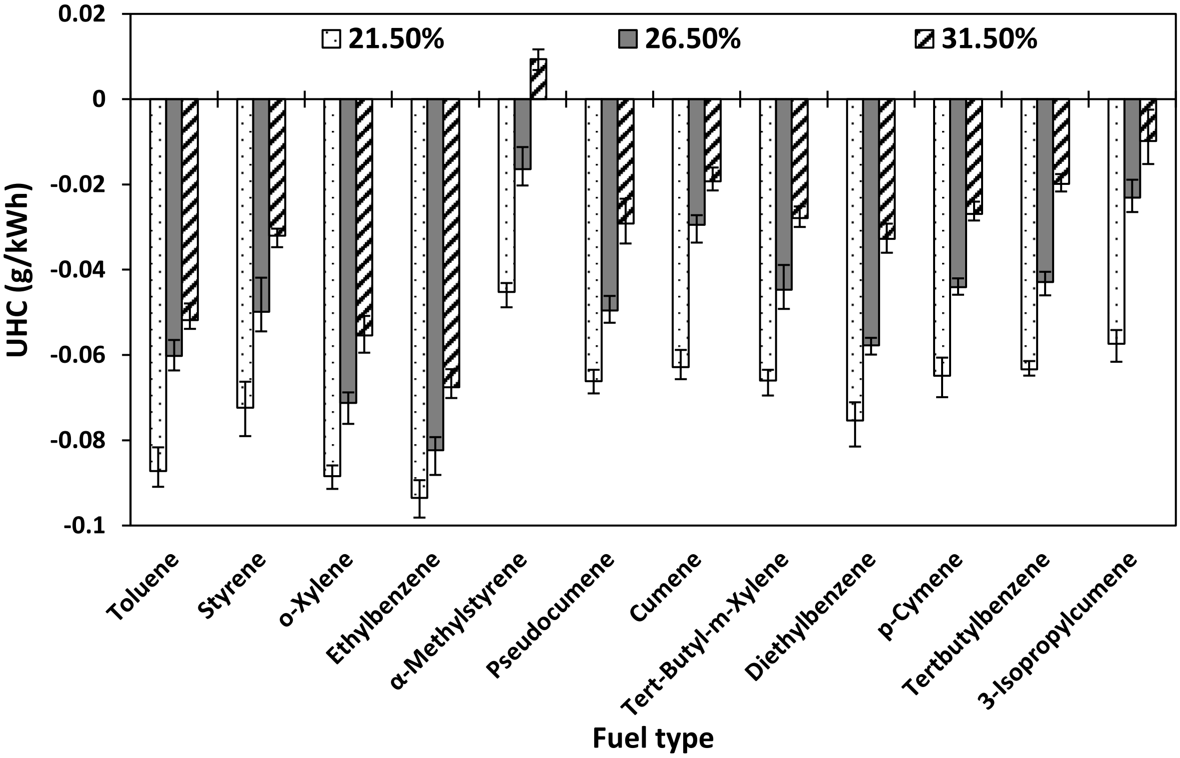

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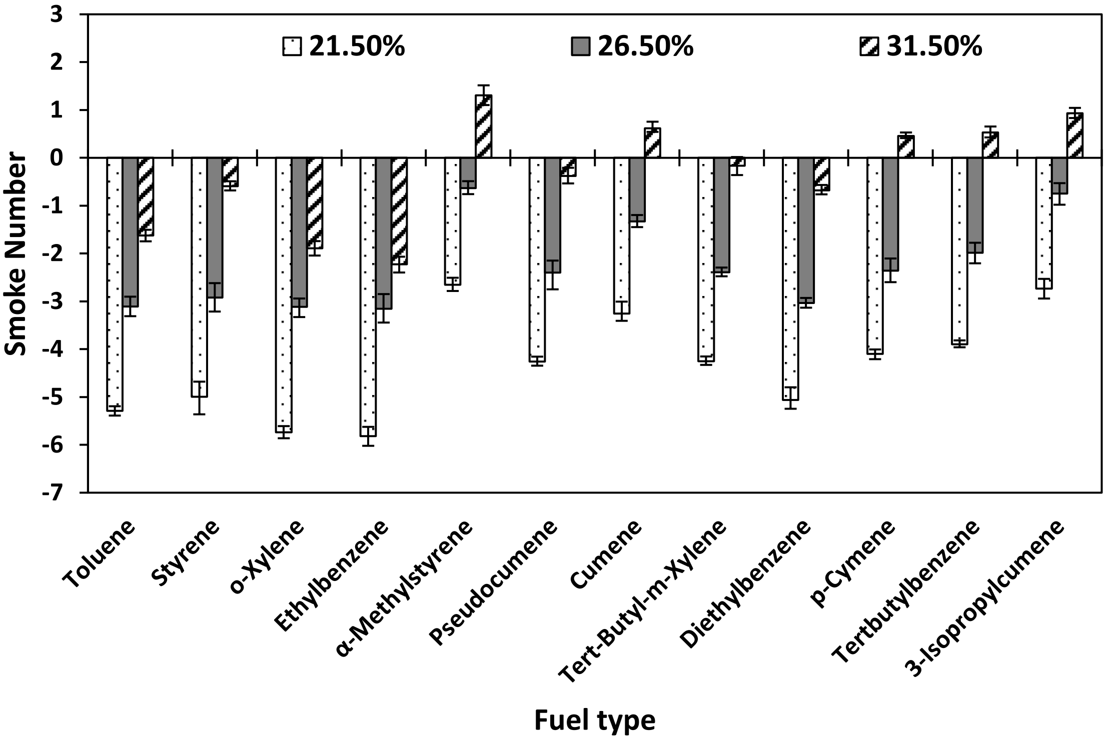
Figure 5.4 UHC results of alkylbenzenes blend fuels compared to diesel fuel

5.3.2 Smoke Emissions

PM components mainly consist of soot particles and it is responsible for the smoke opacity in the exhaust. Figure 5.5 shows the effect of different alkylbenzenes on the smoke emissions at low and high load conditions. For smoke emissions, it was observed that aromatic content in fuel had negative effect on smoke number because of dominant C-C bounds, low H/C ratio and the difficulty of aromatic pyrolysis.

Diesel fuel produced typical high smoke emissions although it contained 23.6 % aromatic content compared to some fuels with 31.5% aromatic content by mass. This was because single-chain alkanes were dominant in the base fuel that was blended with aromatics. While, diesel fuel contains high content of cycloalkanes resulting in high smoke number. Fuels including ethylbenzene and o-Xylene produced low smoke levels because of their better properties such as high H/C ratio, cetane number and low density compared to the other alkylbenzenes. The impact of methyl branch in different alkylbenzenes was insignificant even though their slight increased H/C values compared to other alkylbenzenes. The possible reason may relate with high boiling points of alkylbenzenes with large methyl number resulting in poor spray characteristics and hence incomplete combustion.



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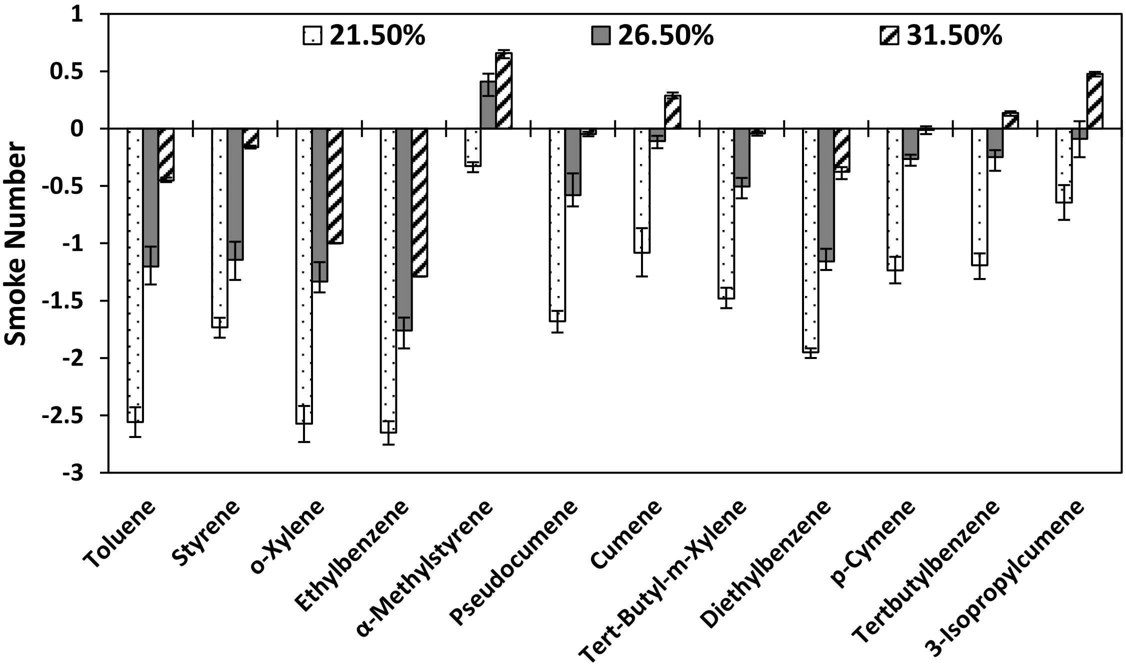


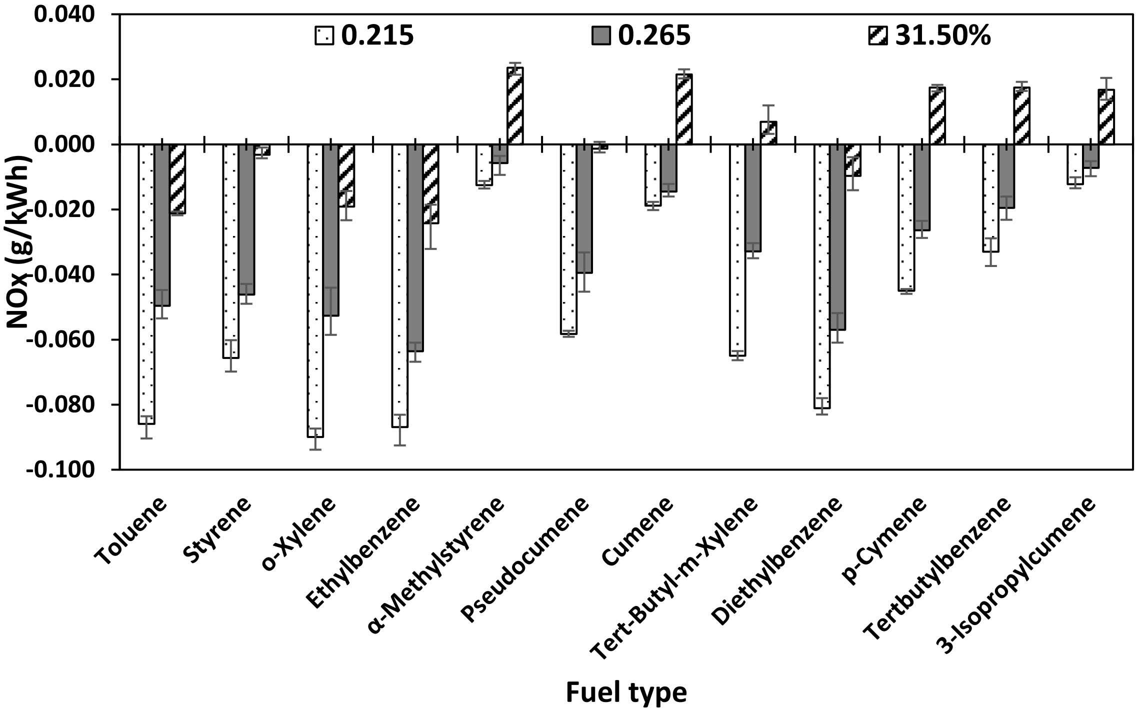
(b) High load

Figure 5.5 Smoke results of alkylbenzenes blended fuels on compared to diesel fuel

5.3.3 NO_x Emissions

The air-fuel mixture was too lean at low load which led to low combustion temperature due to air dilution [13]. With increasing engine load, more fuel was required with constant induced air. Burning more fuel resulted in more heat generated and an increased combustion temperature as well as NO_x emissions. It was also observed that increasing alkylbenzene content in test fuels impacts NO_x emissions as illustrated in figure 5.6. As hydrocarbons with ring structures have high flame temperatures compared to other fuel components, test fuels with high aromatic content produced a locally high-temperature region which has a tendency to increase the NO_x emissions [177, 201].

NOx levels varied from one alkylbenzene to another according to each alkylbenzene properties such as H/C ratio and density as shown in figure. 5.7 and 5.8 respectively. Neill et al. [181] indicated that there is a strong relation between hydrogen content in fuel and NOx emissions.. As the aromatic content in the fuel blends increases, H/C ratio decreases and hence NOx emission increase. Due to higher aromatic content fuels, a premixed combustion zone is formed in the early phase of the combustion. This results in increased in-cylinder temperature and consequently higher NOx emissions. The advancement in the occurrence of the maximum in-cylinder temperature due to aromatic content perhaps results in increased residence time, a favorable condition for NOx formation [202] This is the reason for high NOx emissions of fuel blends with 31.5% aromatic content by mass as compared to 21.5% and 26.5% aromatic content fuels.



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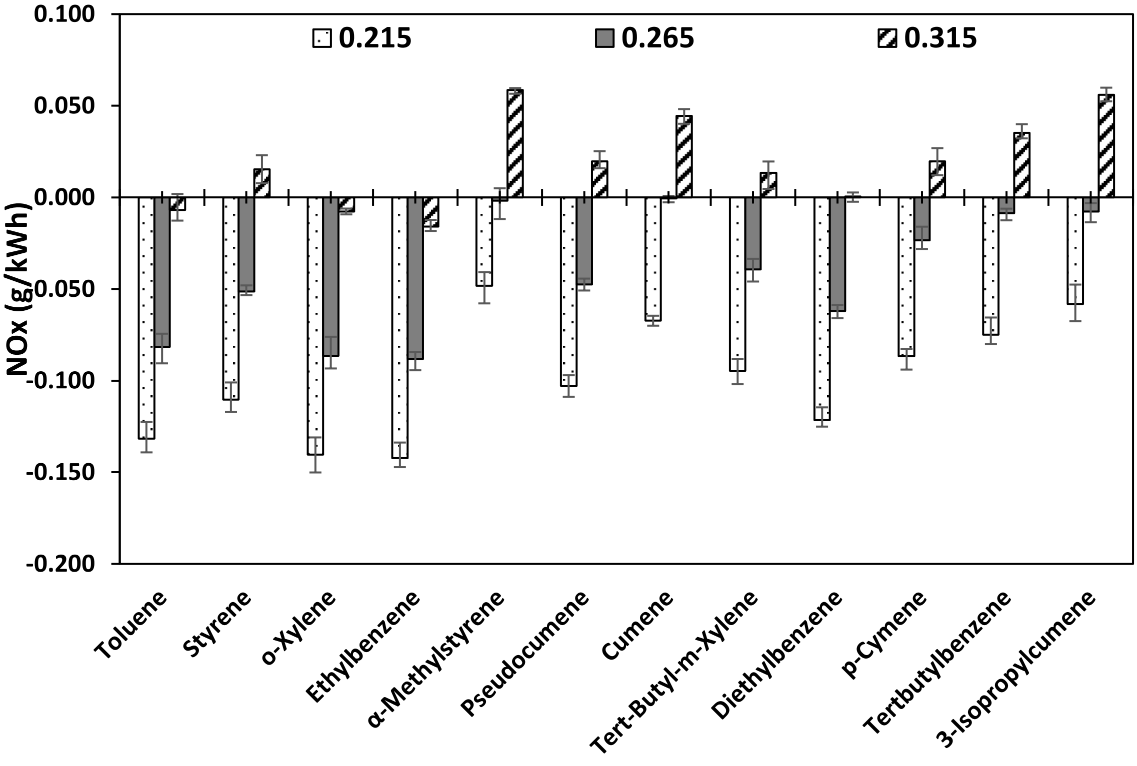

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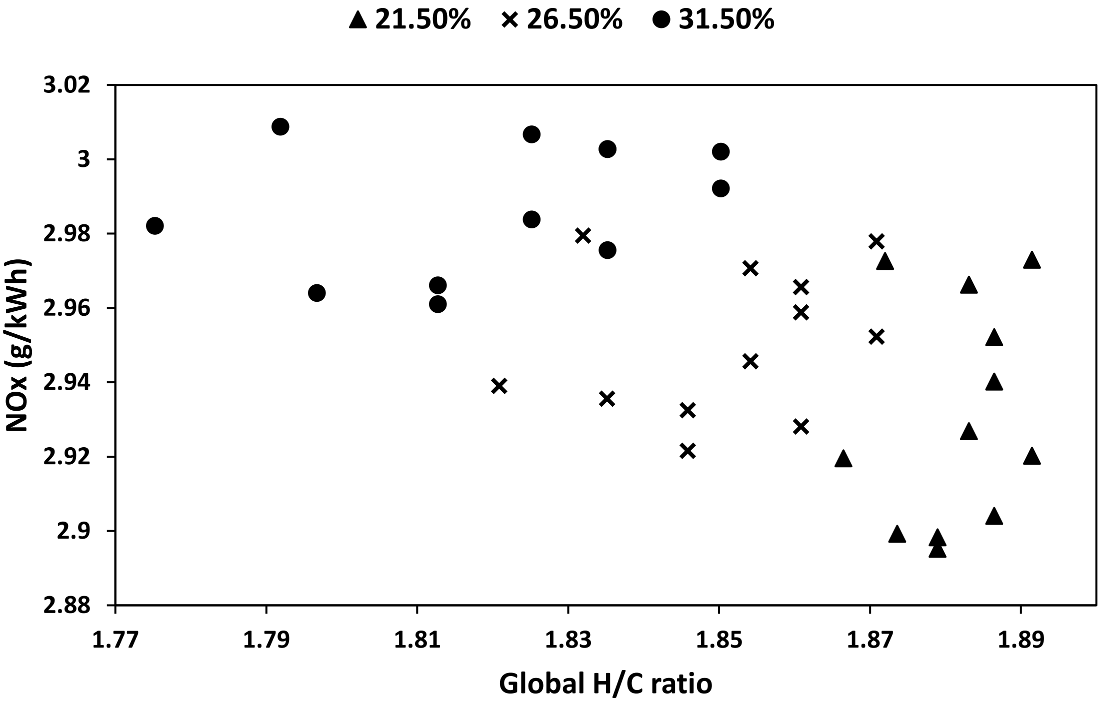
Figure 5.6 NO_x emissions of alkylbenzenes blended fuels compared to diesel fuel



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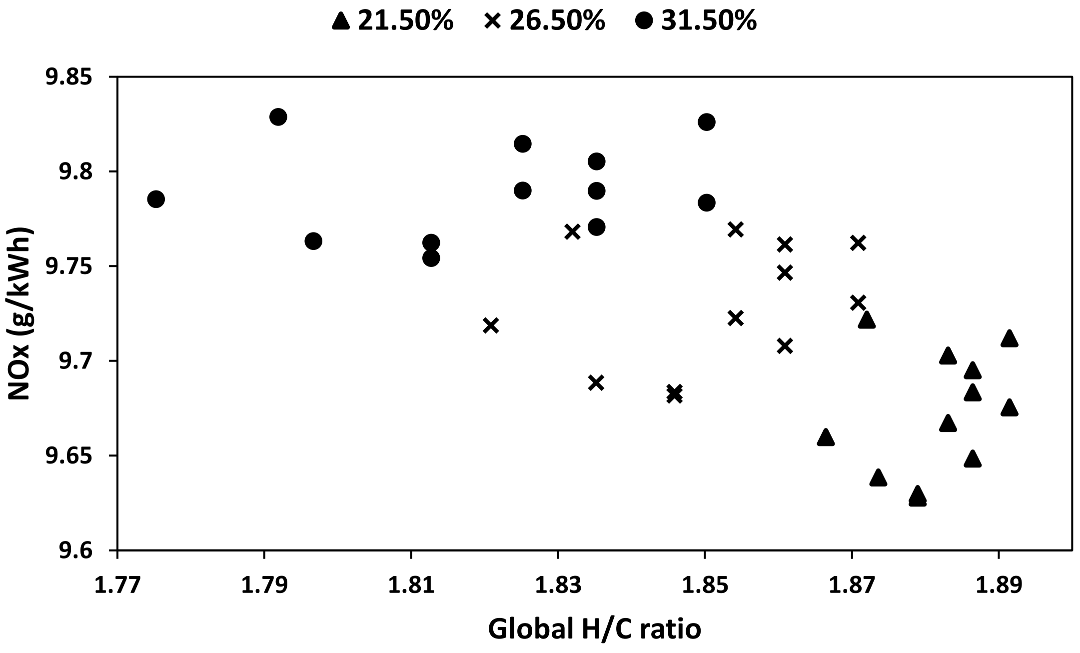

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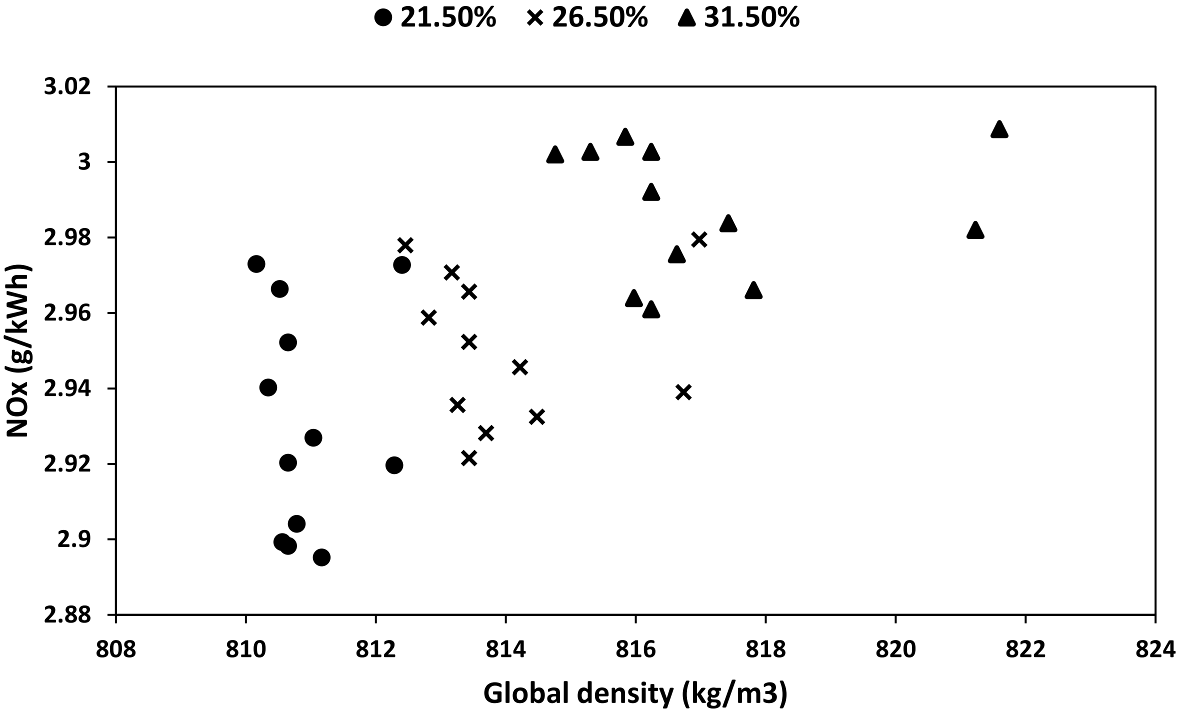
Figure 5.7 Effect of global H/C ratio on NO_x emissions of tested fuel blends



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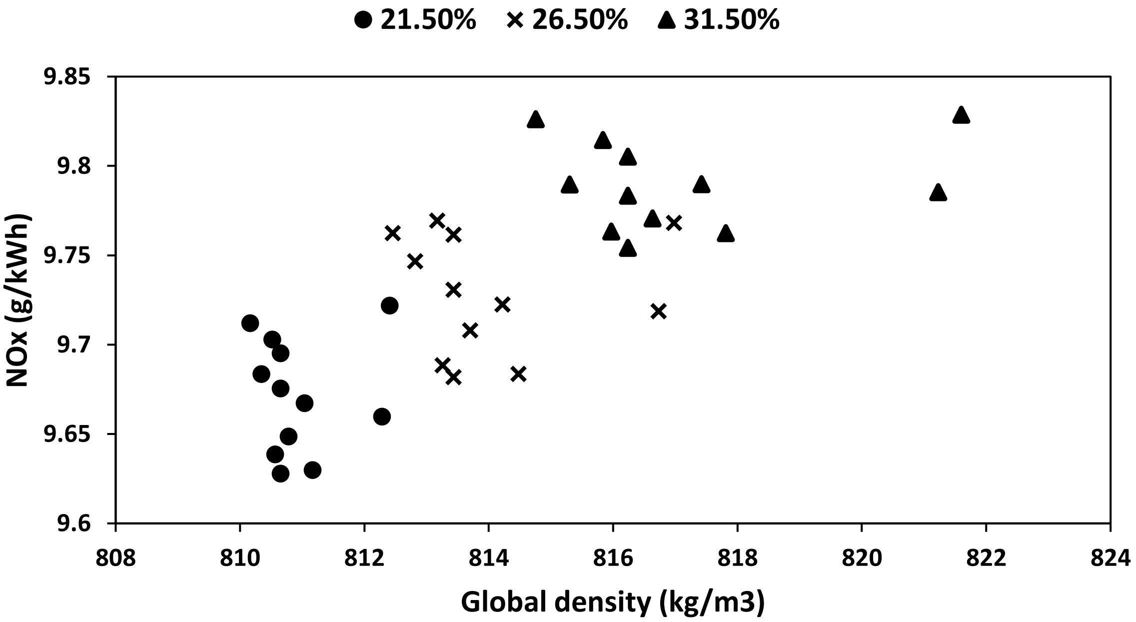


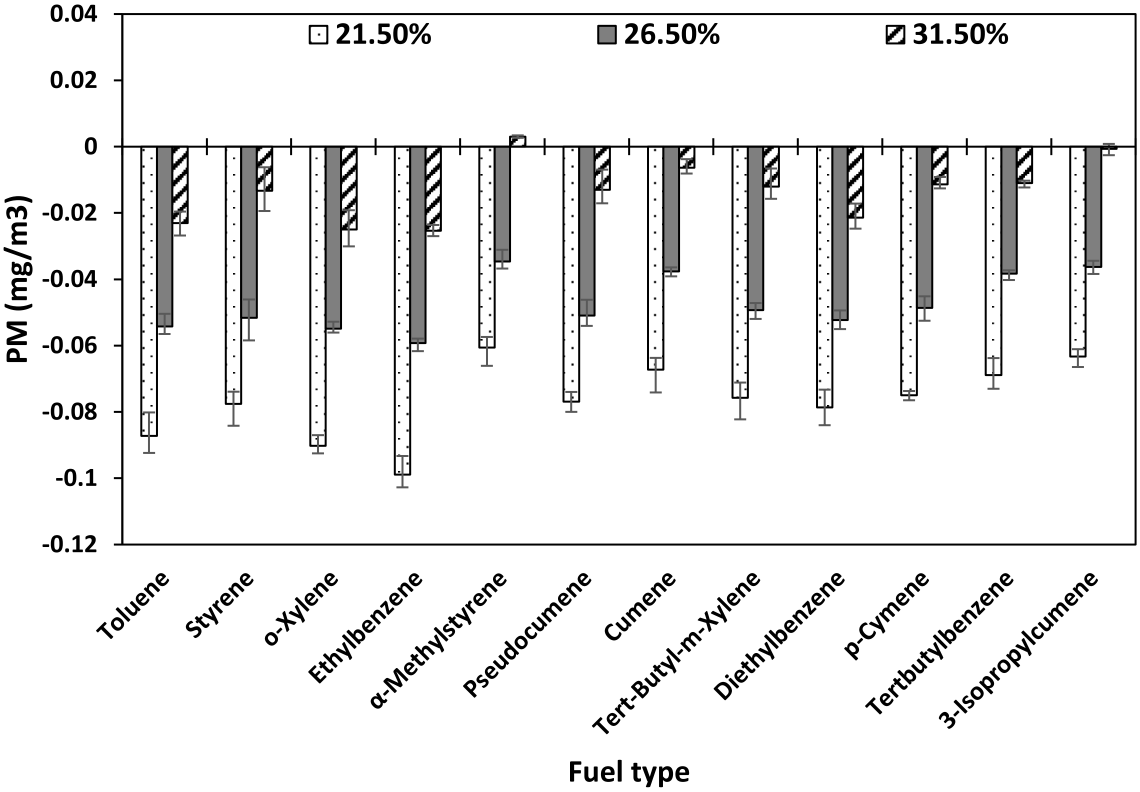
(b) High load

Figure 5.8 Effect of global density on NO_x emissions of tested fuel blends

5.3.4 PM Emissions

At high engine load, high PM concentrations were produced due to lack of induced air at typical high temperatures [12, 19]. Figure 5.9 shows increased PMs with increasing aromatic content. This is similar to the aromatic-PM impact available in many studies [39, 43, 175, 203-206]. Kidoguchi et al. [177] and Keda [207] stated that higher PM concentrations are related to pyrolysis difficultly of aromatics. Therefore, more PMs are formed through incomplete oxidization process because of direct polymerization products from aromatics.

Aromatic density and H/C ratio also play a role in the formation of PM. Figure 5.10 and 5.11 show the effect of H/C ratio and density on PM emissions at varying load conditions respectively. As carbon atoms are the main source of particulates, blending alkylbenzene increased carbon content in fuel composition leading to more soot formation. Therefore, lower PM concentrations were found for the tested fuels that have low density and high H/C ratio. fuel blends that have 21.5% and 26.5% aromatic contents emit lower PM emissions in the exhaust compared to fuel blends with 31.5% aromatic content by mass at both low and high load conditions. Higher PM emissions are recorded for fuels with higher aromatic contents in the binary mixture of base fuel and aromatics. Lower H/C ratio of blends with higher aromatic contents adversely affect the combustion characteristics of blends and hence, PM emission increase. Among the alkylbenzenes, ethylbenzene has better physicochemical properties like a higher calorific value, higher H/C ratio, lower boiling point, etc. These properties result in better combustion characteristics with a shorter ignition delay, higher flame propagation rate of ethylbenzene blended fuel, which reduces the soot formation tendency leading to a reduction in PM emissions [208].



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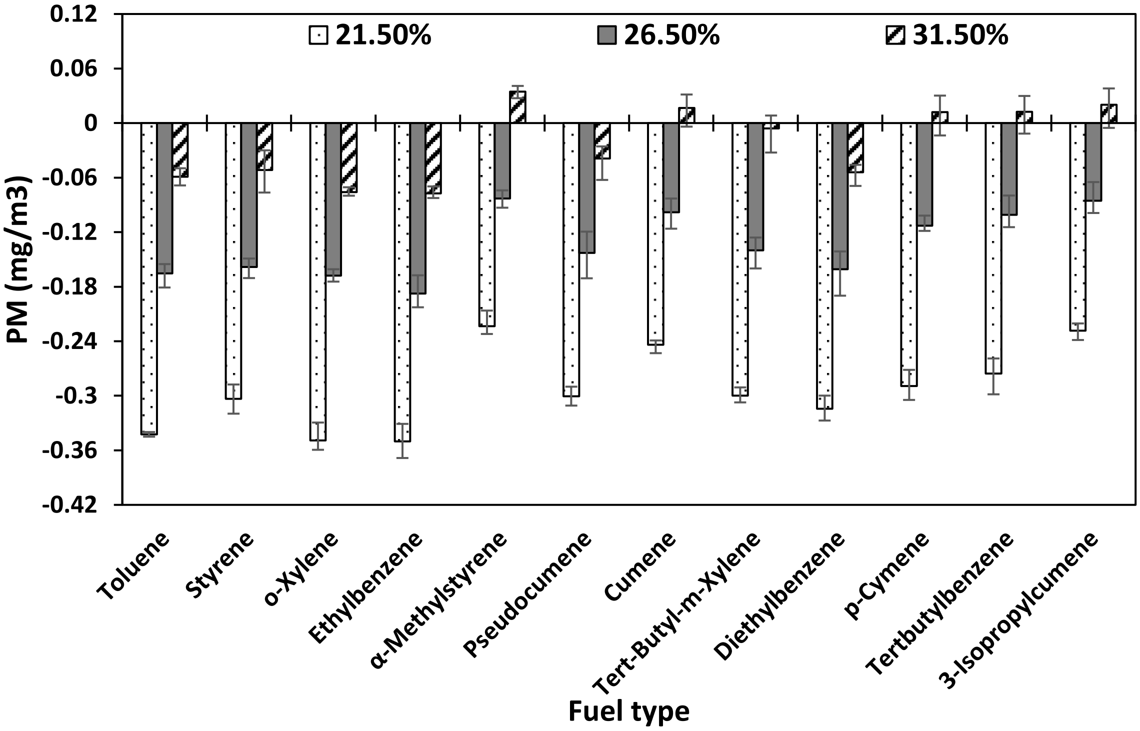

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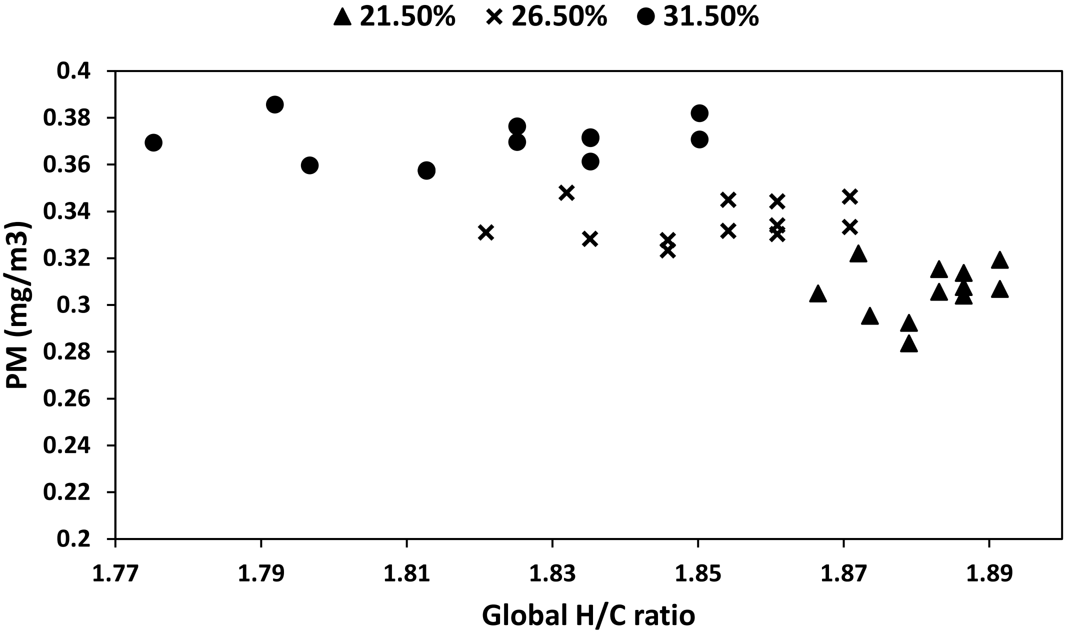
Figure 5.9 PM emissions of alkylbenzenes blended fuels compared to diesel fuel



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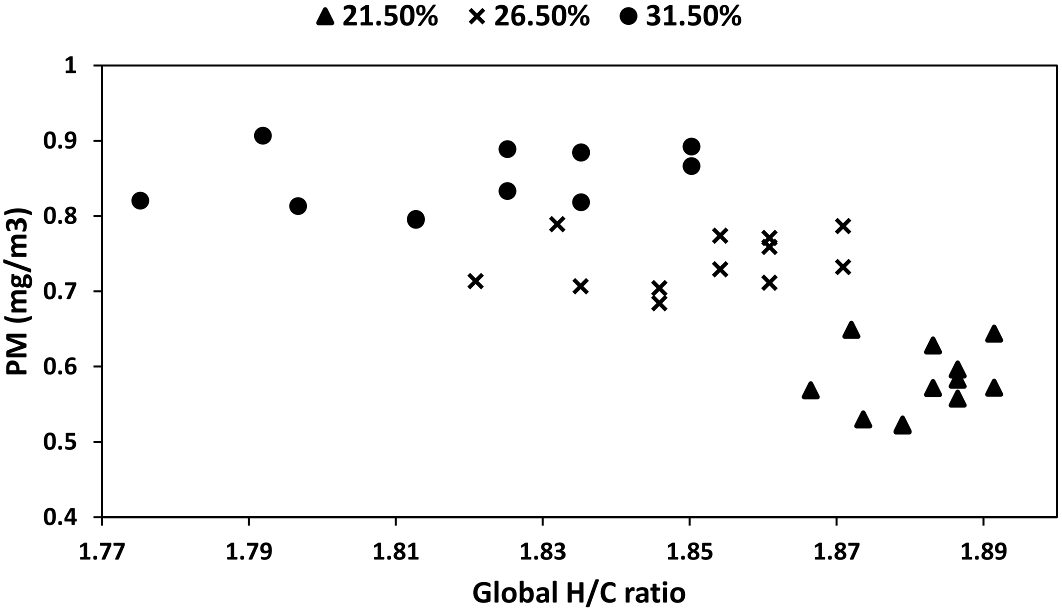

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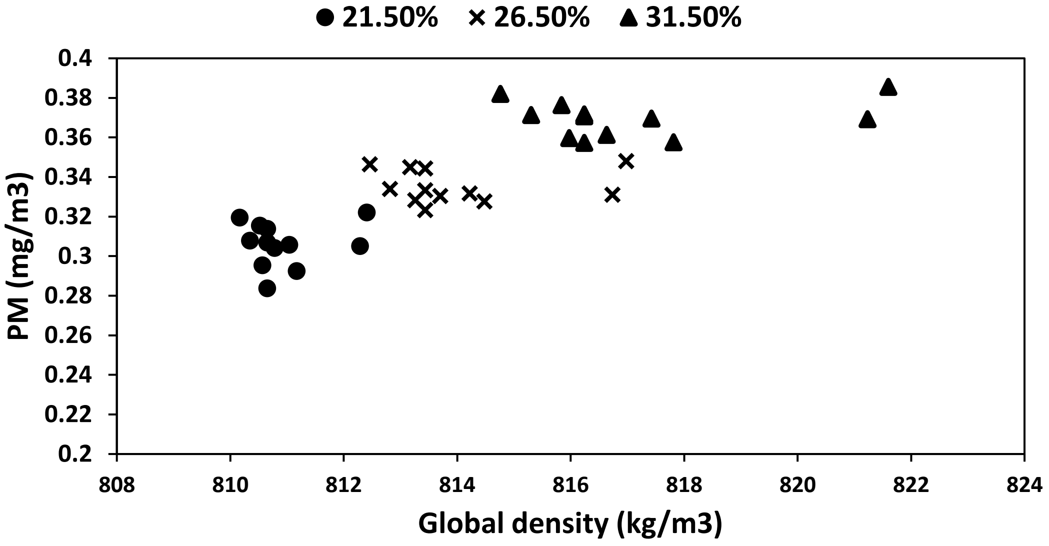
Figure 5.10 Effect of global H/C ratio on PM emissions of tested fuel blends



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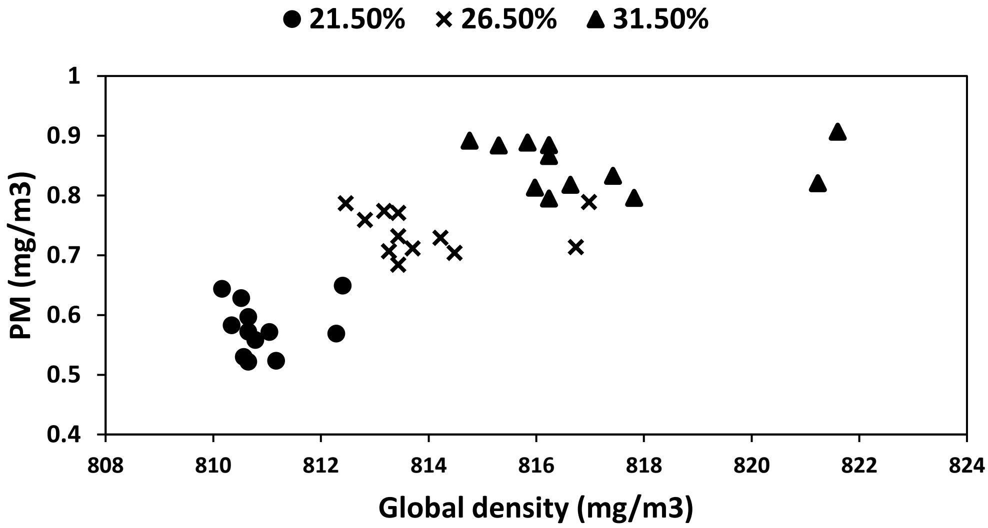


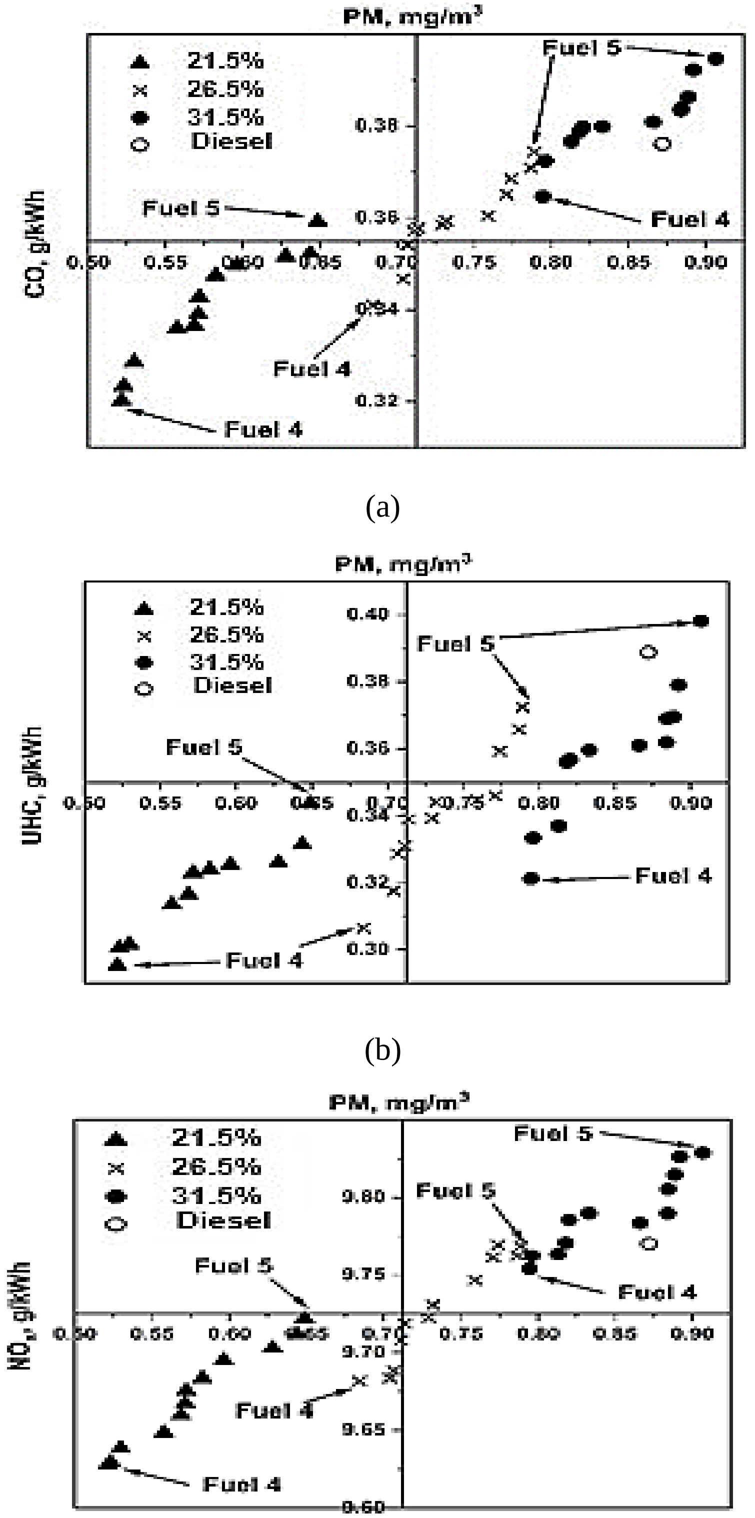
(b) High load

Figure 5.11 Effect of global density on PM emissions of tested fuel blends

5.4 Correlations

5.4.1 Correlations of PM with Other Emissions

Figure 5.12 shows the correlation of the PM emissions with CO, UHC and NO_x at high load conditions. As shown in the figure, Fuel 4 (ethylbenzene) and Fuel 5 (α-methyl styrene) show the limiting cases, where the former stands for lower side and the later stands for higher side of CO, UHC and NO$_x$ emissions.



(a)

(b)

(c)

Figure 5.12 (a-c) Correlation of PM with CO, UHC and NO$_x$ emissions at high load

From this data, it can be concluded that the selection of a single added aromatic with optimal concentration is necessary for better engine performance and lower emissions. For the present study, ethylbenzene is observed to be an appropriate choice for surrogate fuels for a diesel engine.

5.4.2 Development of NOx and PM Correlations

It was observed that PM and NO_x emissions were impacted by global fuel properties such as aromatic content, H/C ratio and density. In agreement with experimental results, PM correlation were developed as function of aromatic content (P_1), H/C ration (P_2) and density (P_3) as follow;

(a) Expression of change of PM emissions due to different aromatic concentrations (i.e. 5, 10 and 15% by mass) are obtained according to mathematical analysis as shown in Eq (5.1).

$$\Delta \mathrm{PM}(\mathrm{P}_1) = -0.0039\mathrm{P}_1^2 + 0.154\mathrm{P}_1 + 0.326 \qquad \text{(Eq 5.1)}$$

(b) Expression of change of PM emissions because of engine load was obtained. The changes in PM results due to load effect were calculated and hence, load coefficients were calculated to be 0.27 at high load and 0.0001 at low load. In order to consider load effect on PM emissions, Eq (5.1) is multiplied by load coefficient (L) as illustrated in Eq (5.2).

$$\Delta \mathrm{PM} = -0.0039\mathrm{P}_1^2\mathrm{L} + 0.154\mathrm{P}_1\mathrm{L} + 0.326\mathrm{L} \qquad \text{(Eq 5.2)}$$

(c) Correlation between PM emissions and global H/C ratio obtained at 5% tested aromatic content and low load. Eq (5.3) shows the correlation between PM concentrations and H/C ratio.

$$\mathrm{PM}(\mathrm{P}_2) = 16.19\mathrm{e}^{(-2.094\mathrm{P}_2)} \qquad \text{(Eq 5.3)}$$

(d) Correlation between PM emissions and global density also developed at 5% tested aromatic content and low load. Eq (5.4) shows the correlation between PM concentrations and density.

$$\mathrm{PM}(\mathrm{P}_3) = 2 \times 10^{-9}\mathrm{e}^{(0.0232\mathrm{P}_3} \quad \text{(Eq 5.4)}$$

(e) From Eq 5.3 and Eq 5.4, it was obtained that the sum of PM(P_2) and PM(P_3) is equivalent to 2×PM(P_2,P_3).

$$\mathrm{PM}(\mathrm{P}_2) + \mathrm{PM}(\mathrm{P}_3) = 16.19\mathrm{e}^{(-2.094\mathrm{P}_2)} + 2 \times 10^{-9}\mathrm{e}^{(0.0232\mathrm{P}_3} = 2 \times \mathrm{PM}(\mathrm{P}_2, \mathrm{P}_3) \quad \text{(Eq 5.5)}$$

Dividing Eq 5.5 by 2

$$\mathrm{PM}(\mathrm{P}_2, \mathrm{P}_3) = 8.095\mathrm{e}^{(-2.094\mathrm{P}_2)} + 1 \times 10^{-9}\mathrm{e}^{(0.0232\mathrm{P}_3)} \quad \text{(Eq 5.6)}$$

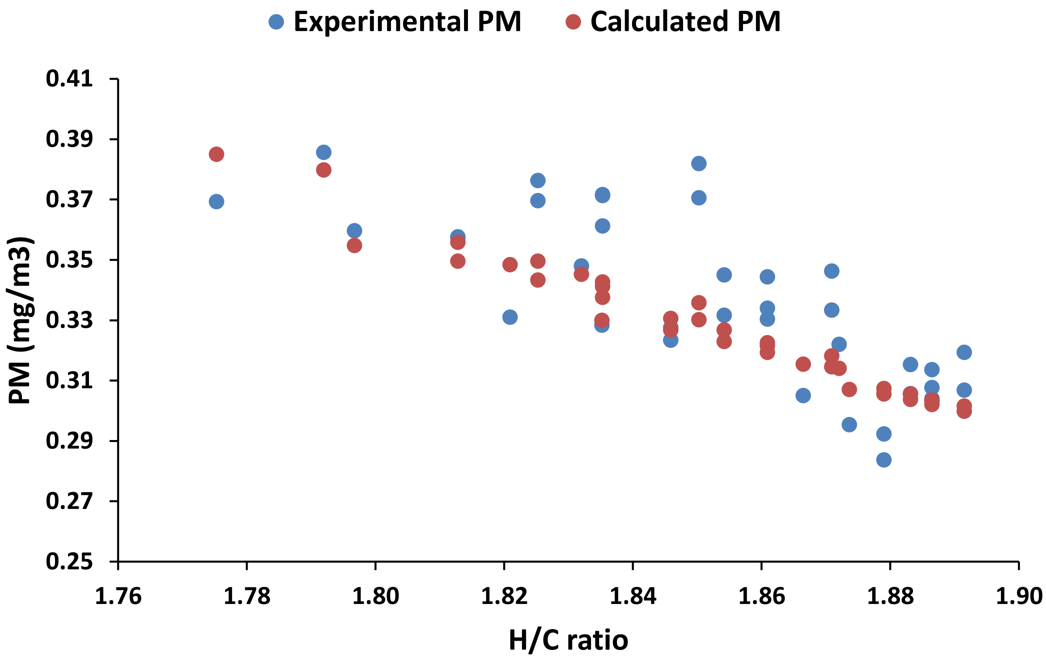
(f) Final PM equation is the sum of Eq 5.6 and Eq 5.2 as provided in Eq 5.7.

$$\mathrm{PM}(\mathrm{P}_1, \mathrm{P}_2, \mathrm{P}_3) = -0.0039\mathrm{P}_1^2\mathrm{L} + 0.154\mathrm{P}_1\mathrm{L} + 0.326\mathrm{L} + 8.095\mathrm{e}^{(-2.094\mathrm{P}_2)} + 1 \times 10^{-9}\mathrm{e}^{(0.0232\mathrm{P}_3)} \quad \text{(Eq 5.7)}$$

NO_x equation was also developed as function of d aromatic content, H/C ratio and density using the same procedure applied for PM equation. Load coefficient is 0.3 at low load and 1015 at high load.

$$NO_x(\mathrm{P}_1, \mathrm{P}_2, \mathrm{P}_3) = -4 \times 10^{-5}\mathrm{P}_1^2\mathrm{L} + 0.0016\mathrm{P}_1\mathrm{L} + \mathrm{L} + 316.37\mathrm{e}^{(-0.19\mathrm{P}_2)} + 33.74\mathrm{e}^{(0.0023\mathrm{P}_3)} \quad \text{(Eq 5.8)}$$

Figure 5.13 and 5.14 show comparison between experimental results and calculated PMs using Eq (5.7). Maximum error in calculated PMs is 8.25% as compared to experimental results, whereas Figure 5.15 and 5.16 show experimental and calculated NO_x results with 2.14% maximum error. The trends of the correlations presented above met a combustor test results. However, the combustor test results cannot be presented in this study as they belong to Chenxing Ling (PhD student at the University of Sheffield). Chenxing Ling and the author of this thesis are preparing a join paper including both results. However, there are many methods in literature that can be used to develop fuel properties correlations such as Threshold Sooting Index (TSI) and Double Bond Equivalence (DBE). These methods are defined in Appendix A.4.



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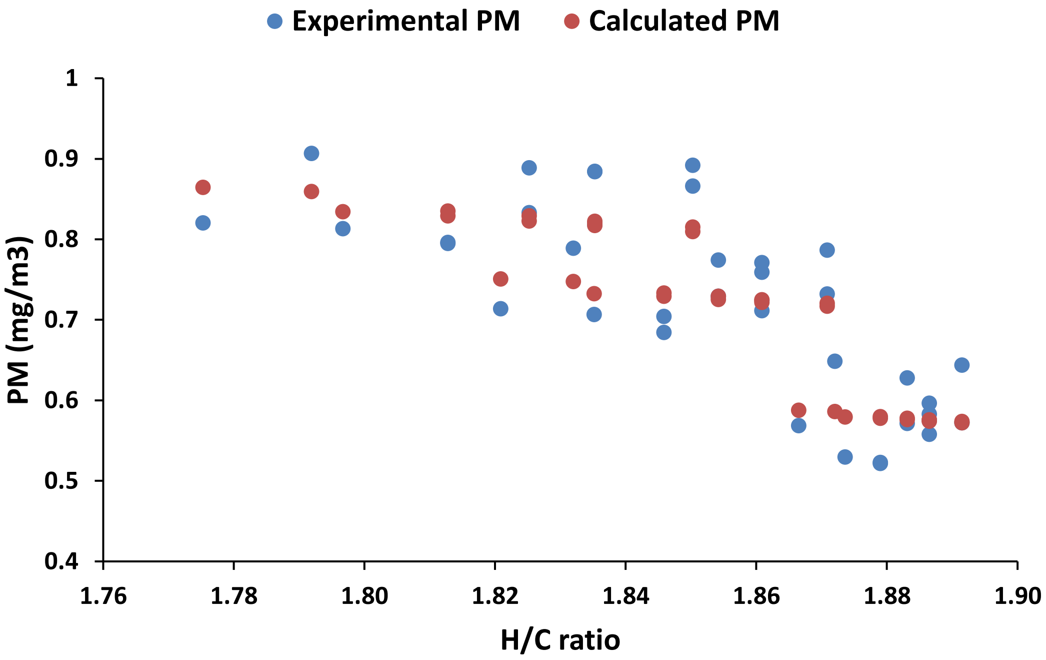
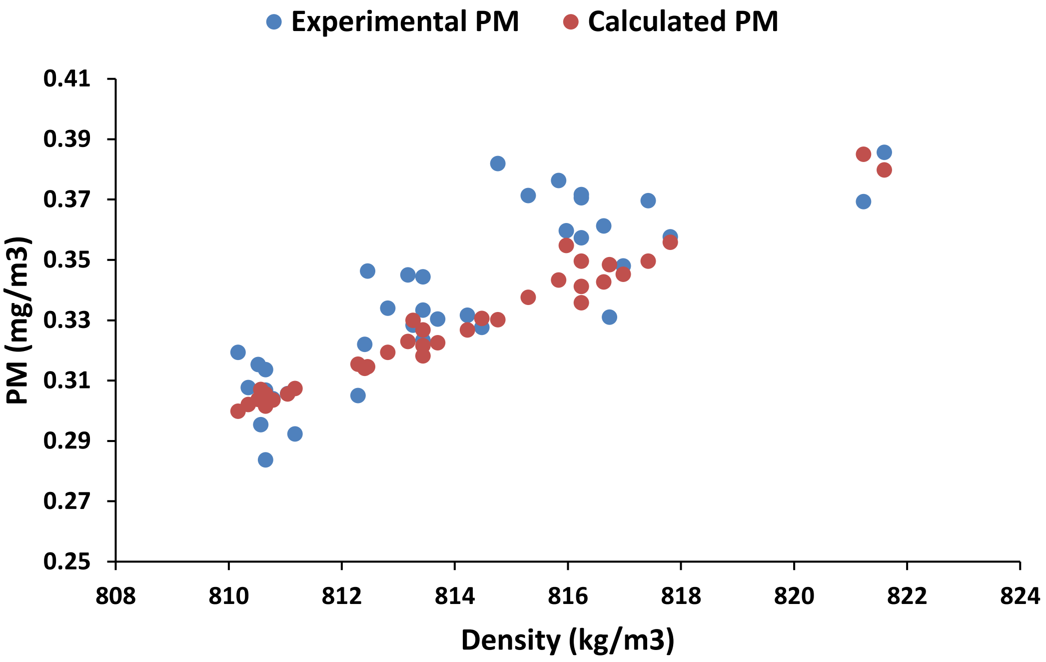


(b) High load

Figure 5.13 Experimental and calculated PMs against global H/C ratio



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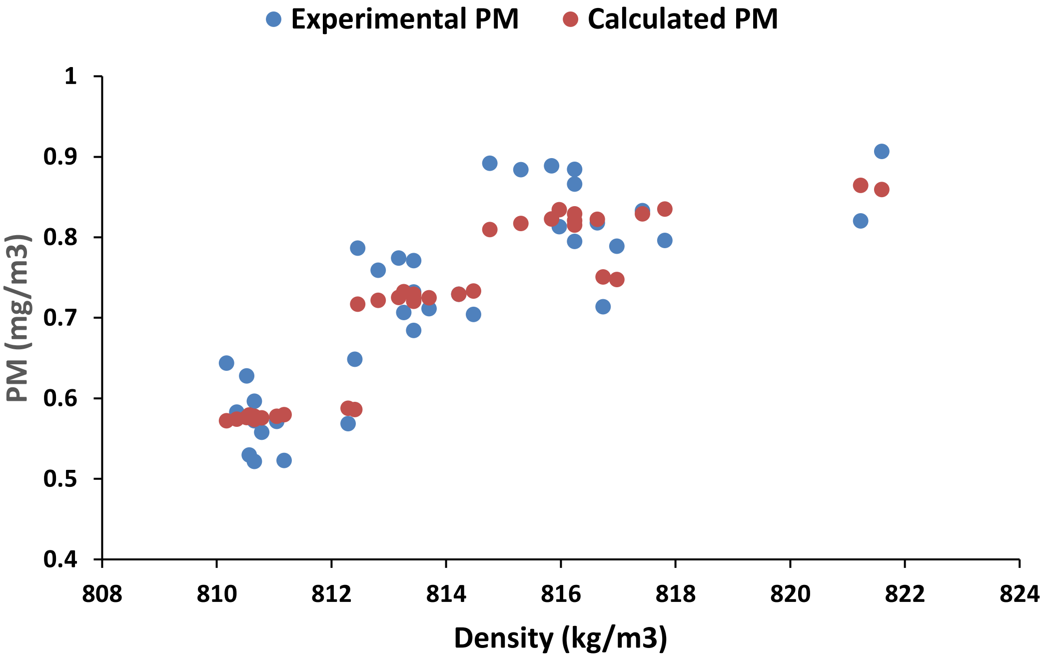
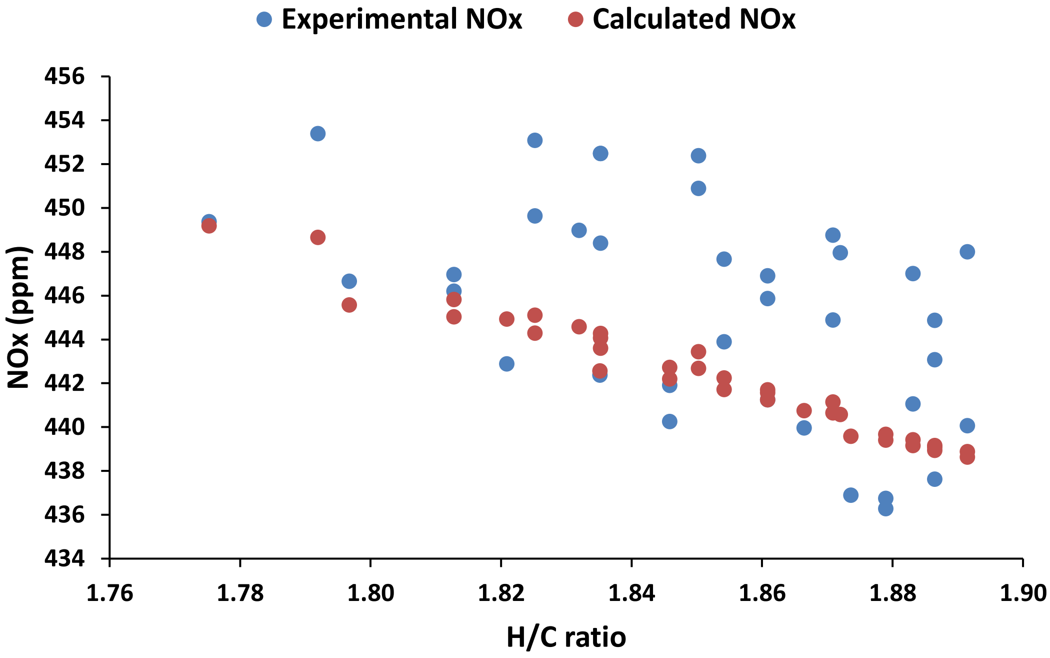


(b) High load

Figure 5.14 Experimental and calculated PMs against global fuel density



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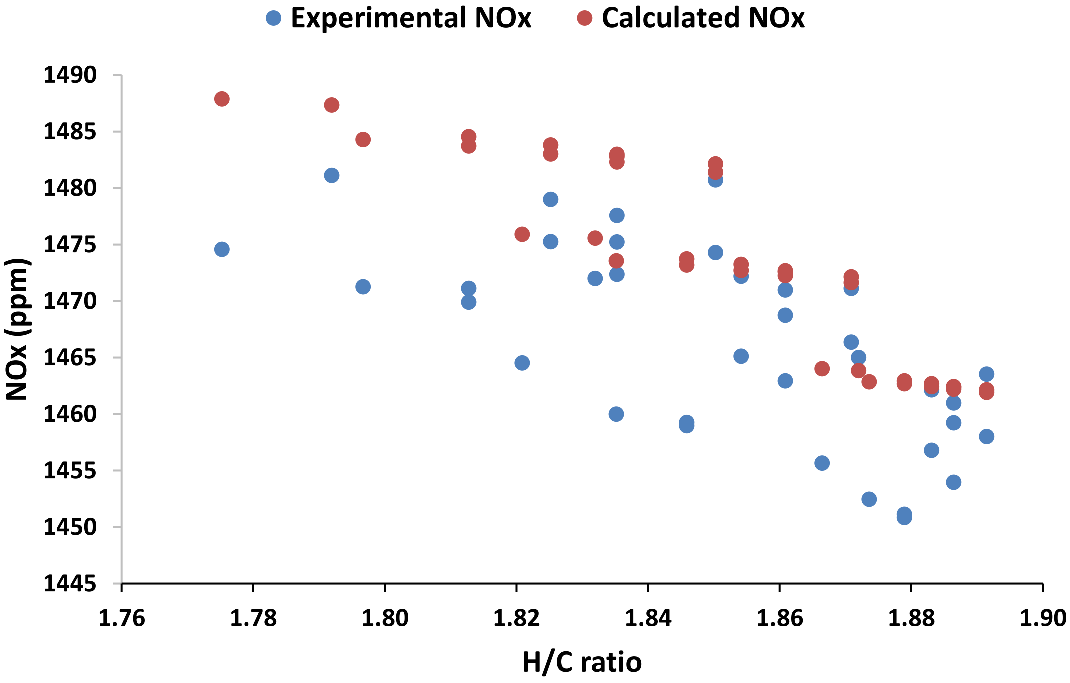

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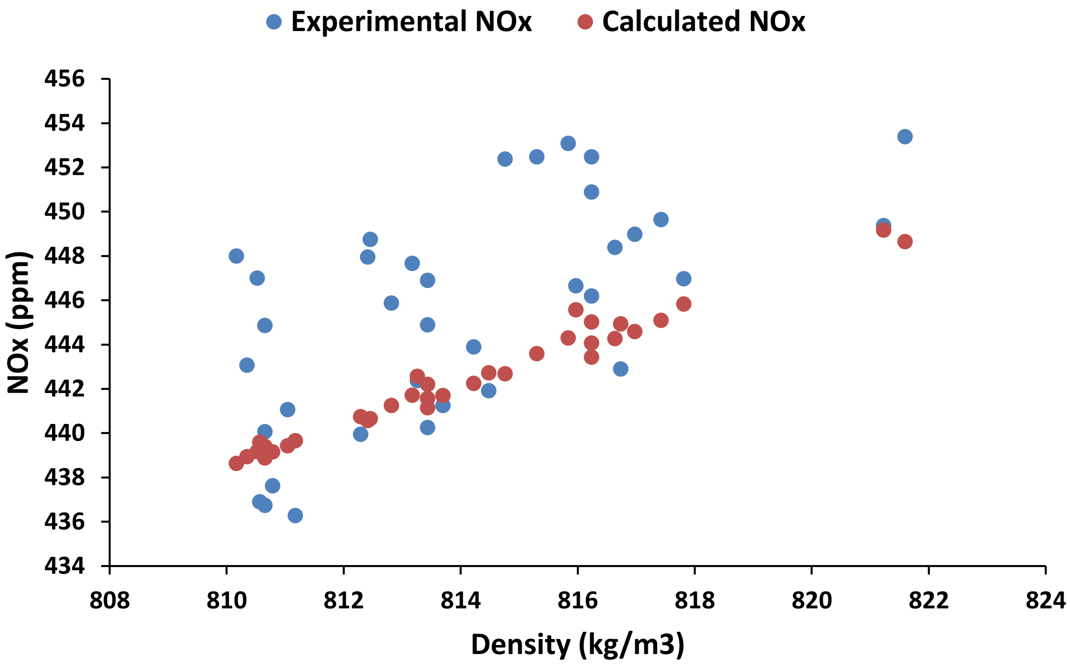
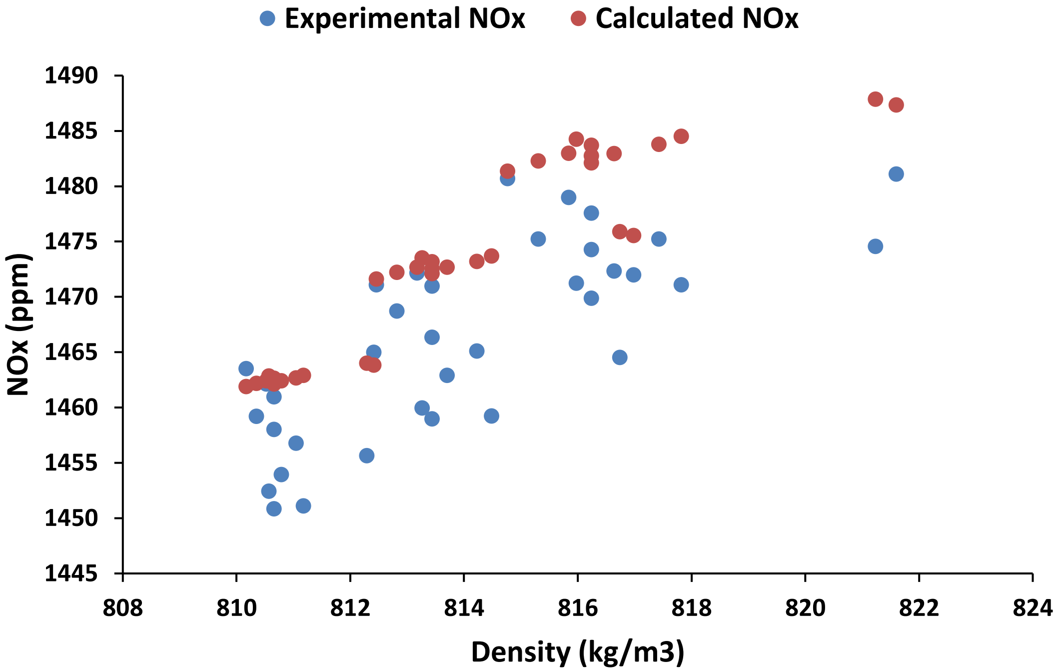
Figure 5.15 Experimental and calculated NO_x against global H/C ratio



(a) Low load



(b) High load

Figure 5.16 Experimental and calculated NO_x against global fuel density

5.5 Conclusion

The effect of different alkylbenzenes on performance and emissions of the CI engine were investigated experimentally. Engine performance and emission characteristics are highly affected by the fuel blend. BTE and BSFC were decreased and increased respectively with blending increased of aromatics because of associated lower cetane number and calorific value. High CO and UHC emissions were produced with higher aromatic contents of the fuel blends. NOx and PM emissions were increased because of high flame temperature and difficultly in pyrolysis of alkylbenzenes. Among all the tested blending ratio of 21.5%, 26.5% and 31.5% aromatic contents by mass, it has been found that 21.5% and 26.5% aromatic fuels have better performance in terms of BTE and BSFC as compared to fuels with 31.5% aromatic content by mass and diesel fuels due to better properties like calorific value, H/C ratio, cetane number, etc.

Comparison among test alkylbenzenes showed that α-methylstyrene impacted CO, NO_x and PM emissions associating with their lower calorific value, high boiling point and lower H/C ratio. Instead of lower calorific value of diethylbenzene, it shows better performance and lower emissions as compared to styrene because of higher H/C ratio**.** Ethylbenzene produced low PMs, NO_x, BSFC and high BTE due to its better physicochemical properties. Study of different alkylbenzenes can help in reforming aromatics in future diesel fuels with particular types displaying low environmental impact and better engine performance. NO_x and PM correlations are developed as a function of significant impacted properties. The correlations show highly agreeing with experimental trends of the results.

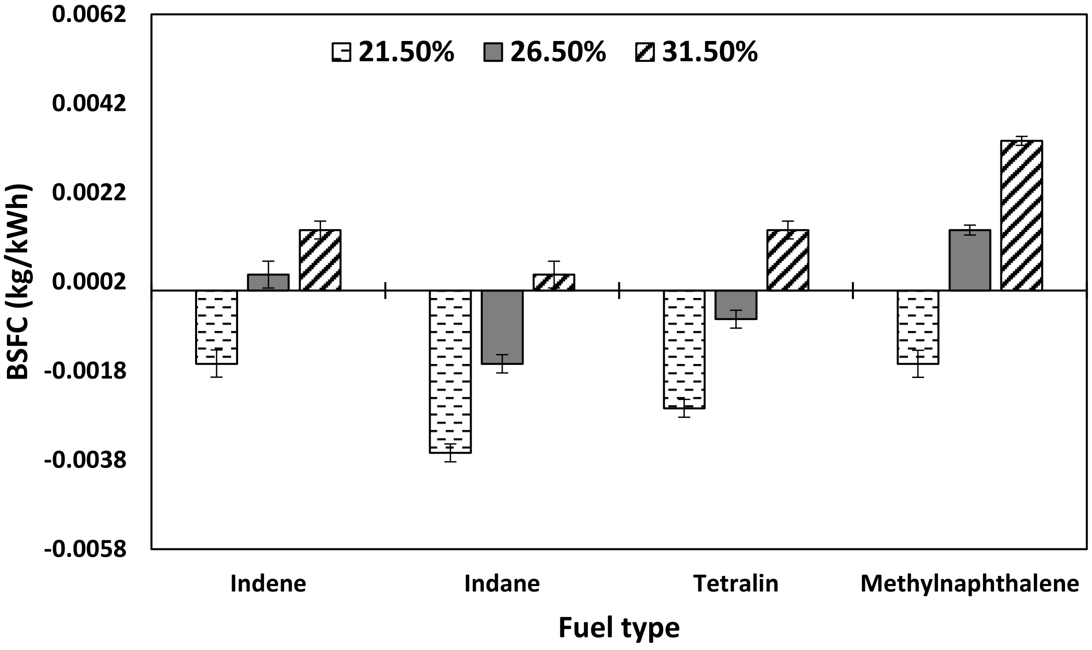
6 IMPACT OF POLYCYCLIC AROMATICS IN CI ENGINE

6.1 Overview

In this chapter, three polycyclic single-ring aromatics (indene, indane and tetralin) and a double-ring aromatics (methylnaphthalene) were examined using the water-cooled single-cylinder DI engine at two load conditions. Low aromatic base fuel was blended with each tested aromatic in three concentrations i.e. 21.5%, 26.5% and 31.5% by mass, respectively as provided in table 3.3. This chapter is divided into three parts; performance, emissions and correlations. In first part, the effects of polycyclic aromatics on CI engine performance are discussed whereas, the impacts on emissions are provided in detail, in the second part. Finally, NO_x and PM correlations are developed and compared to experimental results.

6.2 Performance

Figure 6.1 and 6.2 shows that BSFC for all tested blends decreased with increasing load although, BTE increased. BSFC reduction with engine load is mainly due to the high heat losses from the walls of the combustion chamber at low load condition, which adversely affects the efficiency and hence, more fuel is required for the same output power at low load condition. BTE at high load improved for two reasons. First, more fuel induced with constant air led to richer fuel-air mixtures compared to relatively lean mixtures at low load. Second, high combustion temperature contributed to better oxidization of fuel and hence, the BTE increased.



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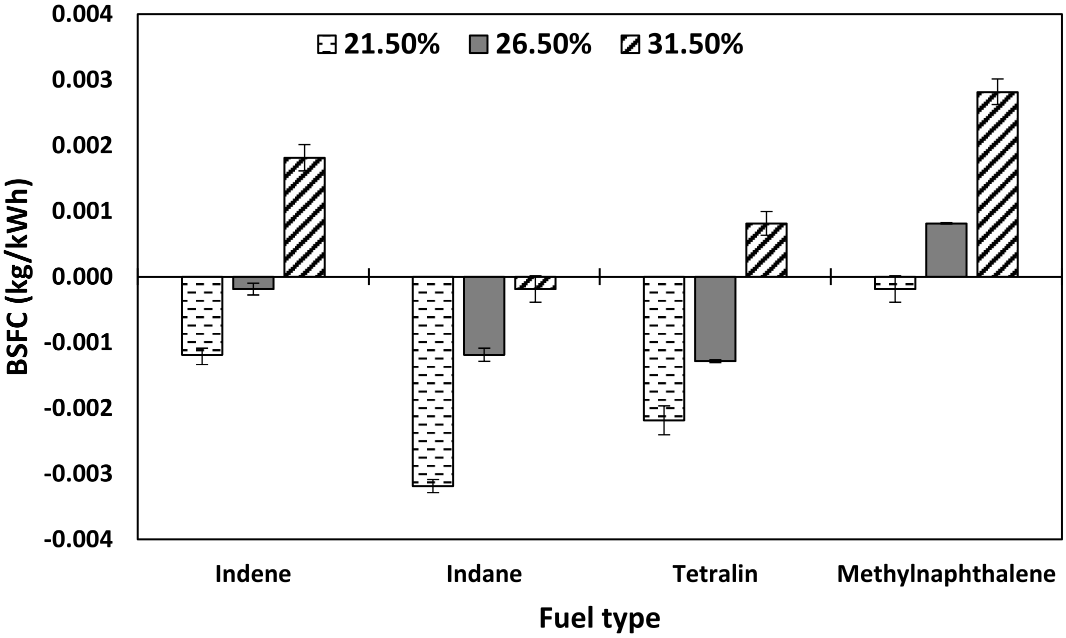
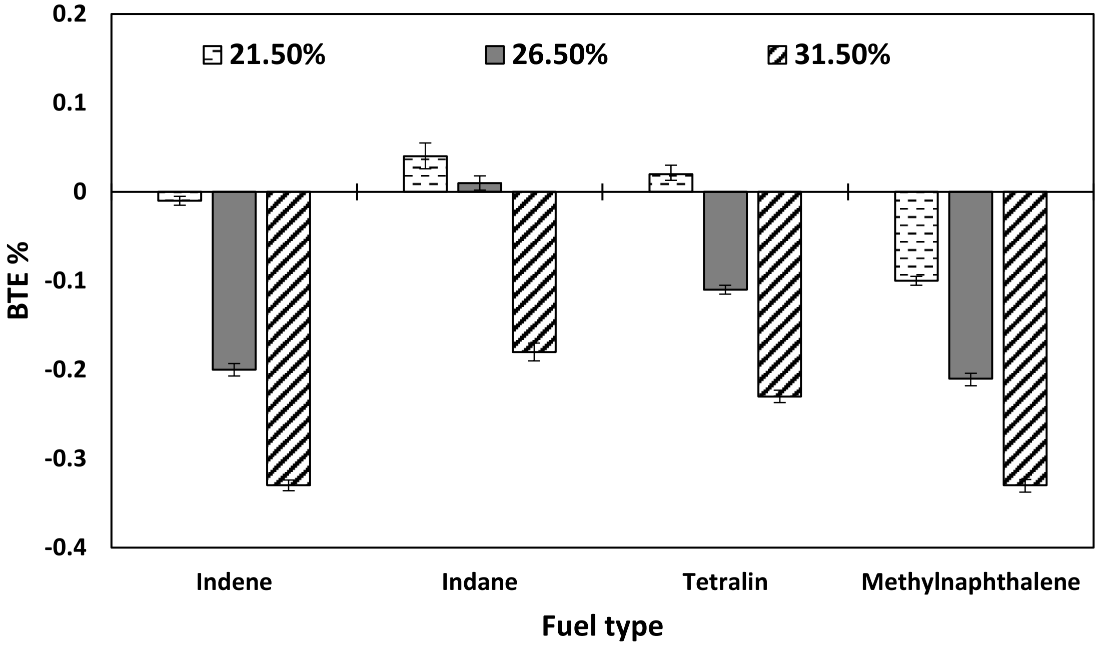


(b) High load

Figure 6.1 Variation in BSFC for tested blends compared to diesel fuel



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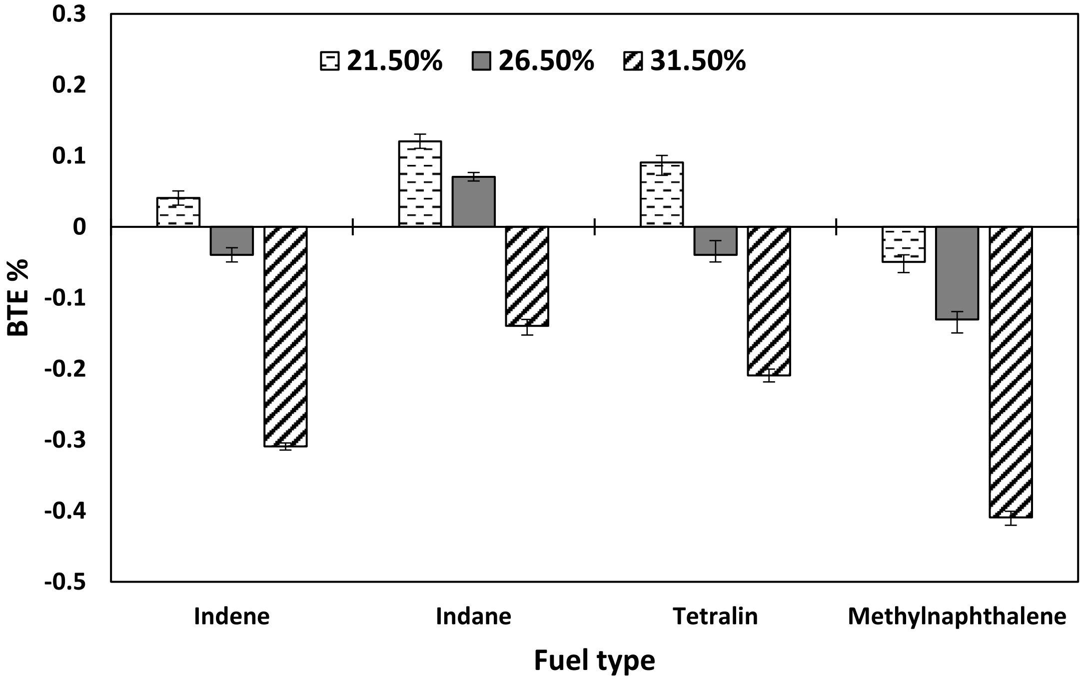


(b) High load

Figure 6.2 Variation in BTE for tested blends compared to diesel fuel

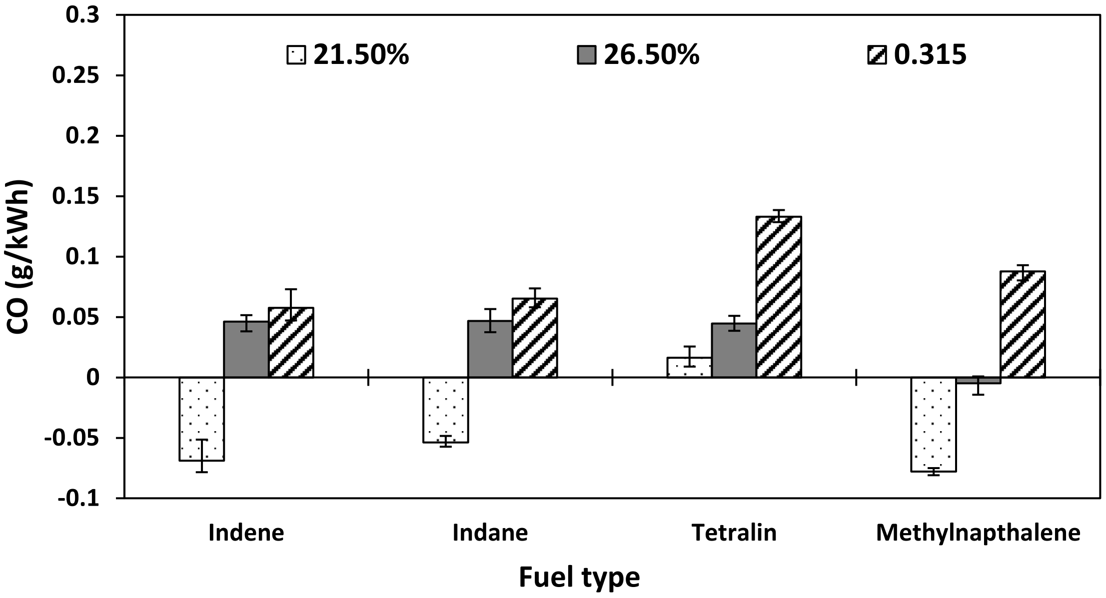
Slight increases in BSFC and reductions in BTE were concluded with increasing aromatic content in the blends. Blending aromatics with the base fuel contributed in global low calorific value and cetane number. Due to low cetane number, higher concentration of aromatics increased the ignition delay and adversely affected the engine performance [197].

Among the tested polycyclic aromatics, indane blended fuels exhibited better performance in terms of increased BTE and decreased BSFC. Higher H/C ratio of indane also led to the better combustion. The performance of indane blended fuels were followed by tetralin, indene and methylnathalene. Methylnaphthalene has lower BTE and higher BSFC because of its higher degree of unsaturation. Moreover, higher density of methylnaphthalene led to poor spray characteristics that adversely affected the combustion of the fuel.

6.3 Exhaust Emissions

6.3.1 CO and UHC Emissions

Figure 6.3 illustrates low CO concentrations with increasing load due to better oxidization resulting from high combustion temperature at high load condition. The aromatic content impact on CO emissions was found significant. CO emissions were increased with aromatic content because of low H/C ratio and dominant C-C bonds of aromatics. Hochhauser [175] also found that there was a relationship between aromatic percentage in fuel and CO concentrations. Blends including indene and methylnaphthalene produced higher CO compared to those with tetralin and indane. The possible reason for this may associate with higher H/C ratios of indane and tetralin compared to the other tested aromatics. High boiling point of methylnathalene was also a probable reason for high emissions due to increased fuel penetration and hence, incomplete oxidation occurred.



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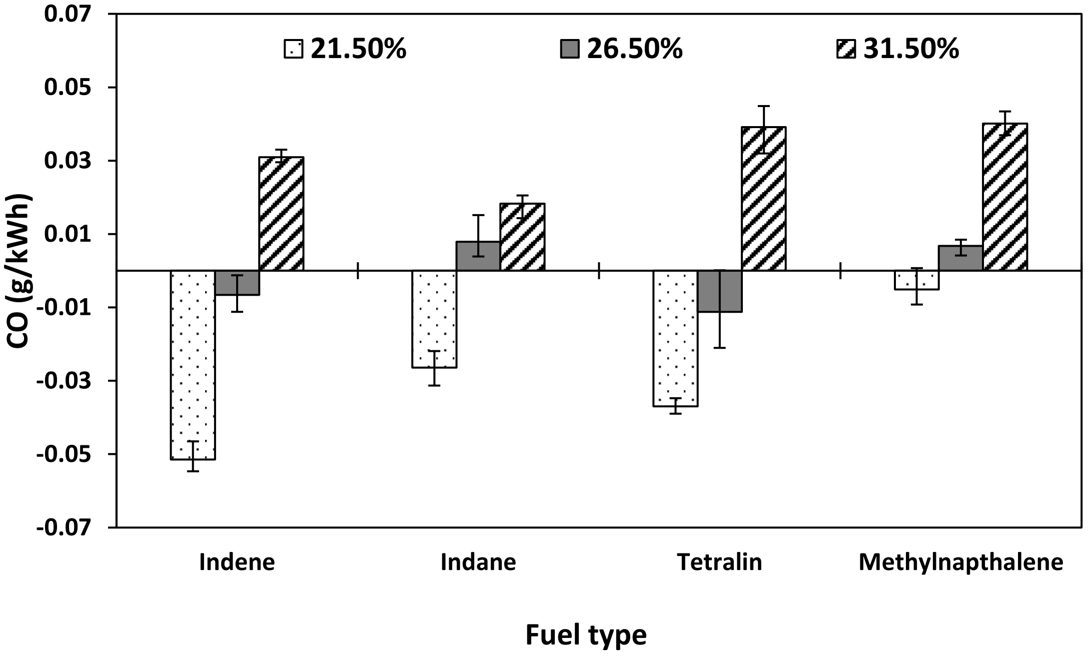
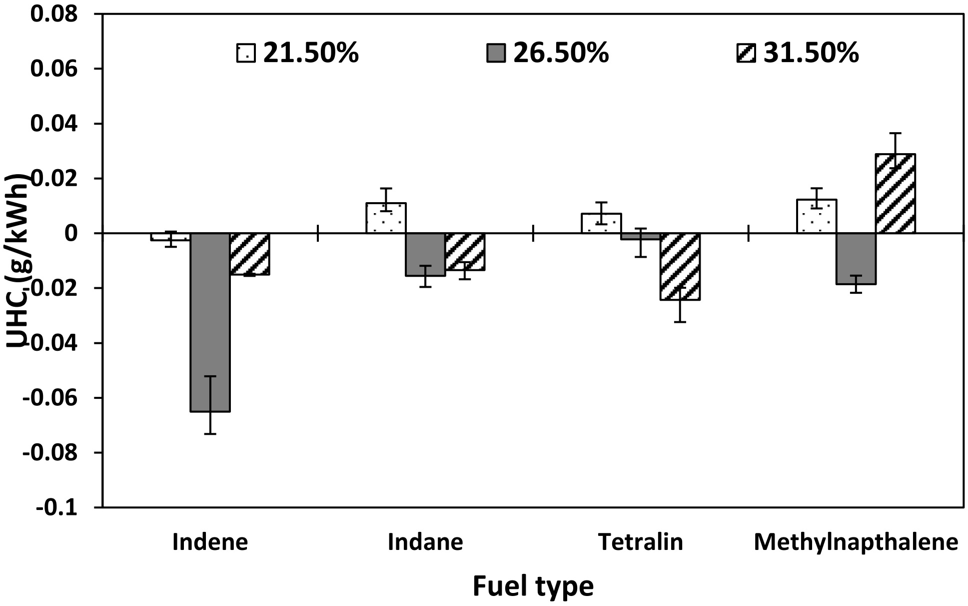


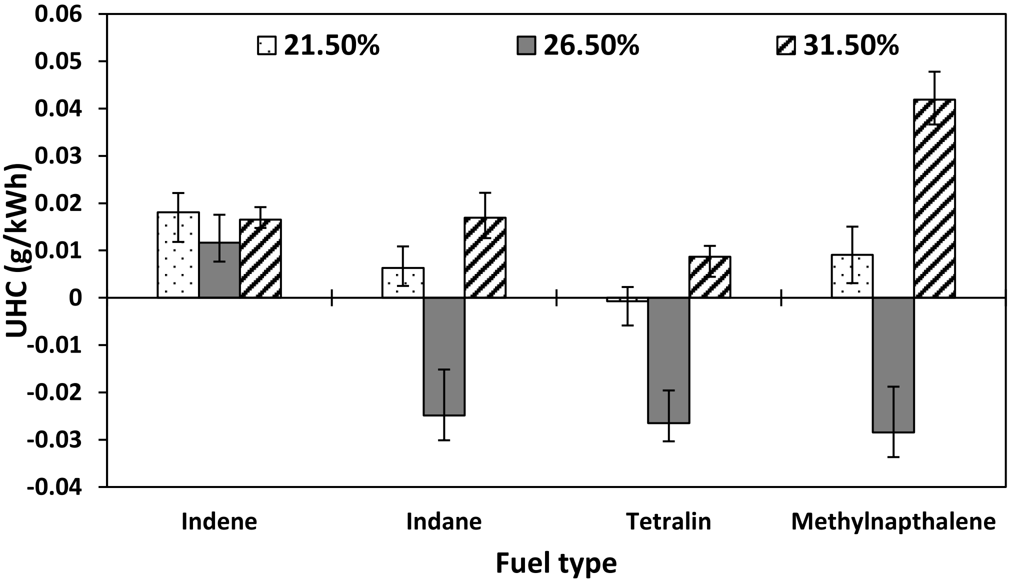
(b) High load

Figure 6.3 Effect of tested fuel blends on CO emissions compared to diesel fuel

As shown in figure 6.4, UHC emissions reduced with increasing engine load. As combustion temperature increased gradually with load, further UHC emissions in combustion chamber oxidized. Blending aromatics with the base fuel resulted in high global density. This can increase the spray penetration causing fuel impingement on the wall of combustion chamber leading to increased UHCs [209]. However, spray penetration distance was also affected by global boiling point of blends [176].



(a) Low load



(b) High load

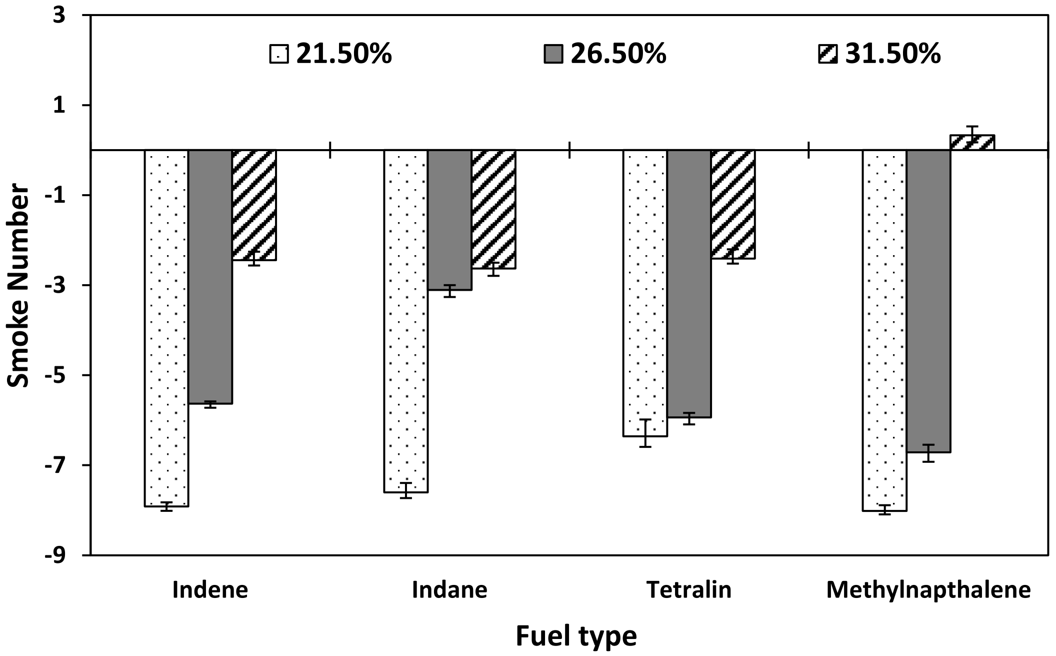
Figure 6.4 Effect of tested fuel blends and diesel fuel on UHC emissions compared to diesel fuel

The fact that fuel with low boiling point can atomize quickly and hence release low UHC emissions. Moreover, higher H/C ratio of indane and tetralin i.e. 1.111 and 1.2 respectively also promoted the fuel oxidation. Methylnaphthalene has higher boiling point (240 °C) and high density (1000.1 kg/m^3) that adversely affected the fuel spray and vaporisation and hence the combustion of the fuel deteriorated. These factors are responsible for higher UHC emission with this aromatic type. The higher degree of unsaturation due to its chemical bonding structure also led to higher UHC emissions.

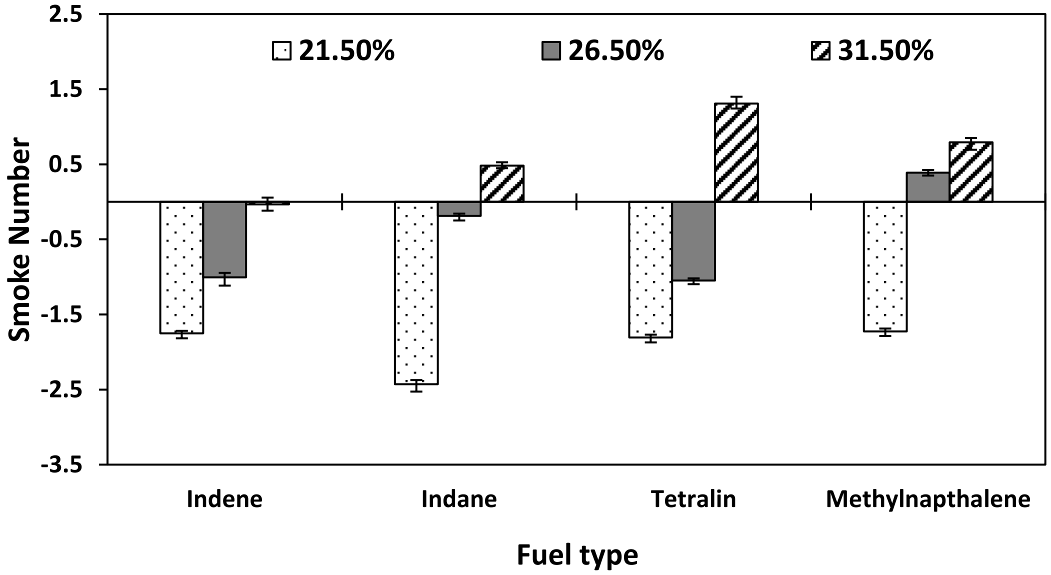
In addition to the impact of aromatic type, UHC emissions were also impacted by aromatic content. As shown in figure 6.4, increasing aromatic content from 21.5% to 26.5% by mass led to slight decreased UHC emissions at low and high loads, respectively. However, further increase in aromatic content (from 26.5% to 31.5% by mass) contributed to higher UHC levels. It can be seen that the relationship between UHC emissions and aromatic content in fuel was not proportional. Therefore, fuel blends with 26.5% aromatic content produced lower UHC emissions than those of 21.5% and 31.5% aromatic content.

6.3.2 Smoke Emissions

Smoke emission is a visually apparent pollutant in the exhaust of CI engines. These emissions give an indication of the PMs. The PM components mainly soot is responsible for the smoke opacity [210]. Smoke number was affected by load condition and aromatic concentration in blends as shown in figure 6.5. When load increased, high combustion temperature and better fuel-air homogeneity improved combustion efficiency and then, low smoke emissions. Among tested blends, the highest smoke emissions were produced from 15% methylnaphthalene- 85% base fuel blend compared to the other blends, especially at high load.



(a) Low load

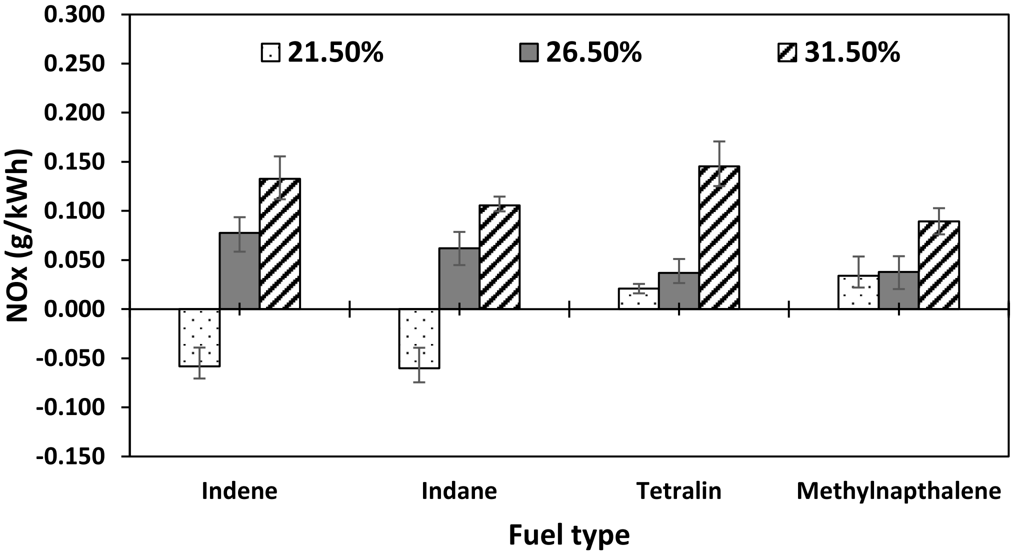


(b) High load

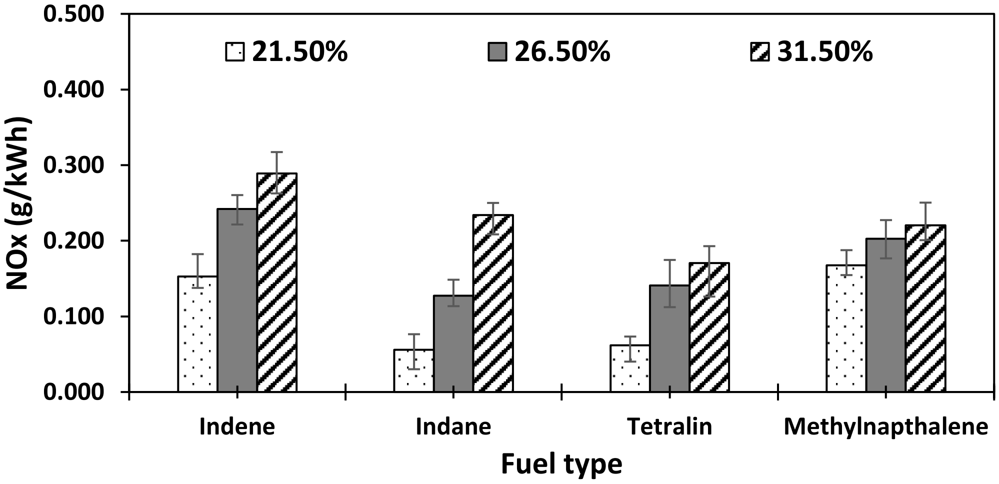
Figure 6.5 Variation in smoke numbers of tested blends compared to diesel fuel

6.3.3 NO_x Emissions

NO_x emissions were increased with increasing load due to increased combustion temperatures. At high load, more fuel is feed to the combustion chamber and burned with low diluted air leading to high combustion temperature and increased NO_x formation. Blending aromatic content also impacted NO_x levels as shown in Figure 6.6. This may associate with typical high flame temperatures of aromatics compared to alkanes resulting in high NO_x emissions [177, 201]. Blending aromatics with the base fuel led to high global density and low H/C ratio. Neill et al. [181] evaluated that there is a relationship between hydrogen content in fuel and NO_x formation. NO_x emissions were also increased due to physical aromatic density impact on fuel injection characteristics [181].



(a) Low load



(b) High load

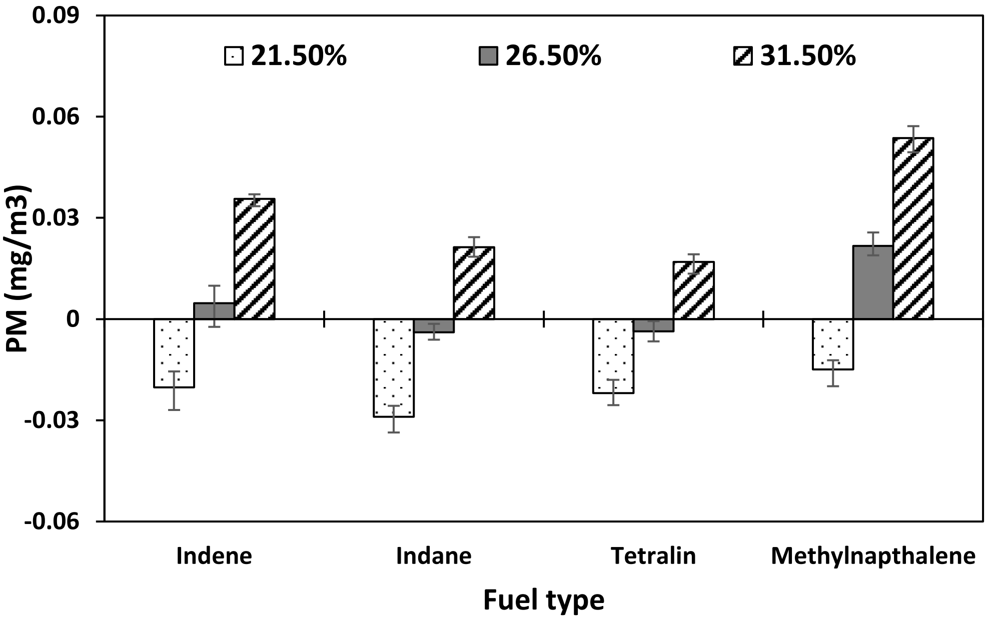
Figure 6.6 Effect of tested fuel blends and diesel fuel on NO_x emissions

Among tested aromatics, blends including indene produced high NO_x levels compared to the other blends, especially at high load due to low hydrogen content or H/C ratio (0.889) and high density (996 Kg/m^3). Due to the better physicochemical properties of indane that led to better combustion, NO_x concentrations were found low for indane blended surrogate fuels.

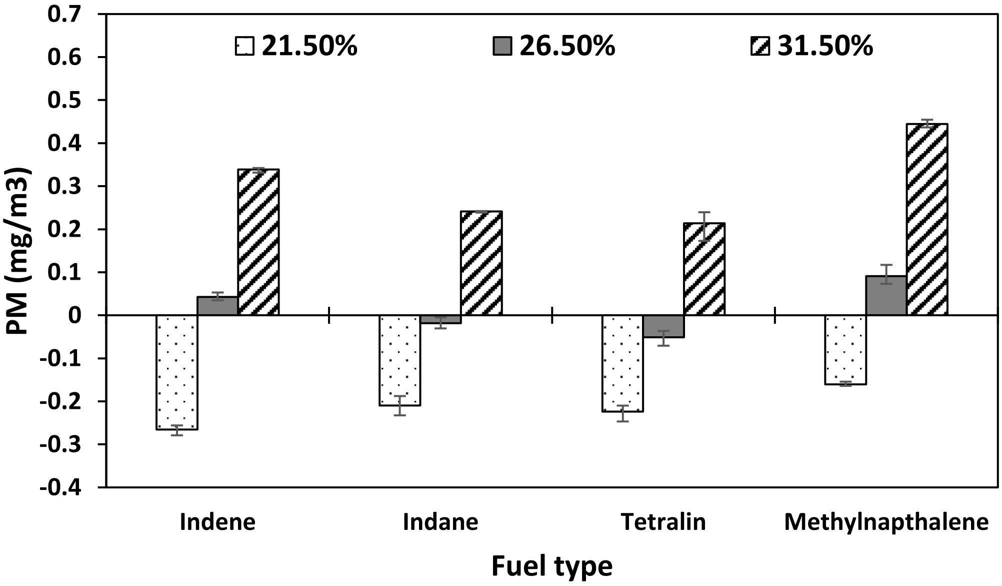
6.3.4 PM Emissions

As shown in Figure 6.7, high PM emissions were observed at high engine load because of higher fuel concentration in air-fuel mixture. This led to richer combustion which had tendency to promote soot formation. PM concentrations were also increased with increasing aromatic concentration in blends due to difficultly of pyrolysis of aromatics [207]. In addition, increasing aromatic content reduced cetane number and increased ignition delay time resulting in high PMs [175].

A correlation was found between global H/C ratio and PM emissions as provided further in section 6.4. The increase of aromatic content in blends contributed to decreased global H/C ratio and hence, increased PM emissions. Increasing global density due to blending of aromatics also impact PM emissions. Comparison between test aromatics showed that blended methylnaphthalene produced higher PMs than the other blends because of its high density and low H/C ratio.



(a) Low load



(b) High load

Figure 6.7 Effect of tested fuel blends on PM emissions compared to diesel fuel

6.4 PM and NO_x Correlations

Regression analysis was used to study fuel property effects on exhaust emissions. It was found that there are intensive correlations between PM emissions and parameters such as H/C ratio, density and aromatic content. Therefore, equations were developed for PM emissions that are in agreement with experimental results as shown below. For the present study, the PM is considered as the function of aromatic contents, H/C ratio and density as it is shown to be significantly affected by these factors.

$$PM = f\ (P_1, P_2, P_3)$$

Where again P_1 = aromatic contents in the fuel blend, P_2 = global H/C ratio of the tested fuel blends and P_2 = global density of the tested fuel blends

(a) Change in PM emissions due to increasing aromatic content obtained using mathematical analysis. While, P_1 represents tested aromatic content, i.e. 5, 10 or 15% by mass.

$$\mathrm{PM}(\mathrm{P}_1) = 0.003\mathrm{P}_1^2 + 0.06\mathrm{P}_1 + 0.64 \qquad \text{(Eq 6.1)}$$

(b) The change in PM emissions because of load impact was calculated. Load coefficient at low and high load were -0.0007 0.398, respectively. To consider the load impact on PM emissions, Eq (5.1) is multiplied by a factor of lad (L) as illustrated in Eq (6.2).

$$\Delta\mathrm{PM}(\mathrm{P}_1) = 0.003\mathrm{P}_1^2\mathrm{L} + 0.06\mathrm{P}_1\mathrm{L} + 0.64 \qquad \text{(Eq 6.2)}$$

(c) Correlation between global H/C ratio of blends and PM emissions was obtained at low load and 5% tested aromatic content.

$$\mathrm{PM}(\mathrm{P}_2) = 7.409\mathrm{e}^{(-1.657\mathrm{P}_2)} \qquad \text{(Eq 6.3)}$$

(d) Correlation between global surrogate fuel density and PM emissions developed at low load and 5% tested aromatic content.

$$\mathrm{PM(P_3)} = 8 \times 10^{-5} \mathrm{e}^{(0.0103\mathrm{P_3})} \qquad \text{(Eq 6.4)}$$

(e) From Eq. 6.3 and Eq 6.4, it was obtained that the sum of PM (P_2) and PM (P_3) is equal to 2×PM (P_2, P_3).

$$PM(P_2) + PM(P_3) = 7.409e^{(-1.657P_2)} + 8 \times 10^{-5} e^{(0.0103P_3)} = 2 \times PM(P_2, P_3) \quad \text{(Eq 6.5)}$$

Dividing Eq (6.5) by 2

$$\mathrm{PM(P_2, P_3)} = 3.7045\mathrm{e}^{(-1.657\mathrm{P_2})} + 4 \times 10^{-5} \mathrm{e}^{(0.0103\mathrm{P_3})} \qquad \text{(Eq 6.6)}$$

(f) Final correlation that can be used for PM emissions at any load and aromatic contents. It is the sum of Eq. (6.6) and Eq (6.2) as shown in Eq (6.7)

$$\begin{aligned}\mathrm{PM(P_1, P_2, P_3)} = {} & 0.003\mathrm{P_1^2L} + 0.06\mathrm{P_1L} + 0.64\mathrm{L} + 3.7045\mathrm{e}^{(-1.657\mathrm{P_2})} \\ & + 4 \times 10^{-5} \mathrm{e}^{(0.0103\mathrm{P_3})}\end{aligned}$$

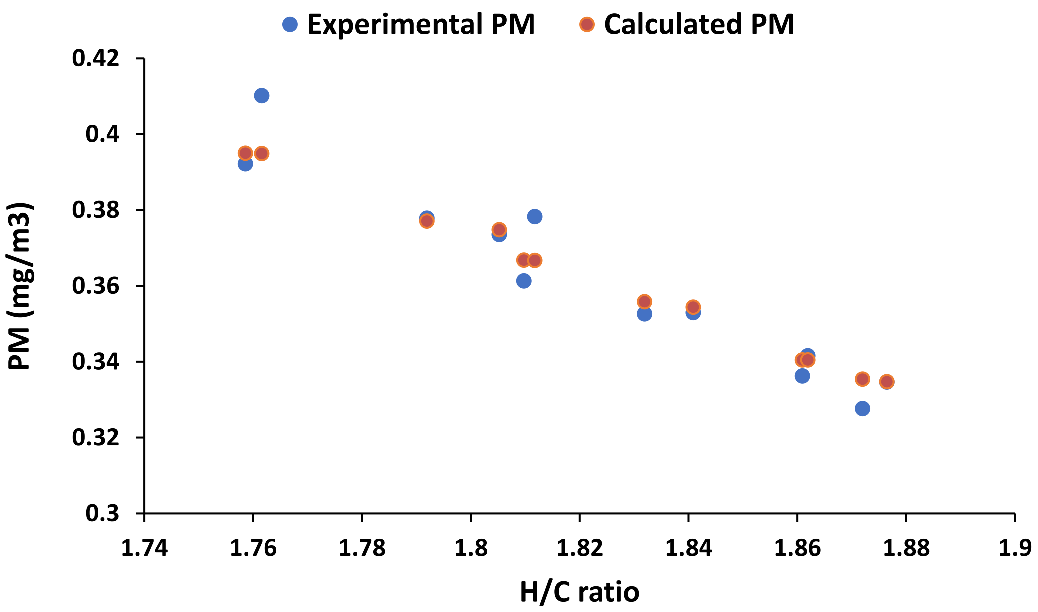
(Eq 6.7)

Correlation for NO_x emissions was also developed as function of density, H/C ratio and aromatic content by using the same procedure as for PM equation. Load coefficient is 0 at low load and 1020 at high load.

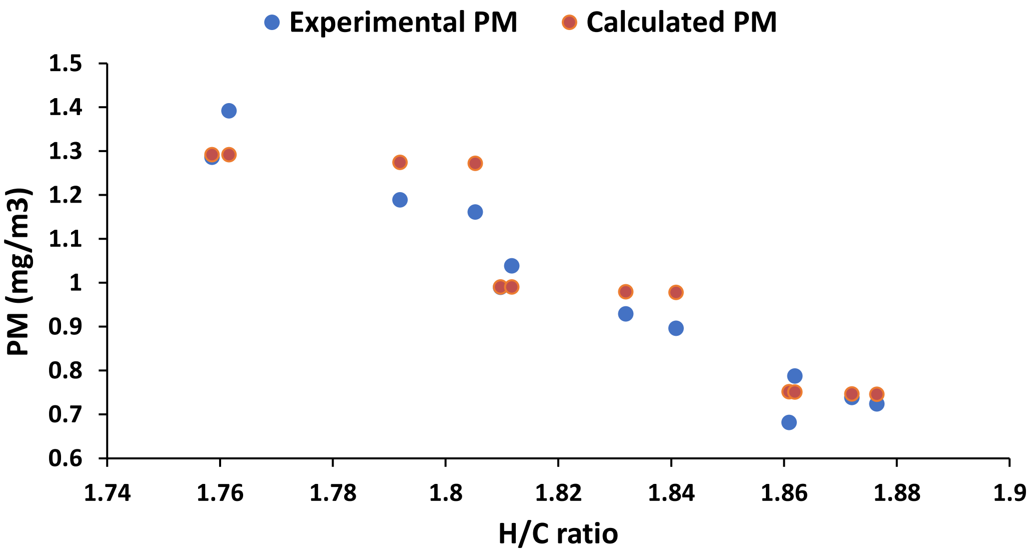
$$\begin{aligned}\mathrm{NO_x(P_1, P_2, P_3)} = {} & 9 \times 10^{-5}\mathrm{P_1^2L} + 0.0018\mathrm{P_1L} + 0.9932\mathrm{L} + 441.38\mathrm{e}^{(-0.359\mathrm{P_2})} \\ & + 29.6\mathrm{e}^{(0.0025\mathrm{P_3})}\end{aligned}$$

(Eq 6.8)

Figures 6.8 and 6.9 show comparison between calculated PMs using Eqn. (6.7) and experimental results. Maximum error in calculated PMs is 10.18% as compared to experimental results. While, Fig. 6.10 and 6.11 show experimental and calculated NO_x results with 2.87% maximum error.

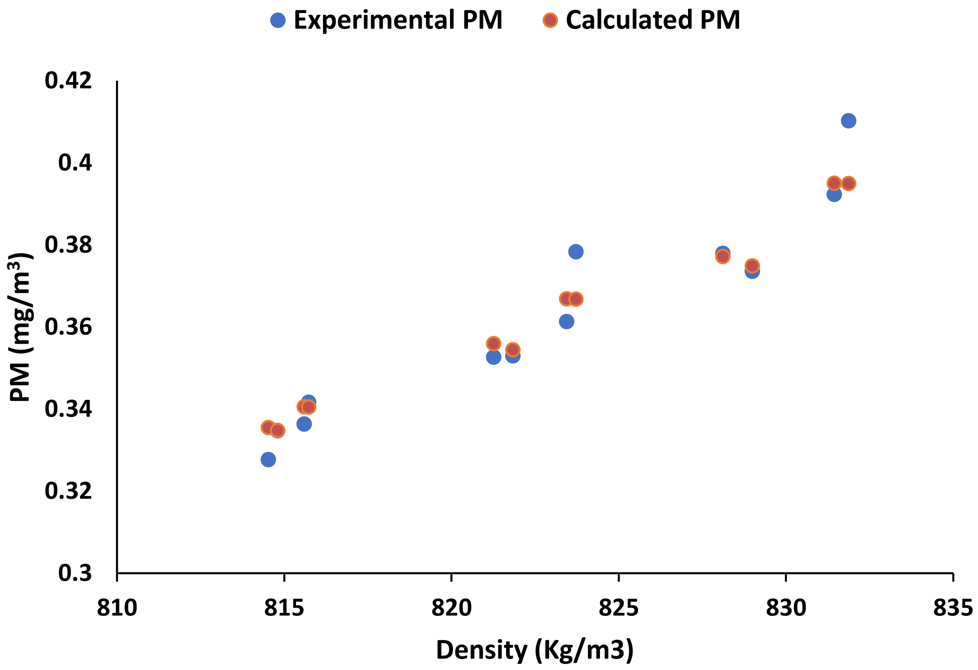


(a) Low load

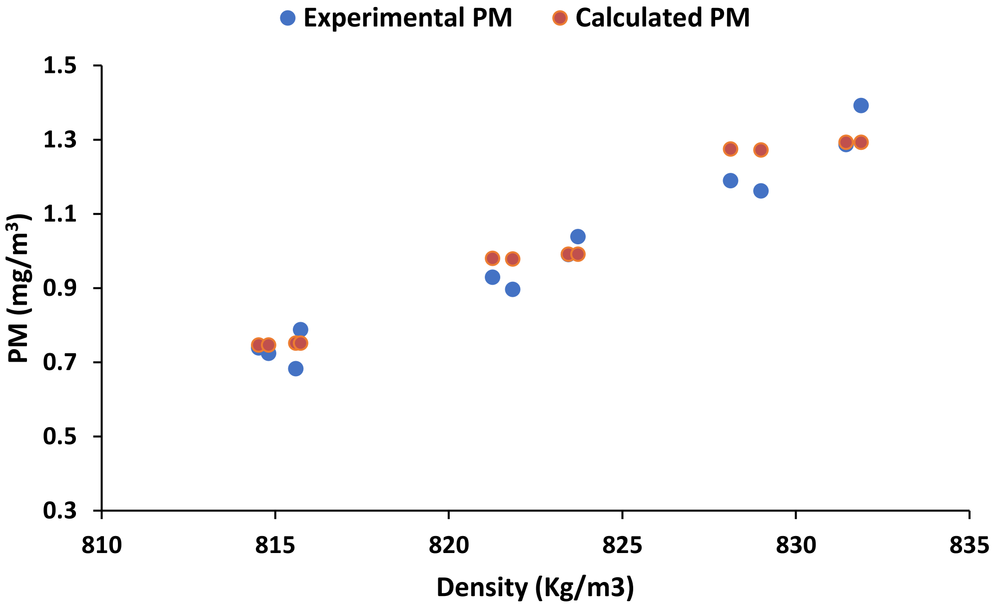


(b) High load

Figure 6.8 Comparison between experimental and calculated PM emissions based on global fuel H/C ratio

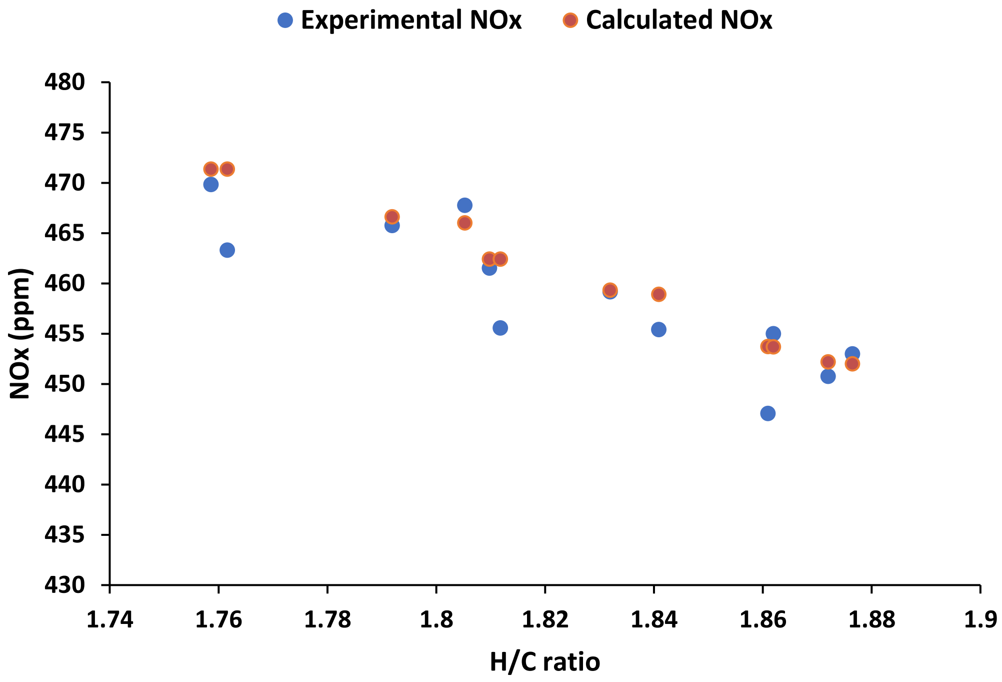


(a) Low load

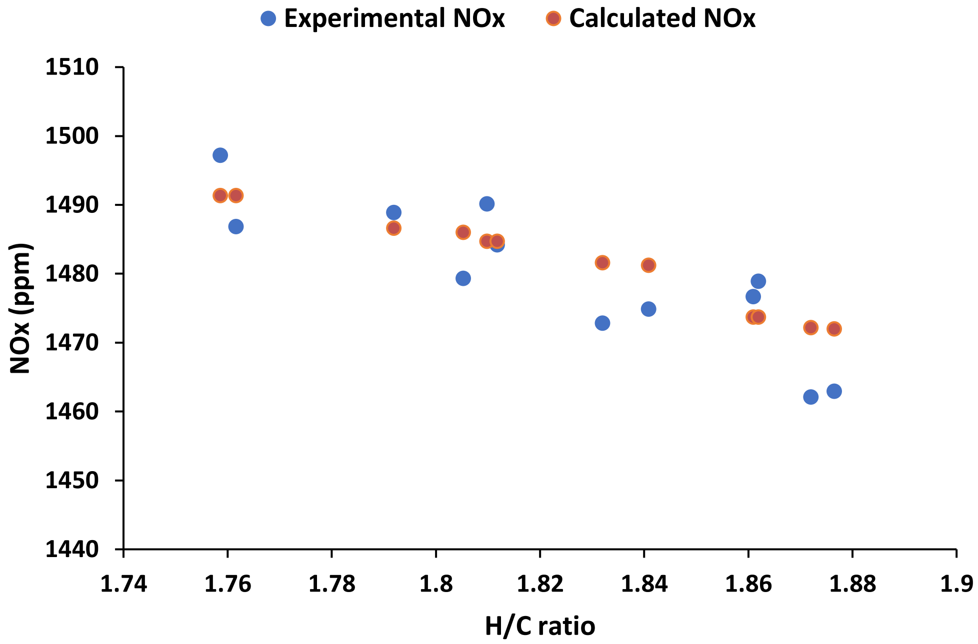


(b) High load

Figure 6.9 Comparison between experimental and calculated PM emissions based on global fuel density

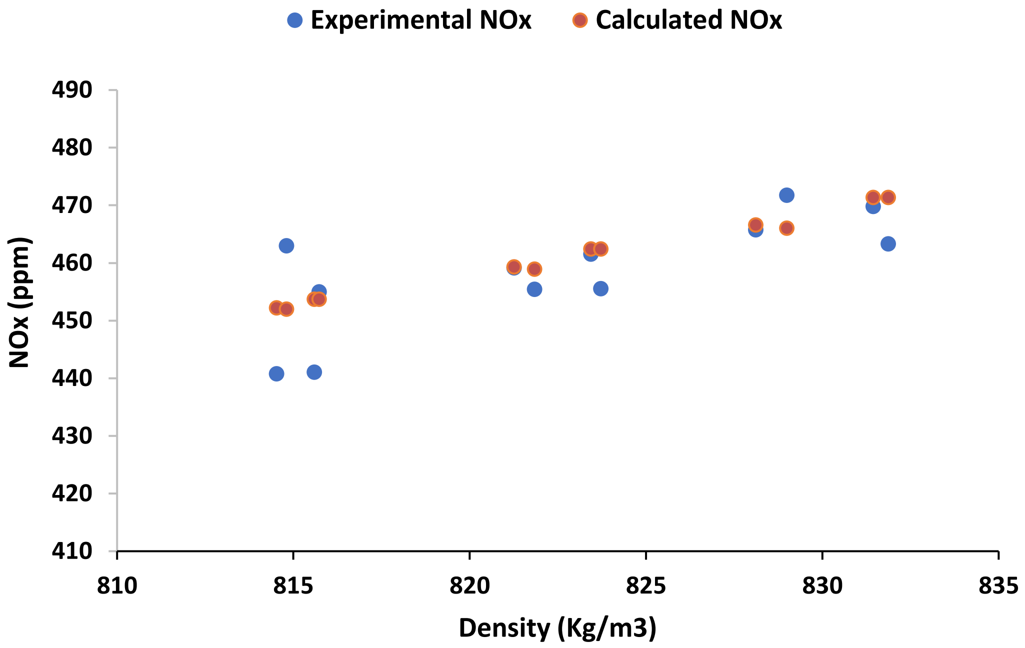


(a) Low load

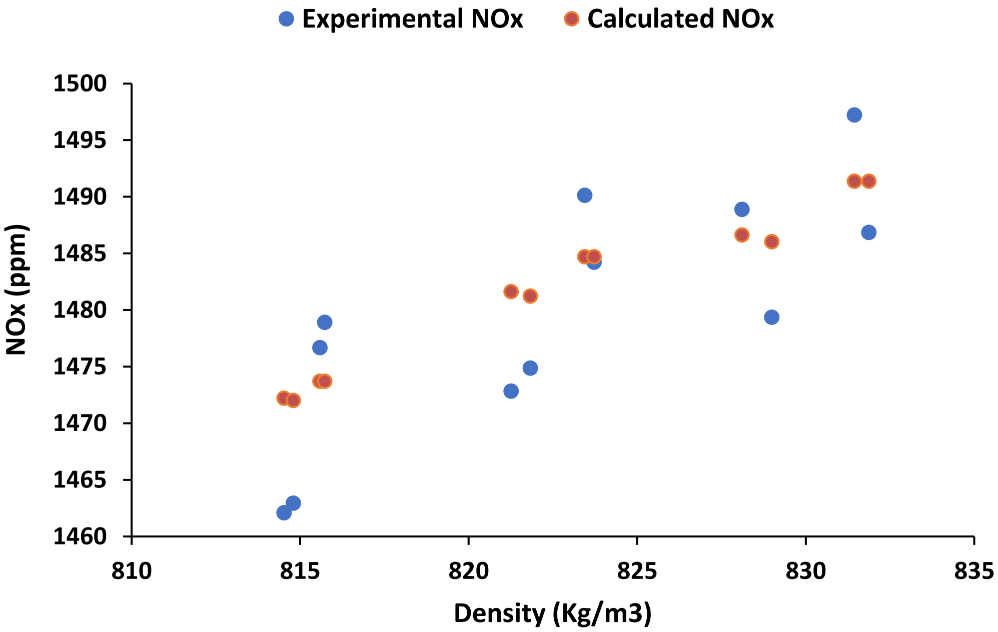


(b) High load

Figure 6.10 Comparison between experimental and calculated NO_x emissions based on global H/C ratio



(a) Low load



(b) High load

Figure 6.11 Comparison between experimental and calculated NO_x emissions based on global fuel density

6.5 Conclusion

Aromatics are one of major diesel components and have significant effect on global fuel properties such as density, H/C ratio, cetane number and boiling point on diesel fuel surrogate. Therefore, four different polycyclic aromatics blended with low aromatic base fuel with different contents (5, 10 and 15% by mass, respectively) were tested experimentally using the DI CI engine. The main aim was to evaluate polycyclic aromatics impacts on exhaust emissions and performance. The overall results show that increasing aromatic content in base fuel contributes to high emissions and slight increase in BSFC and reduction in BTE at high and low load conditions. CO, PM and smoke emissions increase due to high carbon content and associated difficultly of pyrolysis of aromatics. While, typical high flame temperature of aromatics compared to alkanes attributes to high NO_x emissions. Low cetane number and calorific value resulting from blending of aromatics with base fuel impact BSFC and BTE at both loads.

Comparison among tested aromatics shows variations in emissions and performance due to physical and chemical properties of each aromatic. Blends containing methylnaphthalene produce high levels of UHC, PM and smoke emissions because of high density, high boiling point and low H/C ratio compared to the other blends. Indane shows better results as compared to other tested blends due to their better physicochemical properties. In addition, correlations are developed for NO_x and PM emissions that have high agreement with the experimental results.

7 COMPARISON OF OPTIMUM BLEND AND DIESEL FUEL

7.1 Overview

From the outputs of chapter’s 5 and 6, an optimum diesel surrogate blend was formed with specifically selecting of alkylbenzene and polycyclic aromatics to produce low emissions and improve engine performance. In the first section of this chapter, the properties of the optimum blend and diesel fuel are compared. The influence of the optimum blend on engine performance are briefly discussed in the second section, while third section of this chapter covers the investigation of emissions. In both the second and third sections, the experimental results of optimum blend and diesel fuel are analysed and compared with aim of demonstrating the advantages and disadvantages of optimum blend as CI engine fuel.

7.2 Optimum Blend Selection and Properties

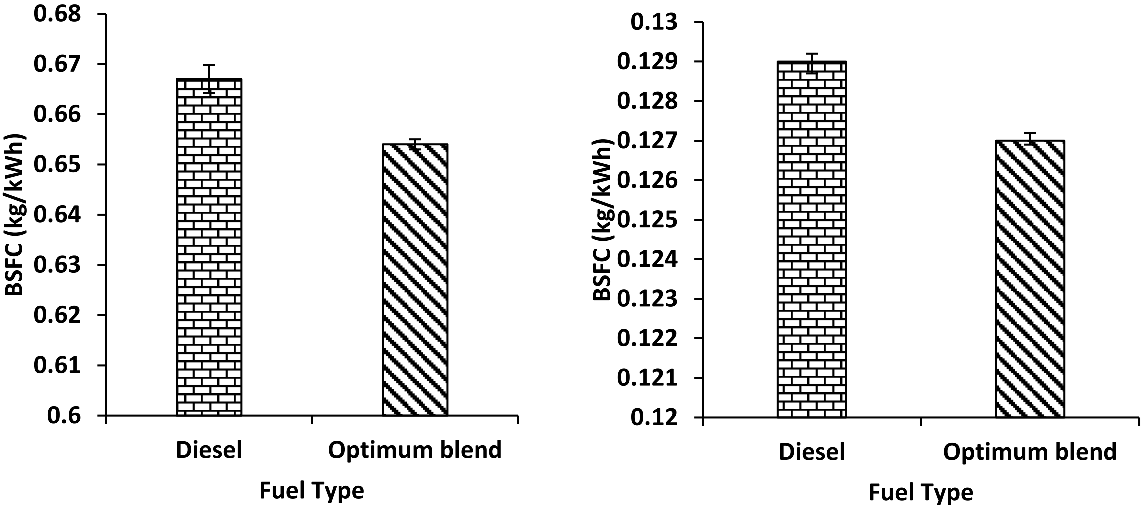
The investigation of 36 alkylbenzene-base fuel blends in chapter 5 showed that blends including ethylbenzene produced lowest exhaust emissions and better performance as compared to the other alkylbenzene-base fuel blends. For 12 polycyclic aromatic surrogate fuel blends, indane contributed to better results. Therefore, the optimum blend is formed with better aromatic selection. Ethylbenzene is selected to represent monocyclic aromatics (alkylbenzenes) and indane is used as polycyclic aromatic representative. As discussed in section 2.7.2, single alkanes produce less PM emissions than cycloalkanes. Therefore, ethylbenzene and indane are blended with straight single alkane blends which were used as a base fuel for optimum blend. The properties of the base fuel are provided in Appendix A.3. The contents of aromatic species in optimum blend are like that of diesel fuel based on diesel sample tested by in Intertek Cleb Brett, in London as provided in Table 7.1. The monocyclic content is 20.5% by mass, whereas polycyclic aromatic is 3.1% by mass based on IP 123. In the following sections, fuel blend is investigated experimentally.

Table 7.1 Optimum blend and diesel fuel properties

Property	**Diesel Fuel**	**Optimum Blend**
Monocyclic Aromatic % by mass (IP 391)	20.5	20.5 (represented by ethylbenzene)
Polycyclic Aromatic % by mass (IP 391)	3.1	3.1 (represented by indane)
Cetane Number (ASTM D613)	51.4	56.47
Density (measured in LCCC lab)	835	781.41
Final Boiling Point (IP 123)	390	242.11
H/C ratio (ASTM D5291)	1.86	1.84

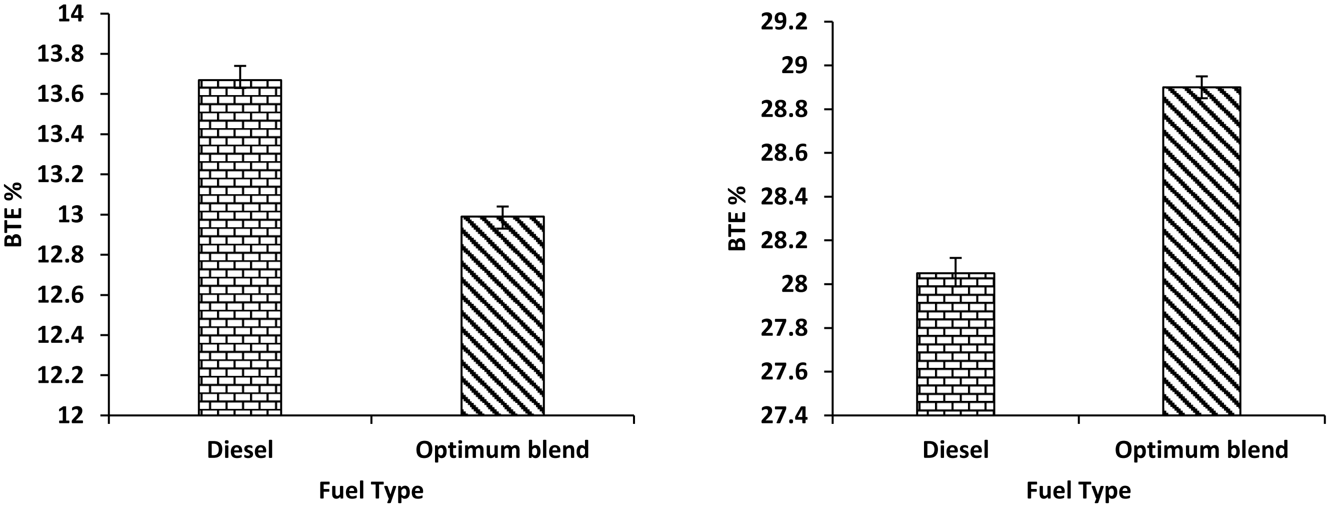
7.3 Performance

From figure 7.1, it can be observed that BSFC results of optimum blend and diesel fuel decreased with increasing load. The possible reason for this associated with the high heat losses from the combustion chamber walls at low load condition, that adversely affected the efficiency and hence, more fuel was needed for the same output power at low load condition. However, as shown in figure 7.2, BTE results of both optimum blend and diesel fuel increased with increasing load for two possible reasons. First, combustion temperature increased at high load which led to better fuel oxidization and then, high BTE. Second, at high load, more fuel was injected into the combustion chamber with constant air which resulted in better fuel-air mixture as compared to too lean mixture at low load.



(a) Low load (b) High load

Figure 7.1 BSFC results of diesel fuel and optimum blend



(a) Low load (b) High load

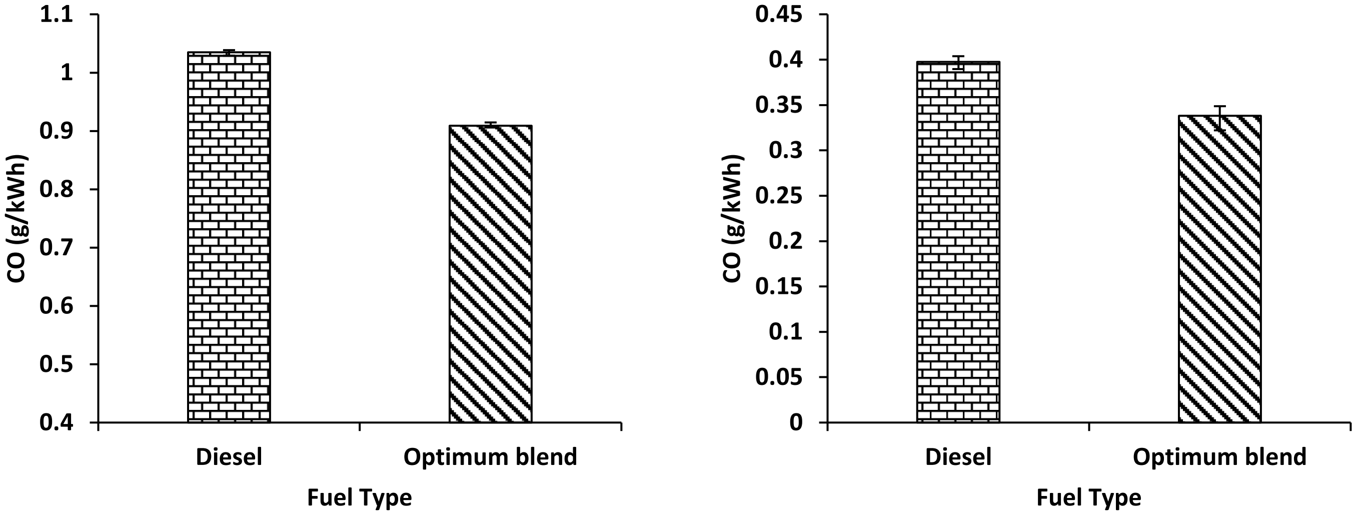
Figure 7.2 BTE results of diesel fuel and optimum blend

Comparison between tested fuels showed that BSFC results of the optimum blend were reduced by 1.95% and 1.55% than those of diesel fuel at low and high load conditions, respectively. BTE of the optimum blend at high load increased up to 3%, but it decreased by 4.97% at low load as compared to diesel fuel. The improvement of both BSFC and BTE at high load related with better combustion gained from better fuel-air mixture. BSFC is influenced by many fuel properties such as calorific value, cetane number and density [198]. The higher calorific value of the optimum blend led to higher energy produced from the burn of the blend and then, less fuel was injected to produce the same power as compared to diesel fuel. Also, low density of the optimum blend improved fuel characteristics by forming small droplets and better oxidization and hence, complete combustion. The higher cetane number of the optimum blend resulted in short ignition delay and high in-cylinder pressure [199]. This enhanced fuel evaporation and fuel-air mixing and hence, low fuel consumption.

7.4 Pollutant Emissions

7.4.1 CO Emissions

CO emissions are formed as a result of incomplete combustion which is caused by heterogeneity of the air-fuel mixture. As illustrated in figure 7.3, at low load (1.1 kW**),** high levels of CO were produced due to excessively lean mixture, whereas better fuel-air mixture at high load (4.5 kW**)** contributed to complete combustion because of more fuel that was injected with maintaining induced air. The formation of CO emissions was also affected by C-C bonds. Single C-C bonds are dominant in optimum blend composition as the optimum blend contains high content of single alkanes (76.4 % by mas). Therefore, low CO emitted from the burn of optimum blend at both engine loads as compared to diesel fuel that contains cycloalkanes.

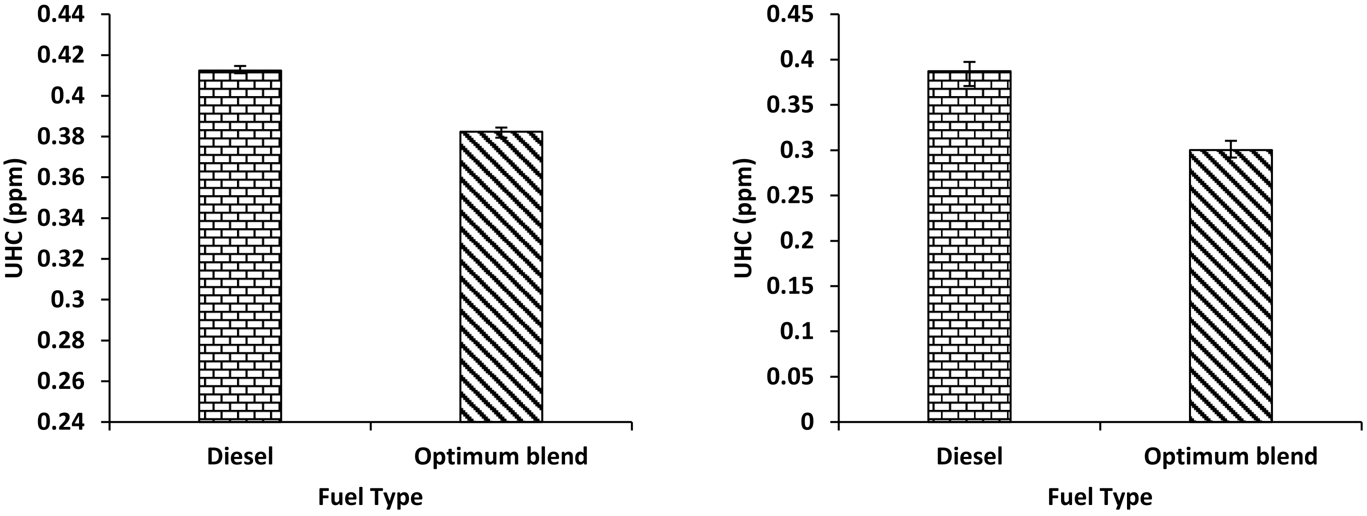


(a) Low load (b) High load

Figure 7.3 CO emissions of diesel fuel and optimum blend

7.4.2 UHC Emissions

As illustrated in figure 7.4, high UHC levels were formed at low load because of poor oxidization resulting from low temperature and lean air-fuel mixture [13]. UHC emissions were also affected by fuel concentrations in the walls of combustion chamber. Comparison between tested fuels shows that UHC emissions of optimum blend were lower by 7.27% and 22.49%, respectively at low and high load conditions than those of diesel fuel. The reason was associated with low density (781.41 kg/m^3) of optimum blend that shortened spray distance and then, reducing fuel impingement in the chamber walls. Consequently, low UHC emissions emitted from the burn of optimum blend. Another reason, decreased boiling point of a fuel contributes to rapid fuel atomization and hence, low UHC levels [200]. Therefore, low boiling point (242.11°C) of optimum blend enhanced fuel atomization and then, low UHC emissions as compared to diesel fuel boiling point (390 °C).

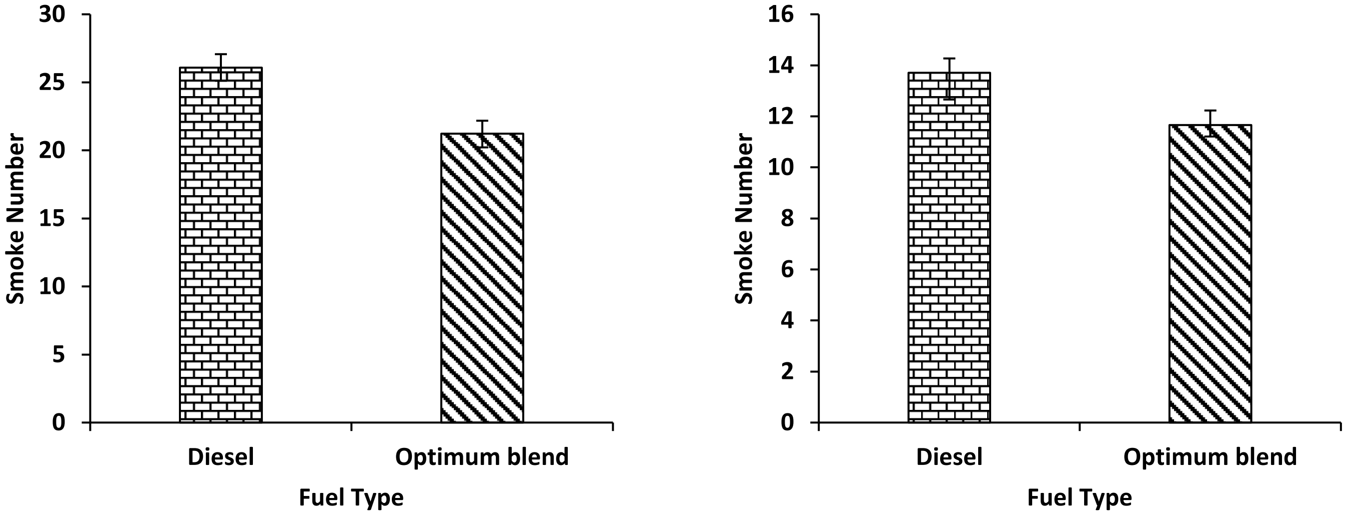


(a) Low load (b) High load

Figure 7.4 UHC emissions of diesel fuel and optimum blend

7.4.3 Smoke Emissions

As shown in figure 7.5, smoke emissions presented in this study as smoke number that was obtained by using Eq (4.1), section 4.2.4. Smoke number was decreased at high load because of increased in-cylinder temperature and better fuel-air mixture, which led to better oxidization process. As compared to diesel fuel, smoke number of optimum blend was decreased by 18.6% and 15% at low and high load conditions, respectively. Boiling point of optimum blend played a role in enhancing fuel atomization and improved homogeneity of fuel-air mixture and then a complete combustion [185]. High H/C ratio and dominant single C-C bonds instead of double C=C bonds in optimum blend composition helped in limiting smoke production.

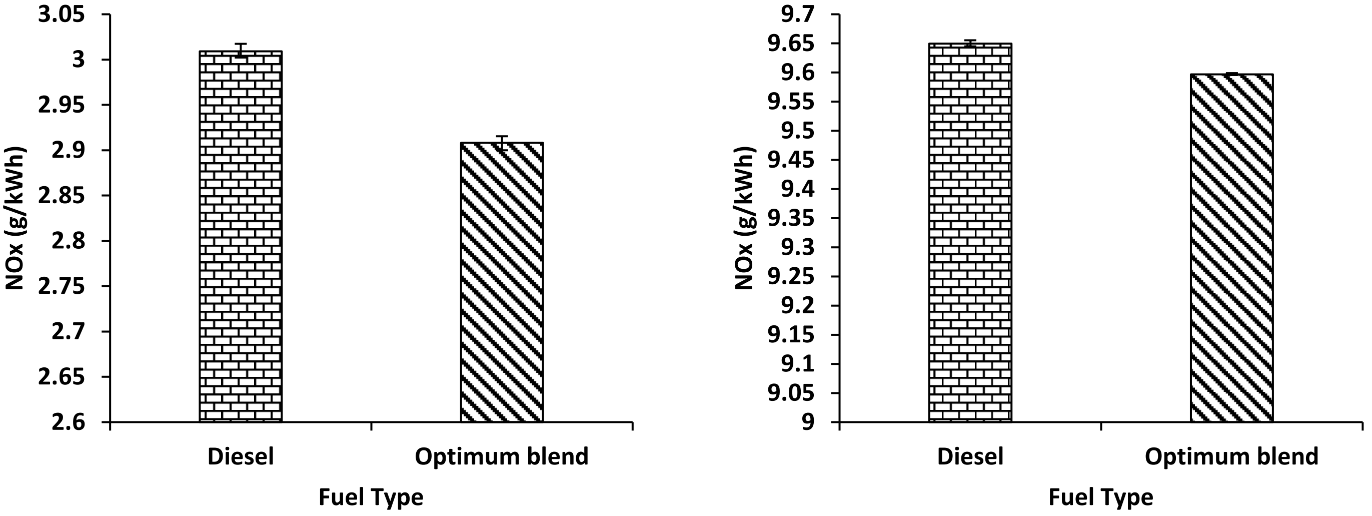


(a) Low load (b) High load

Figure 7.5 Smoke Number of diesel fuel and optimum blend

7.4.4 NO$_x$ Emissions

With increasing load, in-cylinder temperature was increased that resulted in increased NO$_x$ levels as illustrated in figure 7.6. In addition to combustion temperature, NO$_x$ formation was impacted by many fuel properties such as density and H/C ratio. High fuel density impacts the characteristics of fuel spray that attribute to high-temperature rich fuel region in flame. Therefore, diesel fuel with high density (835 kg/m^3) produced high NO$_x$ levels as compared to optimum blend density (781.41kg/m^3). Slight increased H/C ratio of optimum blend may contribute to a decreased NO$_x$ levels [181]. Consequently, NO$_x$ levels of optimum blend were reduced by 3.35% and 0.55% at low and high load conditions, respectively in compared to diesel fuel.

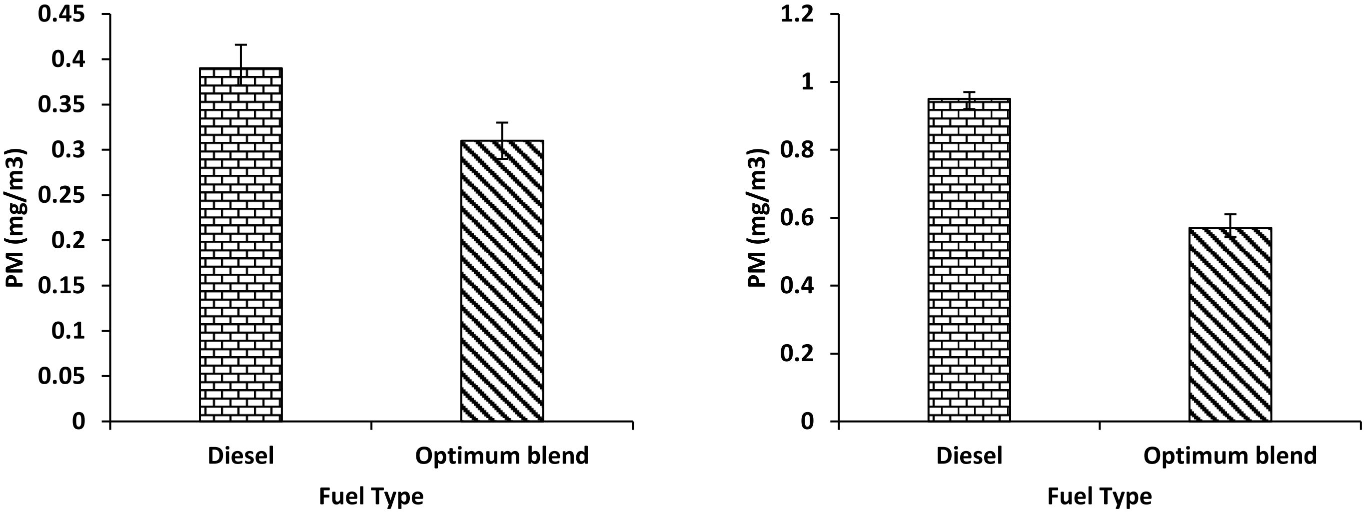


(a) Low load (b) High load

Figure 7.6 NO_x emissions of diesel fuel and optimum blend

7.4.5 PM Emissions

As illustrated in figure 7.7, The concentrations of PM in exhaust emissions were increased with increasing load. At high load, more fuel was injected into the chamber resulting in more carbon content induced and hence, soot formation. Comparison among both tested fuels, significant PM emissions were reduced by 20.5% and 40% at low and high load conditions, respectively with operating CI engine in optimum blend. This achievement was associated with attractive properties of optimum blend such as low density, boiling point and. high H/C ratio. Low density of optimum fuel formed small fuel droplets and better oxidization process and then, low PM formation [10]. Low carbon content or high H/C ratio of optimum blend contributed to low PM emissions because C=C bonded atoms are the main source of PM formation. Optimum blend also has low boiling point that contributed to easier gasification during the injection process [185]. Moreover, optimum blend contains high content of single alkanes (76.4% by mass) instead of diesel fuel including cycloalkanes. Song and Lee [186] reported that cycloalkanes are more tendency for PM formation than other type of alkanes.



(a) Low load (b) High load

Figure 7.7 PM emissions of diesel fuel and optimum blend

7.5 Conclusion

An optimum blend was formed with selected aromatic species and base fuel. Ethylbenzene surrogate blends produced lowest emissions and better performance among alkylbenzenes or monocyclic-aromatics, whereas blends including indane resulted in better emissions and performance as compared to the other polycyclic aromatics. Therefore, ethylbenzene and indane were selected to represent monocyclic-and polycyclic-aromatics, respectively in optimum blend composition, whereas straight single alkanes blend were used as the base fuel. The concentrations of both aromatic species in the optimum blend and diesel fuel are the same. The optimum blend effected both performance and emissions were investigated experimentally at low and high engine load conditions.

Overall results showed that fuelling the CI engine with the optimum blend resulted in significant reduction of PM, smoke, CO and UHCs. The properties of the optimum blend played a role in this achievement. Low density and high H/C ratio of the optimum blend contributed to low PM and smoke emissions. While, CO emissions are reduced because the optimum blend has dominant single C-C bonds instead of double C=C bonds included in diesel fuel. Also, lower boiling point leads to better evaporation and short spray distance which reduce fuel impingement in the walls of combustion chamber and then, low UHC emissions at low and high load conditions, respectively. However, the reduction of NO_x emissions of the optimum blend was insignificant as compared to those of diesel fuel. For engine performance, high calorific value and cetane number of the optimum blend led to slight decreased BSFC and increased BET, especially at high load. From the results of the optimum blend, it can be concluded that reforming aromatics in future fuel composition with better selection of aromatic species will help in reducing exhaust emissions and improving slightly engine performance.

8 CONCLUSION AND FUTURE WORK

8.1 Conclusion

Harmful emissions are a challenge for CI engines and they are increasing with the use of fossil-based feedstock around the globe. Performance improvement is also important to make engines more efficient and reducing fuel consumption. Investigating the effect of fuel components is one of many approaches that can be used to overcome challenges. Aromatics are an important component of the fossil-based diesel fuel. Alkylbenzenes and polycyclic aromatics form the majority of aromatic species in diesel fuel composition and have different physicochemical properties. Therefore, the role of different alkylbenzenes and polycyclic aromatics in emissions formation and engine performance are investigated and a deep explanation is provided in the present study. Contributions to knowledge that have been gained from the present study are summarized as below.

- A knowledge gap in how total aromatic content in fuel can influence BSFC and BTE. Therefore, diesel surrogate fuel blends with three different total aromatic contents; i.e. 21.5, 26.5 and 31.5% by mass are investigated experimentally. The global properties of test fuel blends are affected by aromatic content. Increasing aromatic content in test fuel blends contribute to low global calorific value and cetane number. Consequently, BSFC slightly increases and BTE decreases at low and high load conditions, respectively. Therefore, fossil-based diesel fuel including low aromatic content could be recommended to improve engine performance with the addition of lubricity improver to avoid fuel pump and injection system damages.

- Investigating the influence of different species of the same aromatic type on performance is another contribution from this work. Aromatic impact on cetane number and calorific value differs from one aromatic to another. Among alkylbenzenes, ethylbenzene surrogate blends contribute to low BSFC and high BTE, whereas blends including indane result in better performance as compared to the other polycyclic aromatics. These associate with attractive properties of ethylbenzene and indane such as high calorific value and cetane number.

- The impact of different species of the same aromatic type on exhaust emissions was investigated. Consequently, 12 alkylbenzenes and 4 polycyclic aromatics were investigated. Among alkylbenzenes, α-methyl styrene surrogate blends emit high levels of PM, smoke, UHC and CO emissions, whereas, ethylbenzene surrogate blends produce the lowest levels of emissions. For polycyclic aromatics, blends containing indane produce lower exhaust emissions compared to tetralin, indene and methylnathalene. Ethylbenzene and indane have attractive physicochemical properties such as high H/C ratio, cetane number, low boiling point and density as compared to the other aromatics tested.
- The role of different aromatic contents in gaseous and particulate emissions was explained in details. Increasing aromatic content in test fuel blends leads to high levels of exhaust emissions due to increased ignition delay, density, decreased cetane number, H/C ratio and difficultly of pyrolysis of aromatics. It is recommended that low aromatic diesel fuel with low aromatic content (< 20% by mass) can contribute to low exhaust emissions with the use of lubricity additive.
- Using the experimental results of alkylbenzenes and polycyclic aromatics, a diesel surrogate fuel was blended to drive an optimum blend. Ethylbenzene and inadne represent alkylbenzenes and polycyclic aromatics with straight alkanes blend showed significant reductions of emissions especially at high load as compared to

commercial diesel fuel of similar aromatic content. PM, smoke, CO and UHCs were reduced by 40%, 15%, 14.96%, and 22.49%, respectively. These achievements were gained from high cetane number, H/C ratio, low density and boiling point of optimum blend. However, the reduction of NO_x, BSFC and the increase of BTE were insignificant at low and high load conditions, respectively. Experimental results obtained from the optimum blend demonstrate that reforming aromatics in future fuels with optimum selection of aromatic species is effective approach to limit exhaust emissions of CI engine.

- Prediction models were developed and demonstrated correlations between emissions (namely PM and NO_x) and the properties of aromatics surrogate fuels. NO_x and PM correlations are created as function of highly impacted properties; density, H/C ratio and aromatic content. The correlations agree with the experimental results.

8.2 Future Work

The knowledge that has been gained from the present study increases interest in number of areas that needs further investigations.

8.2.1 The Effect of Different Alkane Species

There are different types of alkanes in diesel fuel composition; n-alkanes, iso-alkanes and cycloalkanes. These types of alkanes are important diesel fuel composition. In the literature, many studies evaluated that cycloalkanes initiate increased tendency to PM emissions than n-alkanes and iso-alkanes. However, further study is needed in order to investigate the impact of different alkane species of the same type on exhaust emissions and performance. This will may help inform future fuels with optimum selection of alkane species. Also, total alkane content impact on performance is another contribution that could be completed.

8.2.2 Engine Technology

Recently, CI engine have integrated with many technologies such as turbocharger and exhaust gas recirculation (EGR). Study of different aromatic species along with engine technology could be covered in future work. This can help in developing correlations between the emissions resulting from the combustion of aromatic species and engine technology.

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APPENDIX A FUEL PROPERTIES

A.1 The properties of alkylbenzenes surrogate fuels

Table A.1 The properties of group A

Blend	H/C ratio	Density (kg/m3)	Cetane Number	Aromatic Content %
Toluene	1.87	810.57	57.15	21.50
Styrene	1.87	812.29	-	21.50
o-Xylene	1.88	811.17	57.42	21.50
Ethylbenzene	1.88	810.65	57.31	21.50
α-Methylstyrene	1.87	812.41	-	21.50
Pseudocumene	1.88	811.04	57.45	21.50
Cumene	1.88	810.52	57.35	21.50
Tert-Butyl-m-Xylene	1.89	810.65	-	21.50
Diethylbenzene	1.89	810.79	-	21.50
p-Cymene	1.89	810.35	-	21.50
Tertbutylbenzene	1.89	810.65	-	21.50
3-Isopropylcumene	1.89	810.17	56.85	21.50

Table A.2 The properties of group B

Blend	H/C ratio	Density (kg/m3)	Cetane Number	Aromatic Content %
Toluene	1.84	813.26	54.30	26.50
Styrene	1.82	816.74	-	26.50
o-Xylene	1.85	814.48	54.83	26.50
Ethylbenzene	1.85	813.44	54.62	26.50
α-Methylstyrene	1.83	816.98	-	26.50
Pseudocumene	1.85	814.22	54.89	26.50
Cumene	1.85	813.17	54.70	26.50
Tert-Butyl-m-Xylene	1.87	813.44	-	26.50
Diethylbenzene	1.86	813.70	-	26.50
p-Cymene	1.86	812.82	-	26.50
Tertbutylbenzene	1.86	813.44	-	26.50
3-Isopropylcumene	1.87	812.46	53.70	26.50

Table A.3 The properties of group C

Blend	H/C ratio	Density (kg/m^3)	Cetane Number	Aromatic Content %
Toluene	1.80	815.97	51.45	31.50
Styrene	1.78	821.23	-	31.50
o-Xylene	1.81	817.81	52.25	31.50
Ethylbenzene	1.81	816.24	51.93	31.50
α-Methylstyrene	1.79	821.60	-	31.50
Pseudocumene	1.83	817.42	52.34	31.50
Cumene	1.83	815.84	52.05	31.50
Tert-Butyl-m-Xylene	1.85	816.24	-	31.50
Diethylbenzene	1.84	816.64	-	31.50
p-Cymene	1.84	815.30	-	31.50
Tertbutylbenzene	1.84	816.24	-	31.50
3-Isopropylcumene	1.85	814.76	50.55	31.50

A.2 The properties of polycyclic aromatics surrogate fuels

Table A.4 The properties of group A

Blend	H/C ratio	Density (kg/m^3)	Cetane Number	Aromatic Content %
Indene	1.86	815.59	-	21.50
Indane	1.87	814.52	57.43	21.50
Tetralin	1.88	814.80	57.45	21.50
Methylnapthalene	1.86	815.73	57.00	21.50

Table A.5 The properties of group B

Blend	H/C ratio	Density (kg/m^3)	Cetane Number	Aromatic Content %
Indene	1.81	823.44	-	26.50
Indane	1.83	821.26	54.86	26.50
Tetralin	1.84	821.84	54.89	26.50
Methylnapthalene	1.81	823.72	54.00	26.50

Table A.6 The properties of group C

Blend	H/C ratio	Density (kg/m^3)	Cetane Number	Aromatic Content %
Indene	1.76	831.45	-	31.50
Indane	1.79	828.11	52.29	31.50
Tetralin	1.81	828.99	52.34	31.50
Methylnapthalene	1.76	831.87	51.00	31.50

A.3 The properties of base fuel used in optimum blend

Table A.7 The properties of base fuel used in optimum blend

Blend	H/C ratio	Density (kg/m^3)	Cetane Number	Calorific Value (MJ/kg)
Straight single alkane blends	2.Appendix 03	751	71.9	47.5

A.4 Threshold Sooting Index and Double Bond Equivalence

The Threshold Sooting Index (TSL) is known as the ratio of molecular weight and smoke point of fuel that represents sooting tendency as provided in Eq (5.9) [211]. Fuel with low TSI number are likely to be low sooting tendency.

$$\mathrm{TSI} = \mathrm{a}\left(\frac{\mathrm{MW}}{\mathrm{SP}}\right) + \mathrm{b} \qquad \text{Eq (5.9)}$$

Where a and b are constants for a given experimental data and MW and SP are molecular weight and smoke point of fuel.

The Double Bond Equivalence (DBE) is a number of rings or double bonds in an organic compound that determine unsaturation level [212]. The Following formula can be used to obtain ring and double bond. For example, DBE of benzene is 4 as one for ring and 3 for double carbon bonds.

$$\mathrm{DBE} = \mathrm{C} - \frac{\mathrm{H}}{2} - \frac{\mathrm{X}}{2} + \frac{\mathrm{N}}{2} + 1 \qquad \text{Eq (5.10)}$$

Where C is number of carbon atoms, H is number of hydrogen atoms, X number of halogen atoms (i.e. Br, F and Cl) and N is number of nitrogen atoms.

APPENDIX B PROCEDURE

B.1 Standard Operating Procedure for CI Engine Testing Rig

The following procedure should be used to test fuels on the CI engine rig:

1. Check all sensors and monitors are working.
2. Check extraction duct is turned on and working, and the other duct is closed.
3. Check all fuel pipes are safely clamped and there are no leaks.
4. Check the cooling water inlet and outlet.
5. Check the engine for any oil leaks.
6. Check both pipes are in a full water tank.
7. Check the stop button (mushroom type) on the control panel and make sure it is switched on.
8. While starting the engine, check the stop mechanism and make sure it is working.
9. Run the engine for 30 min to warm up.
10. Set the engine under low load by turning on only one load unit (1.1 kW) on the control panel.
11. Wait 5 min to ensure stabilisation.
12. Take current and voltage readings from ammeter and voltmeter on the control panel.
13. Measure fuel weight reduction against time (120 s).
14. Measure PM and smoke emissions using the LLI and smoke meter instruments. Follow LII and smoke meter procedures in Appendix B2.
15. Take gaseous emissions measurements from the MEL. Follow the MEL unit procedure in Appendix B2.
16. Set the engine under high load by turning on five load units (4.5 kW).

17. Repeat steps 10–15.
18. Change the fuel tank to test another fuel (see Fuel System Procedure below).
19. Repeat steps 11–17.
20. At the end of the experiment, turn off the control panel.
21. Switch off the engine ignition key.
22. Close water supplier 10 min after turning off the engine to ensure the reduction in engine temperature.
23. Follow shutdown procedures for the MEL unit, LLI, and smoke meter instruments in Appendix B2.

Fuel System Procedure

1. Turn on fuel valve No 1 to feed the engine with tank No 1 and turn off fuel valve No 2.
2. To feed the engine with tank No 2, turn off fuel pipe No 1 and turn on fuel valve No 2.

Emergency procedure

In case of emergency, there are two options to stop the engine running, which are as follows:

- Switch off the emergency stop button (mushroom type) from the control panel.

Or;

- Turn off the stop link in the engine frame.

B.2 MEL, LLI and Smoke Meter Set-up Procedure

Heated lines

1. Make sure the sample in-line pump located under the desk of MEL controlled computer is switch off.
2. Make sure the sample line valve which is in the left of the pump.
3. Switch the sample line plug into white sockets above the desk (requires more than 30 min to warm up).

4000VM analyser

1. Press 0/1 button on the screen to power the analyser. The initial screen will be presented as NOT STEADY and at least 30 min will be required to warm up. Once temperature has stabilised, the condition will appear as STANDBY.

1. Set the span pressure as 30 psi on the nitrogen cylinder (calibration gas cylinder).
2. Set zero gas pressure as 30 psi on the zero gas cylinder.
3. Switch on the vacuum pump installed on the right of the pitch panel.
4. Set upper sampling concentration range to be 4000 ppm using the RANGE button.
5. Calibrate the analyser at three modes: zero, span, and sample, by using first line buttons on the screen.
6. If calibrations are accurately completed, the analyser is ready for sampling.

9000MGA Analyser

4. Press 0/1 buttons on the displays of the three panels (O_2, CO, and CO_2 panels) to power the analyser. The analyser can run immediately and does not need a warm-up period (compared to the 3000HM and 4000VM analysers).
5. Set the span gas pressure as 30 psi on 10% CO_2, 1000 ppm CO cylinder.

6. Calibrate the analyser at three modes: zero, span, and sample, by using first line buttons on the screen.
7. If calibrations are accurately completed, the analyser is ready for sampling.

3000HM Analyser

1. Press 0/1 button on the screen to power the analyser. The initial screen will be presented as NOT STEADY and at least 30 min will be required to warm up. Once temperature has stabilised, the condition will be appeared as STANDBY.
2. Set span gas pressure as 30 psi on hydrogen-helium cylinder.
3. Turn on the air compressor to supply the analyser. Make sure the amount of air pressure is enough by checking analyser setting screen.
4. Set upper sampling concentration range as 1000 ppm using the RANGE button.
5. Press sample button on the screen to ensure that ignition occurs. This is recognised by the sound of an audible humming. If ignition occurs, the analyser is ready for calibration.
6. Calibrate the analyser at three modes: zero, span, and sample, by using first line buttons on the screen.
7. If calibrations are accurately completed, the analyser is ready for sampling.

MEL shutdown Procedure

4. Close the sample line valve, which is to the left of the pump.
5. Purge air through the analysers to clean up them from remaining sampling elements.
6. Turn off the sample in-line pump.
7. Turn off the vacuum pump instructed with 4000VM analyser.
8. Turn off all calibration cylinders.
9. Switch off all the analysers.

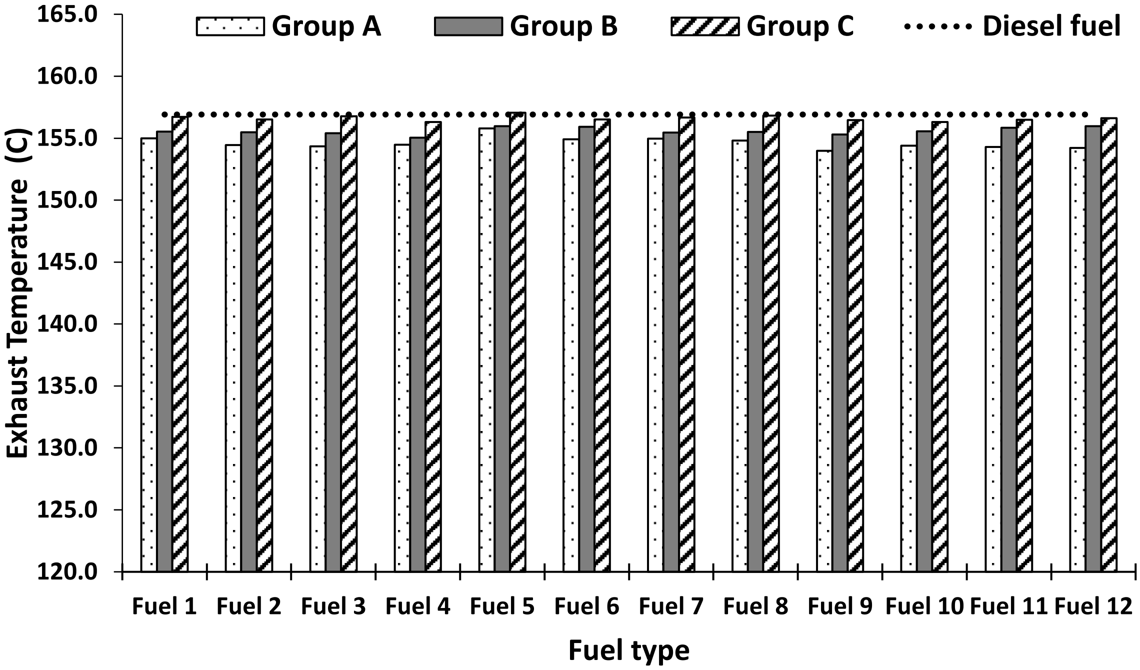
LII Instrument Set-up Procedure

1. Make sure the instrument is connected to the power supply.
2. Make sure sample line and compressed air lines are fitted to the instrument.
3. Press laser power supply underneath the touch screen.
4. Click on START button at the bottom left corner of the touch screen to begin acquisition.
5. Click on RESULTS button on the touch screen to display sampling measurements.
6. At the end of test campaign, click on QUIT button at the bottom left corner of the touch screen.
7. Press laser power supply underneath the touch screen.

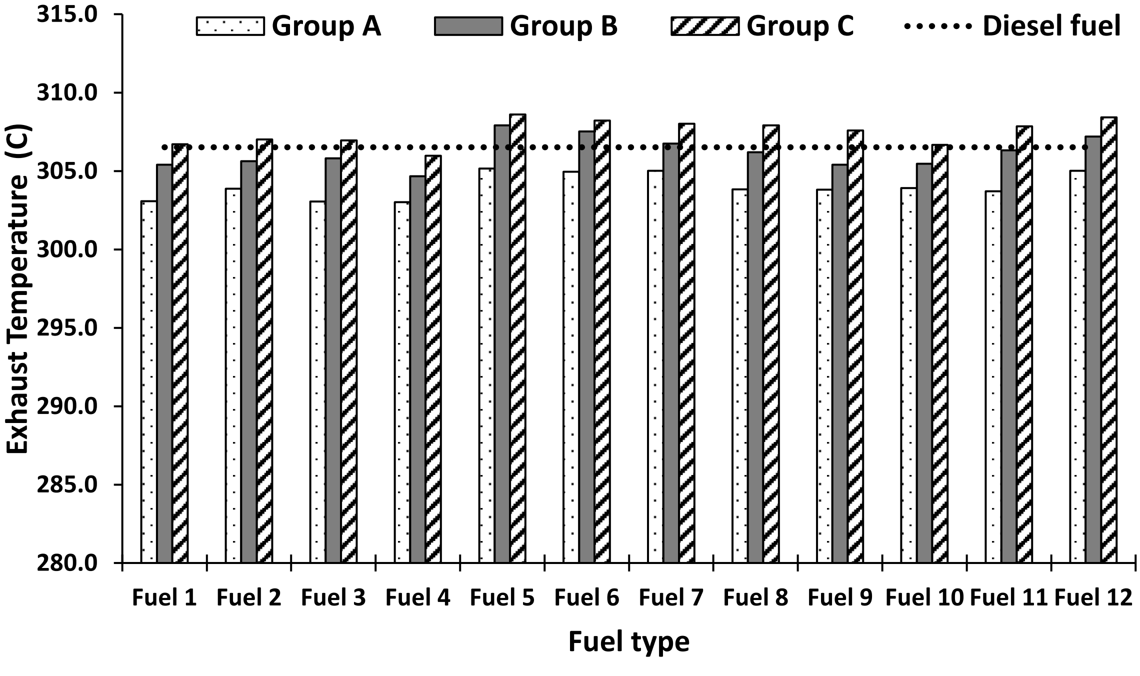
Richard Oliver Smoke Meter Set-up Procedure

1. Switch on 0/1 button to power the instrument and wait until it warms up and reaches 60 °C.
2. Switch on the pump from the front panel of the instrument.
3. Adjust needle valve to maintain the sample flow rate at 9.2 L/min. Make sure the flow rate is fixed during test campaign.
4. Press the RESET button on the front panel of the instrument when the engine is running.
5. Open the sample filter block and insert Whatman no. 4 filter paper.
6. Press SAMPLE button to start sampling.
7. Wait until 9.2 L of sample passes through the filter paper as indicated on the display screen.
8. Open the sample filter block and replace the filter paper with another one.
9. Repeat steps 4–8 for each test point.
10. At the end of test campaign, shutdown the pump and then the instrument

APPENDIX C EXHAUST TEMPERATURES OF TEST FUEL BLENDS

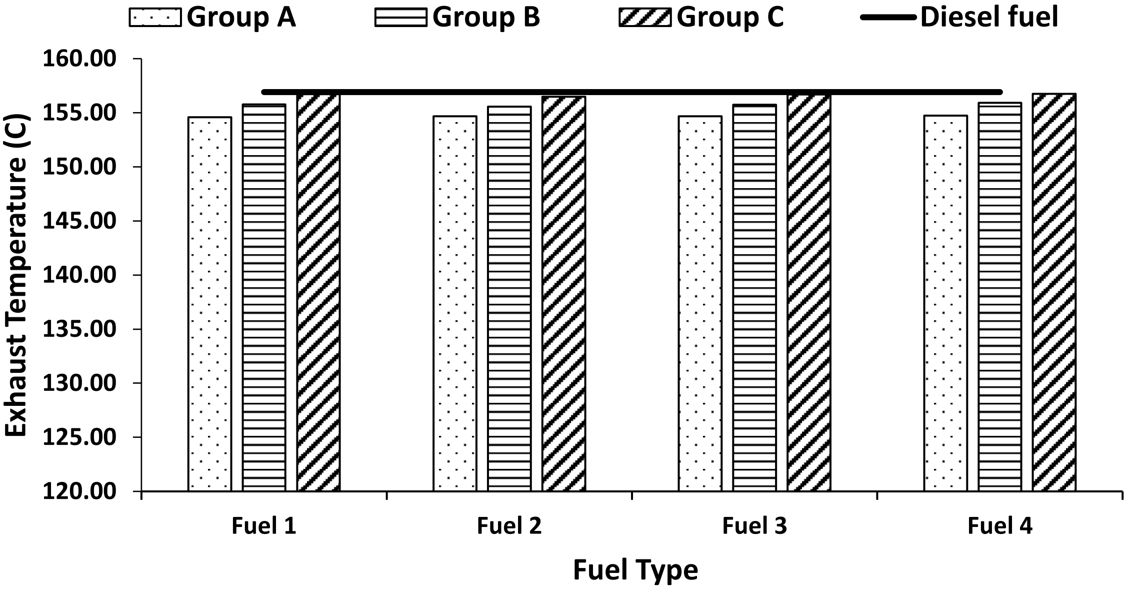


(a) Low load

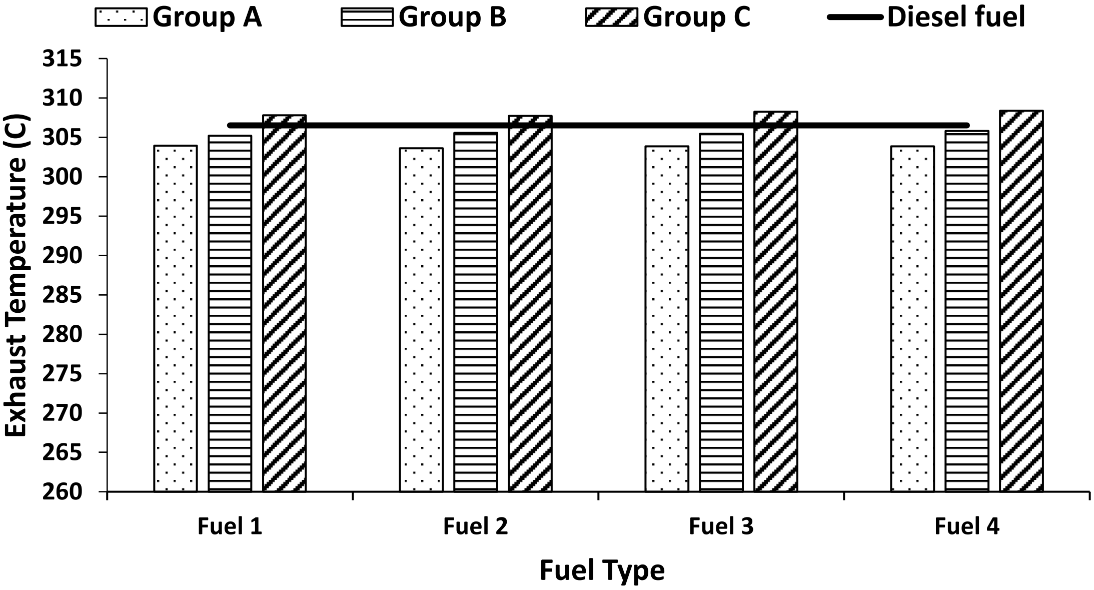


(b) High load

Figure C.1 Exhaust temperature results of alkylbenzenes fuel blends



(a) Low load



(b) High load

Figure C.2 Exhaust temperature results of polycyclic aromatics fuel blends