IMPACT OF ALTERNATIVE FUELS AND HYDROGEN – ENRICHED GASEOUS FUEL ON COMBUSTION AND EMISSIONS IN DIESEL ENGINES

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ABSTRACT

The dependence on fossil fuels in transportation and other sectors, e.g. power generation, has increased concerns for their availability in the future. Therefore, the introduction of various alternative fuels for vehicles is necessary. However, the utilisation of alternative fuels, specifically gaseous fuel, in diesel engines has some disadvantages such as reduced engine thermal efficiency and increased exhaust gas emissions, although showing good results in reducing soot and NO_X, simultaneously. Therefore, the effect of the hydrogen – enriched gaseous fuel (i.e. assuming conversion of part of the gaseous fuel into hydrogen – enriched gas in a fuel reforming process) in the dual fuelled combustion process was studied as a mean of improving further the combustion process and control emissions.

The hydrogen addition was very effective in overcoming the penalty of the biogas or LPG-diesel dual fuelled engine operation. Under hydrogen addition and high engine load, in the case of biogas-diesel dual fuelling, the HC and CO emissions decreased up to 59.3% and 49.6% respectively and thermal efficiency increased by 9.1%. However, NO_X increased by 21.2%. In LPG-diesel dual fuelling, the HC and CO reduced by 32.6% and 48% respectively, thermal efficiency increased by 7.4%, but NO_X increased by 16%.

The implementation of exhaust gas recirculation (EGR) and advanced injection timing showed great potential for dual fuelled engine. The utilisation of EGR at high LPG concentration further improved soot – NO_X trade-off through low in-cylinder temperatures and reduced amount of liquid fuel used for combustion. At low load and under EGR application, soot and NO_X emissions reduced by 58.9% and 18.4% respectively. In addition, the increased in-cylinder temperature with advanced injection timing improved dual fuelled

combustion process hence reducing both HC and CO by 7.5% and increased engine brake thermal efficiency by 3.6%.

Moreover, the properties of the injected diesel fuels (ULSD, RME and GTL) as a pilot fuel have been shown to significantly affect the combustion process, rate of heat release, and emissions formation and oxidation in the dual fuelling system. Oxygenated fuel like RME contributed to the reduction of emissions, except NO_X, while a high cetane number fuel like GTL showed better tolerance to EGR addition and soot – NO_X trade-off.

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Symbol	Unit	
c_p	J/kgK	Specific heat at constant pressure
c_v	J/kgK	Specific heat at constant volume
LCV	MJ/kg	Lower calorific value
	kg/s	Fuel mass flow rate
N	rpm	Engine speed
p	MPa	pressure
P_b	kW	Engine brake power
Q	J	Heat transfer (Energy)
T_b	Nm	Engine brake torque
V	cm^3	Instantaneous volume of the engine cylinde
	cm^3	Displaced volume
	m^3/s	Volumetric flow rate of measured air with EGR
	m^3/s	Volumetric flow rate of measured air without EGR
γ		Specific heat ratio
	%	Brake engine thermal efficiency
θ	degree	Crank angle
λ		Relative air-fuel ratio
Φ		Relative fuel-air ratio
	rad/s	Angular speed

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATDC	After top dead centre
ATR	Autothermal reforming
BMEP	Brake mean effective pressure
BS	British standard
BTDC	Before top dead centre
BTEX	Benzene, toluene, ethylbenzene and m-/p-/o-xylenes
BTL	Biomass-to-liquid
C/H	Carbon to hydrogen ratio
C_2H_2	Ethylene
C_2H_4	Ethylene
C_2H_6	Ethane
C_3H_6	Propylene/Cyclopropane
C_3H_8	Propane
C_4H_8	Butylene/Cyclobutane
C_5H_{10}	Cyclopentane
C_6H_{10}	3,3 dimethyl-1-butyne
C_8H_{18}	2,2,4-trimethylpentana or n-octane
CAD	Crank angle degree
CH	Carbogen
CH_2	Methylene
CH_2O	Formaldehyde
CH_4	Methane
CI	Compression ignition
CLD	Chemiluminescence detection
CN	Cetane number
CO	Carbon monoxide
CO_2	Carbon dioxide
COV	Coefficient of variation
CPC	Condensation particle number
CTL	Coal-to-liquid
DC	Diffusion charging
DMA	Differential mobility analyzer
DOC	Diesel oxidation catalyst
EC	Electrostatic classifier
EGR	Exhaust gas recirculation
EOI	End of injection
FID	Flame ionization detection
FSN	Filter smoke number

FT	Fischer-Tropsch
FTIR	Fourier transform infrared spectroscopy
GC-FID	Gas chromatograph-flame ionization detector
GD30	Ultra low sulphur diesel and gas to liquid diesel blends
Gt	Giga ton
GTL	Gas-to-liquid
H	Hydrogen atom
H/C	Hydrogen to carbon ratio
H_2	Hydrogen
H_2O	Water
HC	Hydrocarbon
HCCI	Homogeneous charge compression ignition
HCN	Hydrogen cyanide
HCs	Hydrocarbons
HC-SCR	Hydrocarbon selective catalytic reduction
HFID	Heated flame ionization defectors
HSDI	High speed direct injection
IC	Internal combustion
IEA	International Energy Agency
IMEP	Indicated mean effective pressure
LHV	Lower heating value
LPG	Liquefied petroleum gas
MIR	Maximum incremental reactivity
MPA	Magneto pneumatic
MULINBUMP	Multi-pulse fuel injection in bump combustion chamber
N	Nitrogen atom
N_2	Nitrogen
NDIR	Non disperse infrared
NH	Nitrogen monohydride
NH_3	Ammonia
NMHC	Non-methane hydrocarbon
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_X	Nitrogen oxides
O	Oxygen atom
O_2	Oxygen
OECD	Organisation for Economic Co-operation and Development
OH	Hydroxyl
PAH	Polycyclic aromatic hydrocarbon
PFI	Port fuel injection
PM	Particulate matter
POX	Partial oxidation

PREDIC	Premixed lean diesel combustion
PREMIER	Premixed mixture ignition in the end-gas region
R-CHO	Aldehyde
REGR	Reformed exhaust gas recirculation
RME	Rapeseed methyl ester
ROHR	Rate of heat released
SCR	Selective catalytic reduction
SI	Spark ignition
SMPS	Scanning mobility particle sizer
SOC	Start of combustion
SOF	Soluble organic fraction
SOI	Start of injection
SOM	Soluble organic material
SR	Steam reforming
TDC	Top dead centre
TPES	Total primary energy supply
ULSD	Ultra low sulphur diesel
VOC	Volatile organic compound
WGSR	Water-gas shift reaction

CHAPTER 1

INTRODUCTION

1.1 Background

Issues related to the fossil fuels shortage have been recognised for a long time. A heavy dependence upon this energy source as being the main if not the only energy carrier in transportation and power generation for many decades has generated concerns and triggered extensive research into alternative fuels. The concern of the low fossil fuel reserves started a long time ago when a theory about peak oil production was introduced. Although the indicators considered to predict the peak oil production have been improved significantly by considering many new factors, most scientists and organisations agree that the peak oil production date will be before 2020 (de Almeida and Silva, 2009).

In addition, the recently ease of accessibility and availability has made fossil fuels the largest share of fuel for transportation. The International Energy Agency (IEA), in a report published in 2007, states that fossil energy contributes of about 81% of the total world commercial energy while about 98% of it is used for transportation (de Almeida and Silva, 2009). This is a consequence of the increased demand and number of vehicles all over the world and is also triggered by high economic growth of some countries which is followed by the considerable increase in energy utilisation.

Over time fuel prices are significantly volatile, as shown in Figure 1. Apart from the rapid rate of energy demand, the trend of the crude oil price is also sensitive to many factors such as political reasons, currency fluctuation, and supply (von Hippel et al., 2011).
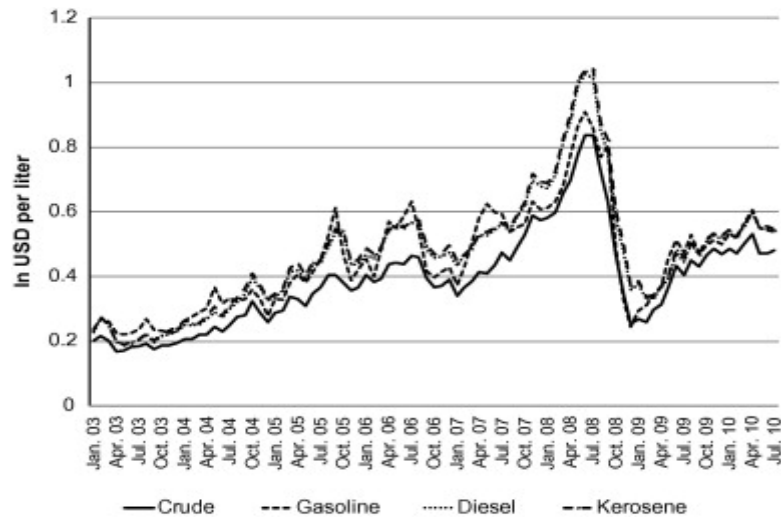
Figure 1.   The world fuel price from 2003-2010 (Arze del Granado et al., 2012)

In addition to fuel security, there is another factor that has encouraged an attempt to replace the whole or part of conventional fossil fuels used in motor vehicles. This is because burning fossil fuel produces harmful emissions (including CO_2) for the public and causes adverse effects on the environment. Emissions of CO_2 produced from the fossil fuels combustion even contribute significantly to global warming.

Therefore, sustainable fuels development and fuel security can be improved with the substitution of fossil fuels with renewable and other alternative fuels, both gaseous and liquid fuels. In addition, further fuel savings in transportation should be improved by enhancing engine technology in order to also be able to utilise gaseous fuels. However, their utilisation in diesel engines still has drawbacks in terms of engine performance and engine-out emissions (Papagiannakis and Hountalas, 2004, Papagiannakis et al., 2007). This is a result of the low energy content and low cetane number (CN) of most gaseous fuels.

To address the challenges described above, research work has been done which aims to explore some alternative fuels (renewable and non-renewable), both gaseous and liquid fuels, to replace part or all of conventional fuels to be used in diesel engines. It also investigates the

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potential of using hydrogen, a good energy carrier resource which has high energy content, as a supplement combined with the gaseous fuels.

1.2 Objectives of the Research

The main objective of the research is to investigate the utilisation of some alternative fuels which also involve strategies to improve engine thermal efficiency and engine-out emissions. In order to achieve the objective, a modification has been carried out to facilitate a dual fuel combustion mode. In addition, different pilot fuels, engine modes of operation, and hydrogen addition were employed where the hydrogen used for this work was obtained from hydrocarbon gaseous fuel (biogas and LPG) reforming. Furthermore, the objectives are described as follows:

- Analyse the effect and feasibility of the induction of biogas and LPG at different concentration levels and engine operating conditions (i.e. engine load) on combustion and exhaust emissions characteristics of a Diesel engine.

- Understand the pilot fuels effect (ULSD, RME and GTL) which have different properties and their combination with gaseous fuels on combustion and exhaust emissions characteristics.

- Investigate the feasibility of advanced pilot fuel injection timing and EGR (exhaust gas recirculation) addition on LPG-diesel dual fuelled engine operation.

- Analyse and understand the effect of reformate addition (both H_2 + CO and H_2 only) in the biogas and LPG-diesel dual fuelling on combustion and emissions characteristics.

1.3   Thesis Outline

This introduction makes up the first chapter which describes a general and brief outline about the background and the aim of the research. Chapter 2 gives a general introduction and reviews the relevant literature on diesel emissions, strategies which can be done to alleviate dependence on oil-based fossil fuel, and a brief explanation of dual fuelled engine combustion mode and how to improve the engine-out emissions. Chapter 3 presents the fuels used and experimental facilities in this research work. These include the diesel engine test bench, exhaust emissions measurement equipment and modifications made to the engine for dual fuelling system purposes. Chapter 4 describes the experimental results from biogas-diesel dual fuelling. It also discusses the effects of the combustion of different injected diesel fuels (conventional diesel fuel, ULSD and alternative fuel, GTL) and their blending (GD30, ULSD-GTL blends 70/30 by volume). This chapter also covers the hydrogen and reformate (H_2 and CO) effects on the engine thermal efficiency and emissions. Chapter 5 focuses on the other gaseous fuel but non-renewable, LPG, on the LPG-diesel dual fuelling with the effect of advanced injection timing and EGR (exhaust gas recirculation). This chapter explains the experimental results that were carried out with two alternative diesel fuels, RME and GTL, compared with ULSD as a baseline condition. Apart from gaseous emissions, soot emission, including soluble organic material (SOM), was investigated and discussed in correlation to gaseous HC. Chapter 6 is an extension of the previous work on LPG-diesel dual fuelling. Gaseous fuel (H_2 and CO) from propane reforming was added along with LPG (propane). Soot formation in hydrogen combustion with relatively high H/C ratio gaseous fuel (propane) was analyzed. This chapter also includes the analysis of some HC species that have lower than three carbon atoms (mainly derived from propane). The last chapter, Chapter 7, summarizes all the research works and the feasibility of gaseous and alternative liquid fuels

on dual fuel combustion. It also offers recommendations for dual fuel systems. Future areas

are proposed to obtain a better understanding of dual fuelled engine operation.

CHAPTER 2

LITERATURE REVIEW

2.1 Diesel Engine Operation

Invented by Rudolf Diesel in 1892, compression ignition (CI) engines have higher thermal efficiency compared with spark ignition (SI) engines. The engine usually operates on a 4-stroke cycle and the basics of conventional diesel combustion are briefly explained as follows.

In diesel engines, the combustion air is inducted into the combustion chamber through intake manifold. This induction process occurs as the piston moves down while the intake valve opens. The amount of inducted fresh air charge depends on engine speed being higher at high engine speed. The piston then moves up from bottom dead centre to compress air charge where at the same time both intake and exhaust valves are closed. A few crank angle degrees before the piston reaches top dead centre, the fuel is injected at high velocity through small orifices or nozzles in the injector tip and atomises the fuel. The high pressure and temperature of the in-cylinder air then mixes with the vaporised fuel. When the air-fuel mixture temperature is higher than fuel's self ignition temperature, a series of spontaneous chemical reactions occurs leading to rapid self-ignition (Heywood, 1988). The in-cylinder pressure and temperature then rises to a much higher level. As the expansion process takes place, where the piston moves downward, the remaining injected fuel still undergoes atomisation and evaporation due to the high combustion temperature. The combustion process continues for a further few crank angle degrees after the end of injection (EOI).

Just as the piston reaches the bottom dead centre, the exhaust valve opens. The difference in pressure between the in-cylinder and exhaust manifold allows the burned gases to escape the cylinder. The burned gas is pushed out by the piston in the exhaust stroke into the exhaust manifold then the next cycle starts again.

The overall combustion process includes four phases; ignition delay, premixed combustion, diffusion combustion and late combustion, which is associated with the rate of heat release diagram as depicted in Figure 2.
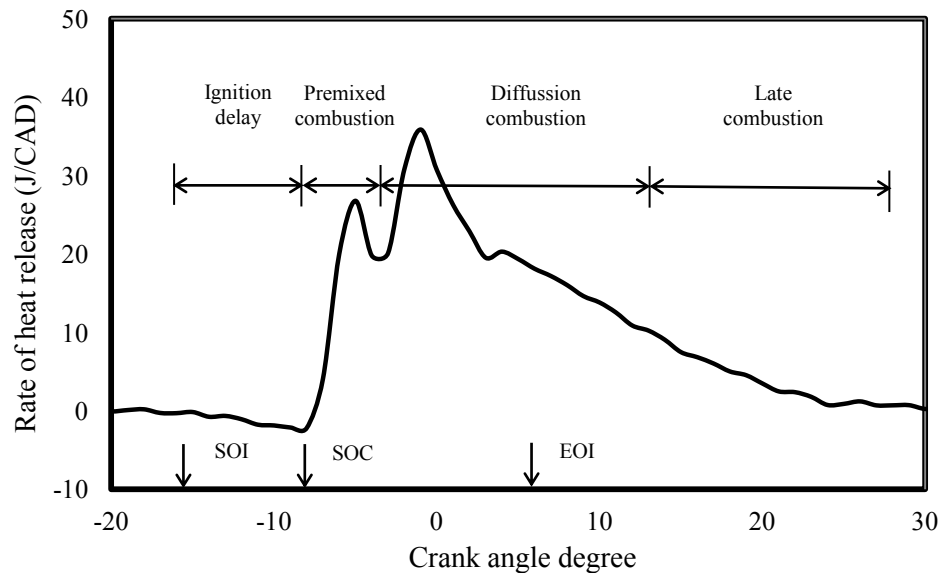
Figure 2.   Typical combustion phase of direct injection diesel engine (Tira et al., 2012)

Ignition delay phase is a time lag between the start of fuel injection (SOI) and start of combustion (SOC). This phase is affected not only by in-cylinder conditions such as temperature, pressure, concentration of charge, oxygen availability but also fuel chemical and physical characteristics (Lata and Misra, 2011). Premixed combustion phase is identified by the increase of heat released in the cylinder due to the combustion of premixed air-fuel mixture within the flammability limit of the fuel. Following this phase is the diffusion combustion phase which is controlled by the rate at which mixture becomes available for

burning. The last phase is late combustion which is generated in the expansion stroke and is determined by the remaining unburned fuel. The heat released at this phase is at lower rate due to the scarcity of air-fuel mixture and in-cylinder temperature drops.

2.2   Diesel Engine-out Emissions

One of the major sources to air pollutant is diesel engines. The concentration of the diesel combustion harmful by-products depends on factors such as engine speed and load, fuel physical and chemical properties, air-fuel ratio, injection timing, and engine design. An understanding in formation and oxidation mechanism of the diesel engine emissions is important as it can lead towards finding solutions to control them.

2.2.1   Carbon Dioxide (CO_2)

Carbon dioxide is the main product of carbon-contained fuel combustion. It is one of the primary emissions of greenhouse gases with nitrous oxide, methane, perfluorocarbons, sulphur hexafluoride and hydrofluorocarbons (Kaewmai et al., 2012). Indeed, CO_2 is already present in the atmosphere but in very low concentration. Unfortunately, the amount has increased over the years at an alarming rate. According to the IEA (International Energy Agency) report, in 1870 the total CO_2 concentration from combustion of fuel is almost zero but in 2009 is measured to be around 29 Gt CO_2. The human activities have changed the balance and cannot compensate the naturally ability of the forest (plants) to remove CO_2. Globally massive utilisation of fossil fuels (i.e. natural gas, coal and oil), exacerbated by deforestation and long lifetime of CO_2 in the atmosphere, impacts adversely to the climate change and makes a serious concern for all nations (IEA, 2011).

Majority of the CO_2 emission in the atmosphere is contributed by activities which heavily use carbon-contained fossil fuels. Those sectors or activities are electricity and heat

generation, transportation and industry. All the sectors account for more than three-quarters of global CO_2 concentration as described in Figure 3 (Ellis and Tréanton, 1998). The increase in population and economic growth of many nations have led to the increased CO_2 emissions concentration (Johansson et al., 1996).
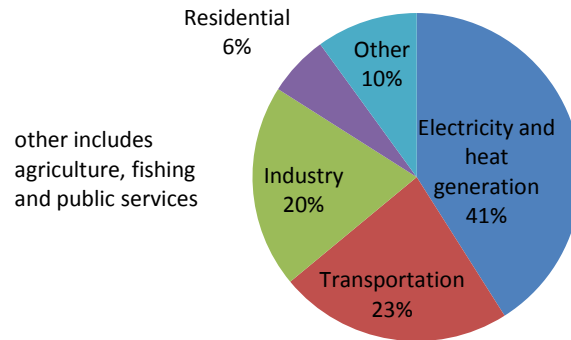
Figure 3.   Sources of CO_2 emissions in 2009 (IEA, 2011)

Though coal represents only one-quarter of the world total primary energy supply (TPES) in 2009, it accounts for 43% of the global CO_2 emissions due to its heavy carbon content per unit of energy released. Moreover, oil and gas accounts 37% and 20% respectively of the global CO_2. This indicates that the more carbon presents in the fuel the more CO_2 is emitted. Figure 4 depicts comparison of CO_2 sharing from different energy sources.

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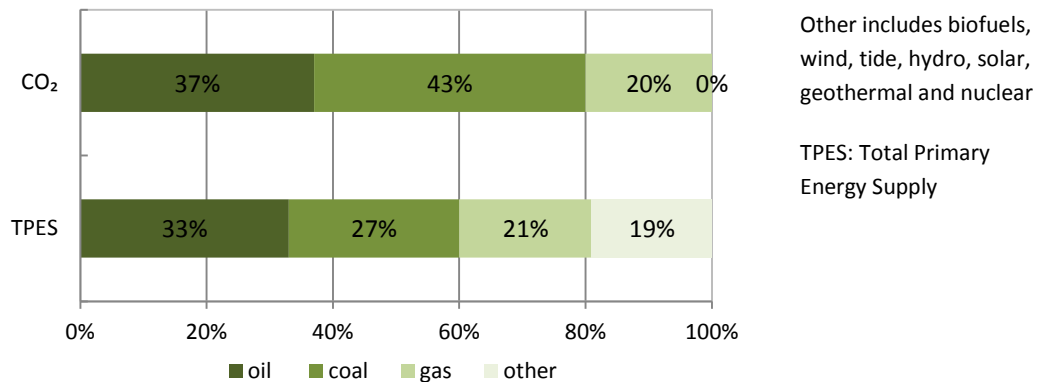
Figure 4. CO_2 emissions associated to type of fuel in 2009 (IEA, 2011)

In transport sector, the second largest CO_2 contributor, some strategies can be implemented to achieve the reduction in CO_2. The use of engine technologies which offer higher fuel conversion efficiently, the use of renewable fuels, the use of fuels having low carbon content, and for longer term the use of hydrogen are some of the proposed strategies (Johansson et al., 1996).

2.2.2   Hydrocarbons (HCs)

Hydrocarbons are produced from the incomplete combustion of hydrocarbon fuel. The concentration level is related to misfire and poor charge mixture due to insufficient mixing between fuel and air. There are several sources for the formation of the HCs emissions such as oil film layers, wall flame quenching, deposits and crevices in the combustion chamber, liquid fuel, and exhaust-valve leakage (Alkidas, 1999). However, the most influential factor for HCs source in fully warmed conditions is combustion chamber crevices (about 38%) whereas under cold start or cold conditions the main HCs sources are wall flame quenching, lubricating oil films and fuel preparation (Alkidas, 1999).

Combustion chamber crevices act as the main place for HCs sources because the very small space available causes flame quenching. The crevices in the cylinder can be head gasket and valve-seat crevices, and piston-ring-pack (Heywood, 1988).

The occurrence of wall flame quenching is when the propagation of flame reaches the cylinder wall forming a thin layer on the surface without oxidation. This layer then is called quenching distance. In this case the cylinder wall can act as an interrupt mechanism of the oxidation reaction and the heat sink results in an in-cylinder temperature drop. Therefore, the cylinder wall temperature is very important in terms of determining the HCs emission level.

Moreover, oil used for lubrication between piston rings and cylinder liner also can contribute to the HCs emission. The oil thin film absorbs fuel thus prevents fuel taking part in the combustion process, and escapes the combustion chamber unburned. In addition, fuel used also affects the HCs emission. Fuels which contain aromatics and olefins generally produce higher concentration of hydrocarbon.

In dual fuel operation, the lower air-fuel ratio due to air replacement results in high HCs emission compared with normal diesel operation. The high heat capacity and lack of oxygen in the combustion chamber leads to a temperature reduction in in-cylinder as a result of misfiring and poor mixing, and hence resulting in slower combustion rate allowing unburned mixture to leave the combustion chamber (Sahoo et al., 2009).

In order to reduce the HCs emission, some techniques are introduced to enhance the mixing time and intensity such as varying the fuel injection timing, increasing fuel injection pressure, and modifying the piston head. The high measured HCs emission concentration can give indication of high cyclic variability as results of partial burning or misfiring cycles (Heywood, 1988).

2.2.3 Carbon Monoxide (CO)

Carbon monoxide is an odorless, tasteless and colorless, and non-corrosive gas that can be poisonous to humans. It is an intermediate product from incomplete combustion of carbon-contained fuels.

The formation process of CO is started by reaction between oxygen and gaseous or liquid hydrocarbon fuel. The CO produced then can react either with oxygen or hydroxyl (OH) radicals to produce carbon dioxide. However, the oxidation rate of CO is slower than those of hydrocarbon species because CO still can be produced although there is enough oxygen (Bagal et al., 2009). Therefore, it is required appropriate in-cylinder conditions in order to minimise the CO formation. The mechanism of the production and oxidation of CO from fuel is described as follows (Adomeit et al., 2006, Bagal et al., 2009).

$$\qquad \qquad (2.1)$$

$$\qquad \qquad (2.2)$$

$$\qquad \qquad (2.3)$$

In diesel engines there are two main sources for the CO formation: over mixing and under mixing between air and fuel (Bagal et al., 2009). Lean combustion during ignition delay period and low temperature combustion are associated to over mixing. In this condition CO cannot be fully oxidised even though there is abundant oxygen. Under mixing condition is associated to the rich premixed combustion where fuel does not mix with air properly hence the CO produced cannot be fully oxidised by OH or oxygen thus leaving high CO level. Dual fuel combustion mode is related to this under mixing condition.

Therefore, it can be summarised that the level of CO produced in the combustion chamber is affected by some factors such as in-cylinder temperature, oxygen concentration,

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gas residence time, and charge mixture turbulence. The OH radical presence is very significant in reducing the emission due to complete combustion. The OH production strongly depends on combustion temperature and it is a product of chain reactions involving oxygen (Heywood, 1988). Therefore, the availability of sufficient oxygen and also high temperature in the combustion chamber are necessary to oxidise CO. However, those two factors are difficult to be achieved in dual fuel combustion which needs to be addressed.

Some efforts have been performed to control the emission to achieve an acceptable level. They include improvements in engine design and engine operating conditions such as the application of fuel injection timing, combustion chamber geometry, and diameter of combustion cavities to obtain uniform air-fuel mixing, and also utilisation of oxygenated diesel fuels (Chen and Iwashina, 2009, Lapuerta et al., 2008a).

2.2.4 Nitrogen Oxides (NO_X)

NO_X is one of the important air pollutants and one of the major diesel emissions which mainly consist of NO and NO_2. However, NO is the predominant compound. The propensity of NO_X formation in the combustion chamber can be described generally by three methods. The first method is thermal NO_X, where the formation depends on the molar concentration of nitrogen and oxygen and high temperature in the combustion chamber. The mechanism of thermal NO_X formation is described by Zeldovich equations. The Zeldovich equations are expressed below:

$$(2.4)$$

$$(2.5)$$

$$(2.6)$$

Secondly is the NO_X formation from the nitrogen of the fuel, where high nitrogen-contained fuels are considered to contribute the NO_X although current nitrogen levels in diesel are not significant. The NO_X formation through this mechanism involves the intermediate species which contains nitrogen such as HCN, NH_3, NH or CN (Fernando et al., 2005).

Thirdly is prompt (Fenimore) NO_X formation, where NO_X is produced by reaction between radicals of hydrocarbon and nitrogen to form HCN in the combustion chamber. When the equivalence ratio is increased, the amount of HC radicals also increases. In addition, the more HC radicals in the combustion process the more NO_X is likely to be produced through this mechanism. The reactions of prompt NO_X formation are shown as follows (Fernando et al., 2005):

$$ (2.7) $$

$$ (2.8) $$

$$ (2.9) $$

$$ (2.10) $$

$$ (2.11) $$

The three pathways of the NO_X formation contribute to the overall NO_X emissions although the contribution of the first mechanism is believed as the most important one (Ban-Weiss et al., 2007). NO_X formation level is also associated to the carbon-to-hydrogen ratio (C/H) of diesel fuels. It has been reported that with the increase in C/H ratio, usually found in fuels with high aromatic content, the adiabatic flame temperature increases which has propensity to produce NO_X (Miyamoto et al., 1994). Most alternative fuels both renewable and non renewable have low C/H ratio which is beneficial to inhibit the emission formation.

Because the harmful effect of NO_X, some internal combustion NO_X limiting technologies have been proposed to reduce the emission. For example, reducing combustion

temperature through steam/water injection or less excess air, denitrogenation of the fuel, reducing the residence time at high in-cylinder temperature through ignition or injection timing adjustment, catalytic combustion or aftertreatment system including the use of selective catalytic reduction (SCR), and premixed or homogeneous intake charge application where dual fuel combustion is categorized in this method. As NO_X emissions are much related to the high in-cylinder temperature, a diluted intake charge by either air or exhaust gas recirculation (EGR) can effectively reduce the emission level.

2.2.5   Particulate Matter (PM)

Particulate Matter (PM) is a typical engine-out emission of diesel engines and much higher than in the case of SI engines. This is caused by a non-homogeneous combustion process in the cylinder. PM concentration increases in line as the engine load increases. At this engine condition the combustion temperature is high thus can reduce the PM formation but a significant high fuel concentration in the combustion chamber generates the PM emission. In addition, the scarcity of oxygen also substantially influences the PM formation by hampering the emission oxidation. Therefore, the air-fuel ratio is considered important in PM emission formation rate.

The aromatic content in fuel also contributes to the emitted PM (Xinling and Zhen, 2009). Therefore, a low aromatic content in a fuel potentially reduces the PM concentration. In addition, Miyamoto et al. (Miyamoto et al., 1996) also has proven that increasing oxygen content and reducing the number of molecular C-C bonds in a fuel substantially reduce PM emission. The sulphur content of injected fuel also affects PM emission. Tan et al. (Tan et al., 2009) has found that PM is decreased as sulphur content in the fuel decreases in the same engine operating conditions. Additionally, the effect of sulphur content to PM emission is more obvious at low engine load conditions. Therefore, modifications on in-cylinder

conditions through dual fuel combustion and changes in fuel properties through the use of oxygenated and free-aromatics fuels are expected to control the PM formation.

Diesel PM shows a bimodal size distribution and lognormal in form. One of the size distributions is called nuclei mode, ranging from 0.005 to 0.05 μm. Due to its smaller size, particles in this mode have little effect on the total mass but have significant impact on total number of particulate. The accumulation mode particles, having larger size, are in the size range from 0.05 to 1.0 μm and dominate the mass of diesel particle.

The structure of PM of diesel combustion mainly consists of ash, solid carbonaceous material (mainly soot), volatile organic and sulphur compound (Graskow et al., 1999). The formation of soot occurs in locally fuel rich region where the ratio of carbon to oxygen atoms is high. In addition, the volatile or soluble organic compounds (SOM/soluble organic material) are formed from atomized and evaporated lube oil and fuel which escapes and is not involved in oxidation process (Cromas and Ghandhi, 2005). The sulphur content in the fuel influences the particulate size and distribution by the formation of volatile compound which is adsorbed onto the soot. However, most of the currently available fuel in the automotive market has relatively low sulphur content which is below the regulated level.

2.2.6   Unregulated Emissions

Apart from the major engine pollutants such as HC, CO, NO_X and PM, CI engines also emit various emissions which are not yet regulated. Some of the unregulated emissions come from HCs species. The following are some of the emissions.

Aldehydes

Aldehydes, member of carbonyl group, are simple compounds which can be identified by a carbon-oxygen double bond with R-CHO structure. Acetaldehyde and formaldehyde are two main aldehydes species emitted from motor vehicles (Zhu et al., 2011b). Aldehydes are

the intermediate compounds which mainly originate from incomplete combustion of saturated aliphatic hydrocarbons (Magnusson et al., 2002, Takada et al., 2003). Concentration of the emitted emission is affected by fuel composition (Zervas et al., 2002). Some experimental results show that the emission increases with biodiesel (Turrio-Baldassarri et al., 2004, Machado Corrêa and Arbilla, 2008) but another show an opposite trend (Krahl et al., 2009). Therefore, it can be suggested that there are multiple sources of parameters which affect the emission when using biodiesel. They are conditions and type of engine, origin of biodiesel, and modes of operation (Machado Corrêa and Arbilla, 2008, Peng et al., 2008a, Zervas et al., 2002).

Alkyl compounds

They are organic chemical compounds that contain only hydrogen and carbon either straight or cyclic chains. Based on the structure, the compounds can be classified into two classes: aliphatics and aromatics. Moreover, aliphatic hydrocarbons are divided into paraffins, cycloparaffins, olefins and acetylenes (Heywood, 1988).

Paraffins (C_nH_{2n+2}): saturated hydrocarbon molecules with single bond open-chain. Examples of the group are methane (CH_4), ethane (C_2H_6), 2,2,4-trimethylpentana (C_8H_{18}).

Cycloparaffins (C_nH_{2n}): unsaturated hydrocarbon molecules with single bond ring chain. Examples of the group are cyclopropane (C_3H_6), cyclobutane (C_4H_8), cyclopentane (C_5H_{10}).

Olefins (C_nH_{2n}): open-chain unsaturated hydrocarbons containing a double bond. Examples of the group are ethylene (C_2H_4), propylene (C_3H_6), butylene (C_4H_8).

Acetylenes (C_nH_{2n-2}): open-chain unsaturated hydrocarbons containing one C-C triple bond. Examples of the group are acetylene (C_2H_2) and 3,3 dimethyl-1-butyne (C_6H_{10}).

Meanwhile aromatics are hydrocarbons that contain one or more benzene rings.

Benzene, toluene, ethylbenzene and m-/p-/o-xylenes (BTEX) compounds

The emissions are characterised by highly flammable and strong odour. They are volatile organic compounds (VOCs) which are emitted by petrol and diesel engines and potentially contribute to ozone formation. The formation of the emissions is affected by conditions of combustion such as high temperature and local stoichiometric which improve fuel thermal pyrolysis (Takada et al., 2003, Nelson et al., 2008). Moreover, the major source for the production of benzene and toluene is from fuel fragments which are produced from oxidative pyrolysis of fuel (Nelson et al., 2008), meanwhile xylene formation is associated to aromatic content in fuel (Zhu et al., 2011b). BTEX is one of the important fractions of non-methane hydrocarbons (NMHC) which are classified as hazardous air pollutants as can actively participate in photochemical reactions (Rappenglück et al., 1998).

Soluble organic material (SOM)

SOM is part of PM which is formed by the unburned fuel or oil which then undergoes the phase change from gas to particulate phase and is adsorbed onto the soot. The concentration of SOM is related to various factors such as engine operating conditions, type of fuel, and sampling technique. At high engine load, the total mass of SOM is lower compared with low engine load even much higher at idle (Stanmore et al., 2001). Moreover, in HCCI or dual fuel engine operation SOM is relatively high compared to that of conventional CI engines. This is caused by unburned low volatile component in fuel which can be adhered on the cylinder wall (Kawano et al., 2004).

It is widely accepted that biodiesel has higher SOM. It is mainly due to lower volatility and higher viscosity which has high propensity to be condensed and adsorbed onto the particles surface, which is more obvious in the cold conditions or low engine load (Lapuerta

et al., 2008a). SOM contains polycyclic aromatic hydrocarbons (PAH) which are toxic and harmful to human and environment.

2.3   Strategy for Fuel Security and Sustainability

The security of fuels availability as energy carrier should be maintained and becomes a priority goal both for short and long term. The indicators for fuel security have evolved not only a physical *availability* of fuel but also considering various aspects. The oil crisis in 1970 and 1980 has formatted the energy policy and *affordability* was included for the fuel security as economical aspect. Concern on environmental deterioration and climate change has driven to formulate stringent emissions legislations. Therefore, *acceptability* of fuel combustion to meet the emission legislations was also taken into consideration. The globally uneven of oil reserves and consumption, Middle East countries have 62% of the global oil reserves while the OECD (Organisation for Economic Co-operation and Development) countries only have 9% but consume 50% of global oil (Lefèvre, 2010), has put *accessibility* as another indicator for fuel security (Kruyt et al., 2009).

The discussion in this section will focus on the use of gaseous and alternative liquid fuels as diversification of fuel for transport sector in dual fuel engine mode. Dual fuelled engine and the use of alternative fuels principally are means to simultaneously reduce fossil fuel consumption, thus keeping the fuel security, and air pollution or greenhouse gases.

2.3.1   Gaseous Fuels Utilisation

2.3.1.1   Biogas

Biogas, a combustible gaseous fuel, is produced by anaerobic fermentation of organic matter by a consortium of microorganism. Biogas can be made from organic residue of agriculture, and by-product of ethanol or biodiesel production. It also can be made from

animal manure, and many wastewaters containing organic compounds such as food processing and industrial and municipal wastewater (Yoon and Lee, 2011). The production process is possible if there is lack of oxygen in all natural environments. The process involves three stages; hydrolysis, acid formation, and methane fermentation (Rahmouni et al., 2002). Biogas is principally a mixture of methane (CH_4) and carbon dioxide (CO_2) along with other trace gases. In addition, the contents and quantities of biogas produced (from digester) heavily depend on the feed stocks and the process conditions such as water content, temperature, pH etc. (Huang and Crookes, 1998). In general, the compositions of biogas can be seen in the Table 1.

Table 1.   Variations of biogas constituents (Rahmouni et al., 2002)

Gas constituent	Variation range (%)	Average content (%)
Methane	30 – 65	45
Carbon dioxide	20 – 40	35
Nitrogen	5 – 40	15
Hydrogen	1 – 3	1
Oxygen	0 – 5	1
Hydrogen sulphide	0 – 0.01	0.003

The use of biogas currently is for heat and electricity production. The other choice of biogas conversion is for fuelling internal combustion engines. However, its utilisation is still hampered by several factors; poorly developed commercial market in biogas technology, low quality of biogas (low concentration of methane), limited biogas fuelling stations and distribution system, and relatively higher cost of dual-fuel vehicles compared to those of running on either ethanol or biodiesel (Lantz et al., 2007).

As mainly composed of methane, the application of biogas in dual fuel engine is relatively easy to form a homogeneous air-fuel mixture and produces low CO_2 emission due to high hydrogen-carbon ratio (Corbo et al., 1995). Biogas is also good in preventing engine

knock due to methane which has a high research octane number (about 120). However, the presence of CO_2 potentially reduces the flammability range resulting in deterioration in combustion process such as increasing cyclic combustion variation, lowering the flame temperature, and prolonging ignition delay (Sahoo et al., 2009).

In addition, the presence of CO_2 in biogas leads to a lower volumetric energy density and fuel conversion efficiency because laminar flame speed and combustion enthalpy is reduced. The high self-ignition temperature of biogas also resists autoignition. However, with the use of improved engine design such as prechamber ignition and higher compression ratio, the engine operating conditions can be optimised through reduction in HC and CO without sacrificing the engine thermal efficiency (Roubaud and Favrat, 2005). The addition or combination with high heating value gases such as hydrogen also can be an option to improve the combustion characteristics. Reducing the content of CO_2 and other inert gases from biogas can improve the flame velocity and calorific value. A process to gain hydrogen and to reduce CO_2 from one source at the same time for application in CI engines will increase the energy content and thus fuel economy.

2.3.1.2 Liquefied Petroleum Gas (LPG)

LPG refers to a group of hydrocarbon-based gases obtained mostly from gas wells and by-product of crude oil refining processes. The predominant constituents of LPG are mainly butane and propane, but the actual composition of commercially available LPG varies widely among countries and depends on season, properties of the crude oil/gas supply used, refining process and cost (Masi, 2012). In cold countries such as UK, propane is the most abundant component of LPG in order to provide adequate vapour pressure in winter, whilst in the warmer countries butane has higher percentage (Price et al., 2004). In the UK, the quality

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specifications of LPG are conformed to BS 4250 which is specified for commercial butane and propane.

The emissions of LPG-driven vehicles are low and LPG is commercially available in most places (Johnson, 2003). It has been proven that LPG-operated vehicles have benefit in reducing emissions compared to that of gasoline. A decrease in main emissions such as HC, CO, NO_X, PM and CO_2 is obtained mainly due to high hydrogen-carbon ratio and no aromatic hydrocarbons of LPG. This is supposed to encourage the utilisation for transportation. However, its utilisation both for heating system and motor vehicle is still limited. Therefore, the UK government has encouraged the utilisation by giving financial advantages to those converting vehicles to operate on LPG (Price, 2004).

Apart from emissions benefit, the LPG-driven engines also have low maintenance, operational cost, and high thermal efficiency. The high thermal efficiency obtained is due to LPG has high flame speed and octane number thus suitable for high compression ratio (Karamangil, 2007, Masi, 2012). Those characteristics lead to the increased heat released and thus increasing in-cylinder pressure which elevates the indicated work (Masi, 2012). LPG also has benefit in storage property when compared with biogas where it can be liquefied in relatively low pressure range of 0.7-0.8 MPa at atmospheric temperature. This makes it easy to be stored in pressurised steel tanks, and hence LPG provides more energy content on mass basis compared to other gaseous fuels.

The characteristic of high octane number but low cetane number makes LPG widely used in SI engines. However, it has been desirable to utilize LPG on the CI engines for gaining both better engine thermal efficiency and emissions. High research octane number enables LPG or propane to be run at high compression ratio like diesel engines with less possibility to detonation.

LPG has low molecular weight due to its simple chemical compound and high vapour pressure compared to conventional diesel fuels. Therefore, in dual fuel application, homogeneous air-fuel mixture followed by premixed combustion can be easily attained. Thus, significantly lower soot and CO_2 emissions from diesel engines operated by LPG are possible (Alam et al., 2001, Campbell et al., 2004). In addition, when the quantity of LPG increases in dual fuel system the premixed combustion rapidly increases. This is because LPG is a reactive hydrocarbon gas fuel (Stewart et al., 2007). However, the ignition delay may increase with the increase in the amount of LPG because of low CN of LPG. A readjust of injection timing may restore the SOC (start of combustion) point while keeping the combustion benefit.

LPG has lower diffusivity (0.12 cm^2/s) compared to hydrogen (0.61 cm^2/s) (Lata et al., 2012). This characteristic may lead to the formation of bigger unburned LPG-air mixture area and hence dissipating the available energy which potentially could reduce the thermal efficiency. Mixing the LPG and hydrogen together is expected to improve the drawback of LPG in dual fuel combustion.

2.3.1.3 Hydrogen

The decrease of primary energy sources (i.e. fossil fuels), the pollutant emissions associated to the combustion of fossil fuel, and the need to maintain the energy supply security has encouraged the use of hydrogen as one of the alternative fuels both for transportation and powertrains systems.

Apart from motor vehicles can run well with hydrogen, the hydrogen emission benefits (no presence of carbon) and its inherent benefits such as high calorific value in terms of mass, wide flammability limits, and flame propagation speed allows better efficiency improvement favouring its application in automotive (Verhelst and Sierens, 2001).

It has been shown that hydrogen is a good substitute fuel for gasoline as hydrogen has high octane number. Therefore, it can resist knock under SI engine operation (Korakianitis et al., 2010). It also offers other advantages such as low pollution, controllability and safety. Hydrogen-fuelled vehicles can operate at low equivalence ratio as hydrogen is able to burn at lean mixture allowing stability combustion at lean operation. Therefore, it is possible to produce low NO_X at this condition. However, at high engine load the hydrogen-fuelled internal combustion engine has a possibility to produce NO_X. This is because the ignition energy of hydrogen is very low which enables hydrogen-air mixture to be ignited even with the presence of hot spots or gases. This can promote advanced start of combustion which then simultaneously increases the heat released and high in-cylinder pressure/temperature. Other issue that may arise is premature ignition and backfire which can cause engine knocking (White et al., 2006).

Hydrogen has high mass specific LHV (lower heating value) compared to other gaseous fuel (such as methane) or liquid fuel. However, its energy density is much lower compared to those fuels as a result from its low density. For stoichiometric combustion, hydrogen requires high mass of combustion air. It requires an air-hydrogen ratio of about 34:1 by mass for complete combustion which is much higher than that of gasoline which has air-fuel ratio about 14.6. However, hydrogen displaces more of the combustion chamber compared with other fuels. This leads to less air in the combustion chamber but at the same time improve energy content of the stoichiometric mixture of air and hydrogen.

The utilisation of hydrogen is expanded to compression ignition engines to capitalise the benefit of hydrogen combustion characteristics. In a recent research, Boretti (Boretti, 2011) modified the combustion chamber through pre-chamber injection of hydrogen with a glow plug unit. In this novel combustion system, the combustion of hydrogen-air mixture will

experience both premixed gasoline and diffusion diesel-like combustion. It is found that the engine thermal efficiency is improved at the same BMEP (brake mean effective pressure) output compared with diesel fuel only operation.

The utilisation of hydrogen is also applied to dual fuel system. Hydrogen as the main fuel can be injected either in the intake port or into the combustion chamber directly. Compared with the port fuel injection (PFI), directly hydrogen injection into the combustion chamber will improve the volumetric efficiency and thus power density (White et al., 2006). However, providing a car with on-board hydrogen is still a technical challenge. A feasibility study on hydrogen utilisation which is obtained from stoichiometric gaseous fuel reforming is required to enhance the gaseous-diesel fuel operation.

2.3.2   Alternative Liquid Fuels Utilisation

The use of 'carbon neutral' fuel like biodiesel is necessary for mitigation of global CO_2 concentration. On the other hand, the limited oil resources while relatively large amount of natural gas resources has encouraged the utilisation of another alternative fuel, GTL, as a new diesel fuel.

In addition, the liquid or pilot fuel used is one of dominant factors in the dual fuelled engine operation. Type and quantity of the pilot fuel have great impact to the engine performance and emissions. Although the amount of the pilot fuel used can be very small, the function in the combustion process is very relevant as it acts as ignition source. Apart from the engine operating conditions (load and speed) and pilot fuel injection system, a good control and selection of the pilot fuel is expected to ensure a stable ignition, well flame distribution and the burning of air-gaseous fuel mixture throughout the combustion chamber and hence leading to minimum cycle-to-cycle variation. This section discusses two alternatives fuels which can be used for pilot fuel.

2.3.2.1 Biodiesel

Biodiesel is one of the alternative fuels that have been gaining a growing interest which is produced from renewable sources such as waste cooking oils, animal fats, and vegetable oils. The utilisation has been started long time ago when diesel engine was invented by Rudolf Diesel. However, due to low cost of diesel and gasoline the utilisation of biodiesel for motor vehicles decreases. As the global crude oil price increases due to its gradually declining sources and the concern for the environmental problem, the attention for its utilisation arise again. In addition, the main raw materials for biodiesel production are abundant, biodegradable and relatively easy to find and hence can reduce the dependency on petroleum (Demirbas, 2007).
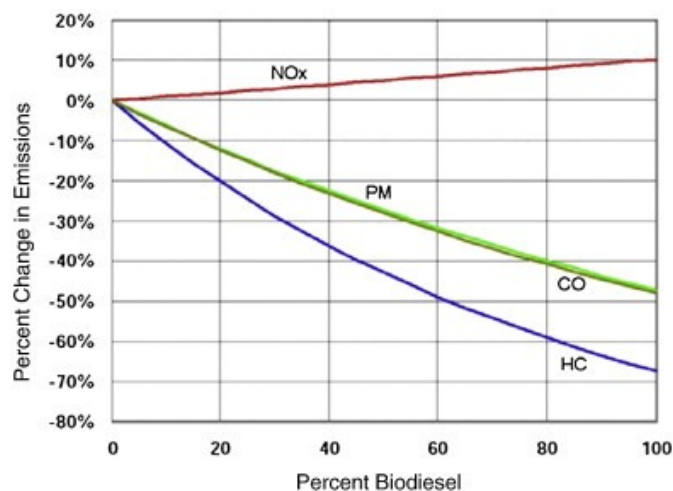
Figure 5.   Characteristic of engine-out emissions from biodiesel and its blend (McCormick, 2005).

Biodiesel, as an alternative fuel, has relatively similar properties to diesel fuel and it can be used in most diesel engines (neat or as an additive) without any significant engine modifications while at the same time can substantially reduce engine-out emissions such as HC and CO (Sun et al., 2010). Apart from its oxygen content it also contains virtually no sulphur and free aromatics thus emit low PM. As additive, the more biodiesel content in the

fuel blend the more emission advantages as depicted in Figure 5. It is also a nontoxic and biodegradable fuel and hence minimizing the risk to environment and ground water (Shahid and Jamal, 2008). Because of all the advantages biodiesel has been used widely as a vehicular fuel.

However, biodiesel has some limitations which need to be addressed. Some major properties that can affect the engine performance and emissions are higher viscosity, less favorable cold flow properties, and lower heating value and volatility. In addition, its high bulk modulus of compressibility can lead to the advanced fuel injection timing which can increase NO_X emissions. The lower heating value results in an increase in fuel consumption while its cold flow property results in difficulty to start the engine in cold weather. However, its high viscosity improves engine lubricity thus can lengthen the engine life (Shahid and Jamal, 2008, Boehman et al., 2005). In addition, it is suggested that the combination of biodiesel and gaseous fuels with their specific characteristics in dual fuel engine may become a solution for dual fuelling system to overcome the emission issues (Selim et al., 2008).

Biodiesel can be produced through transesterification which aims to reduce the viscosity, improve cold flow properties and cetane number of the raw material. In this process ethanol and methanol are usually used due to their relatively low price, and chemical and physical advantages (Ramadhas et al., 2004). The production process and technique used has great influence to the biodiesel chemical and physical properties. Maintaining the quality of the product is important to obtain acceptable biodiesel commercially. All biodiesel should meet the standard of ASTM 6571-3 or EN 14214 for US and Europe respectively.

2.3.2.2 Gas-to-Liquid (GTL)

Gas-to-liquid is a next generation fuel which is created from a Fischer-Tropsch process which was discovered by Franz Fischer and Hans Tropsch, German scientists, in 1920s as a

result of lack of petroleum resources. Nowadays, there has been an interest to the fuel processing due to high recent oil prices, and abundant feedstock. The product name obtained from this process depends on its raw material and it is usually indicated with xTL where x denotes the source of the feedstock. The raw material can be biomass (BTL), coal (CTL) or natural gas (GTL) (Gill et al., 2011, Mancaruso and Vaglieco, 2012).

The production of the FT diesel fuel involves three-step procedure and is described schematically in Figure 6. In the first step, gaseous material is reformed with pure oxygen or air while solid material like coal is gasified (with the presence of steam and oxygen) to produce syngas which contains mainly carbon monoxide and hydrogen. The second step is a phase change process from gas to liquid by utilisation of catalyst. This step is important as it depends on the catalyst used and reaction conditions. They can determine the length or the weight of the hydrocarbon chains produced. To convert the syngas to liquid fuel there are four established reforming technologies including partial oxidation, steam reforming, autothermal reforming and combined or two-step reforming (Gill et al., 2011). With hydrocracking and isomerisation process, in the third process, the waxy synthetic crude produced from second step is upgraded into the acceptable product (middle distillate fuel) (Norton et al., 1998, Alleman and McCormick, 2003).
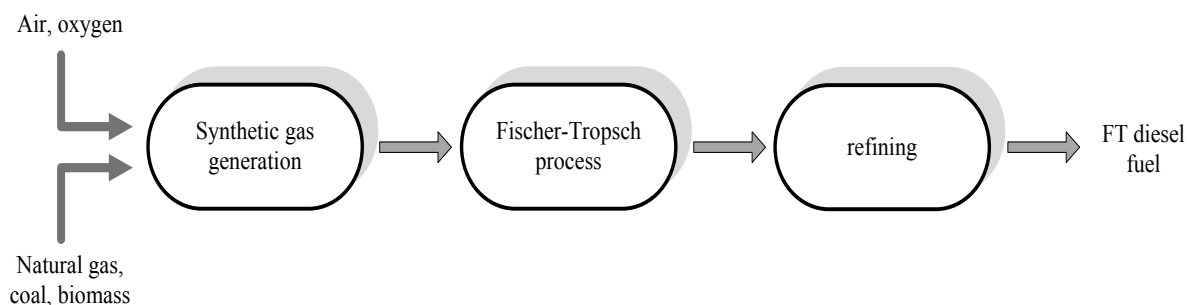
Figure 6.   Schematic diagram of FT diesel fuel production stages (Forest and Muzzell, 2005)

GTL virtually is an ultra-clean fuel, colorless, odorless, low in toxicity, aromatics, sulfur content, and has high cetane number (Gill et al., 2011). The advantageous properties give benefits in reducing HC, CO NO_X, and PM emissions. However, GTL has lower density because of higher H/C ratio compared with the standard European specifications for diesel. Therefore, strategy of fuel injection needs to be reconfigured/modified (Rounce et al., 2009, Larsson and Denbratt, 2007). In addition, GTL also has poor lubricity because of its low aromatic and sulphur content. However, driven by increasingly stringent emissions regulations the use of a 'clean' alternative fuel is an inevitable choice. Therefore, the poor lubricity of GTL can be overcome by addition of biodiesel or additives (Alleman and McCormick, 2003).

2.3.3 Engine Technology through Dual Fuel System

The utilisation of gaseous fuel and diesel-like fuel at the same time is called dual fuel engine. Driven by the fossil fuel depletion, the utilisation of gaseous fuel in IC engines has got more positive response as a possible method, and at the same time can reduce engine emissions (Xu et al., 2010). In addition, dual fuel operating strategy has economic benefits because various alternative fuels can be used which typically has lower cost than that of conventional fossil fuel and requires no major hardware modifications. It also can be operated on any combinations of gaseous and liquid fuel. Moreover, the engine operation can be switched to normal operation when the availability of gaseous fuel has run out. Generally, gaseous fuels have high octane number which is appropriate for engines with high compression ratio. This is particularly advantageous because can resist knock.

Dual fuelled engine concept combines the type of combustion CI engines and SI engines. The admission of gaseous fuels can be performed in several ways such as carburetion, intake manifold injection, intake port injection, and direct in-cylinder injection

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(Saravanan and Nagarajan, 2009). With this engine mode the air intake and gaseous fuel is mixed together then is compressed like in a diesel engine. This mixture cannot auto-ignite because its low cetane number therefore a small amount of injected diesel fuel at the end of the compression phase (called pilot fuel) is required to ignite the mixture (Sahoo et al., 2009).

The use of different fuels with different flammability limits, both liquid and gaseous fuel is a benefit to get better engine-out emissions and performance if appropriate conditions suit for their mixing and combustion.

In dual fuel combustion the amount of heat released is associated to the concentration and type of gaseous fuels. According to Poonia (Poonia et al., 1998) heat released in the combustion chamber can be divided in three phases. Firstly, the premixed combustion of pilot fuel and part of gaseous fuel-air mixture. Secondly, the combustion of gaseous-air mixture close to the pilot fuel sprays zone and diffusive burning of pilot fuel. Thirdly, gaseous fuel-air mixture combustion dues to flame propagation from spray zone.

From some strategies applied to introduce gaseous fuels into the cylinder the fumigation of gaseous fuel in the intake manifold to mix with the intake air is the basic way of gaseous fuels induction. This is a simple method and preferable for the engine which does not have electronically controlled unit for diesel injection (Palke et al., 2001). For stable engine running conditions the dual fuel system is operated at part load condition while at idle and full engine load the engine is operated under normal condition (100% diesel). This is necessary to avoid knocking. Diesel fuel is required to ignite the premixed gaseous fuel-air mixture as gaseous fuel is resistant against auto-ignition. Therefore, the engine cannot be run exclusively on the gaseous fuel (Wagemakers and Leermakers, 2012).

However, in order to save gaseous fuel a technique has been developed with locating the gas injector in the intake manifold which can be controlled electronically. In this method

the quantity and the injection timing of the pilot and gaseous fuels can be set according to the operating conditions. Therefore, a desirable composition of the air-fuel ratio can be achieved and hence knocking and misfiring can be avoided. Improvements in fuel consumption, HC and CO emissions could be obtained without increasing NO_X and PM emissions. However, some problems can arise from this injection mode such as atomisation, the degree of air-fuel mixture homogeneity and liquid fuel layer formation in the intake pipe (Panão and Moreira, 2007).
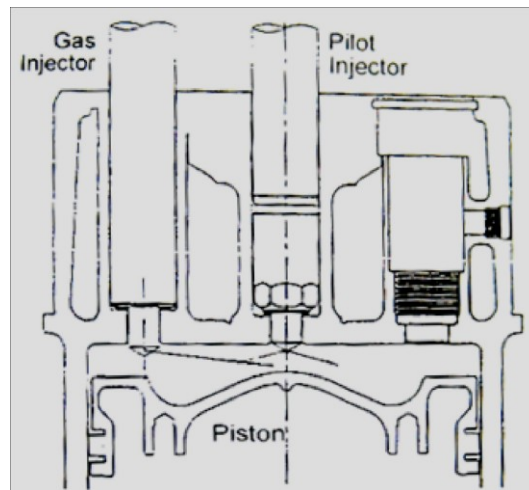
Figure 7.   H-Process dual fuel engine method (Shah et al., 2011)

Other gaseous fuel injection strategy is by high pressure direct injection into the combustion chamber as can be seen in Figure 7. Two fuel injectors are mounted in the combustion chamber both for liquid and gaseous fuels. The engine operation has advantage as it has the ability to be operated on very limited amount of liquid fuel thereby resulting in the engine producing very low PM and NO_X emissions. It is also associated to the improved gaseous and liquid fuel mixing rate because the fuels are injected at high pressure (3500 – 4000 psi of gaseous fuel injection pressure) and supported by appropriate location of the fuel injectors. Better homogeneous mixture and un-throttle valve operation are the reasons for

better combustion efficiency at low engine load which is faced in the basic dual fuel system hence improves thermal efficiency (Shah et al., 2011).

2.4 Engine-Related Strategies for Emissions Reduction

2.4.1 Exhaust Gas Recirculation (EGR)

EGR is the most well-known and established technique for reducing NO_X due to its simplicity and low cost implementation. This effective NO_X emission control method is commonly used in many modern high speed direct injection (HSDI) diesel engines. The application of EGR is simple and straightforward especially in naturally aspirated diesel engine. The exhaust gas flows to the intake manifold through the throttling valve as exhaust pressure is higher compared with the intake (Figure 8) (Zheng et al., 2004).
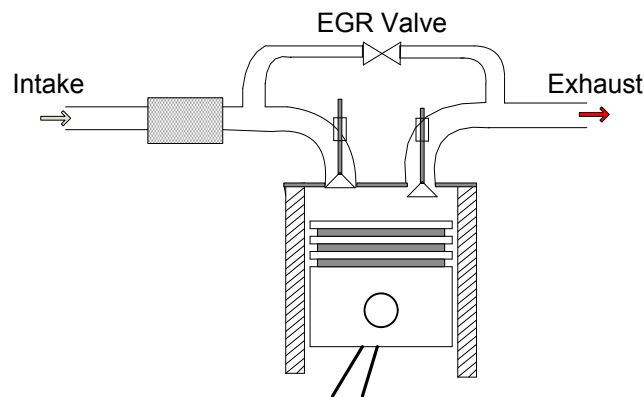
Figure 8.   A schematic diagram of exhaust gas recirculation

The reduction in NO_X is achieved mainly because EGR displaces oxygen concentration in the combustion chamber hence reducing overall flame temperature. The presence of EGR will alter the combustion process and heat released in three major ways. First, the O_2 concentration is reduced as consequence of the exhaust gas presence in the combustion chamber (dilution effect). This causes the injected fuel spreads further to find oxygen for

stoichiometric combustion. Therefore, the flammable region is extended as can be seen in Figure 9. Apart from stoichiometric mixture the region also includes portion which contains CO_2, H_2O, and N_2 from exhaust gas. The reduced oxygen concentration also lowers the oxygen partial pressure affecting the kinetics of NO_X formation reactions (Ghazikhani et al., 2010, Maiboom et al., 2008, Abd-Alla, 2002).

The second effect of EGR is thermal effect. CO_2 and H_2O as the inherent components of EGR have higher specific heat capacity compared to those of substances from ambient air such as O_2 and N_2. Consequently, the overall heat capacity on the cylinder charge is reduced and hence lowering flame temperature and propensity in NO_X production.
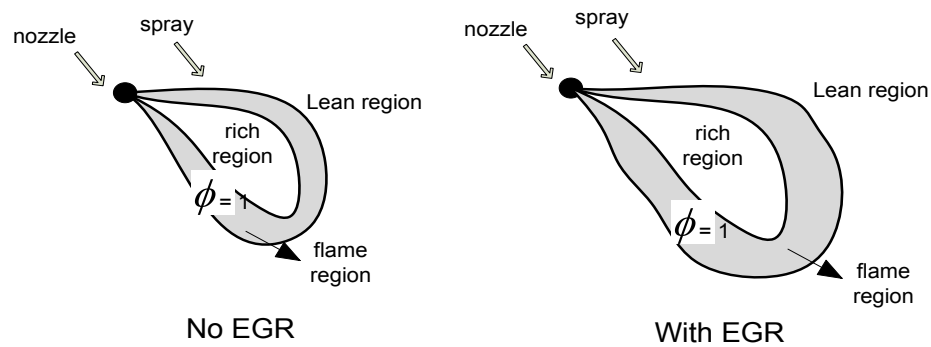
Figure 9.   The change of spray flame volume due to EGR (Abd-Alla, 2002)

The third effect is chemical effect. The combustion process occurred in the combustion chamber is altered because of the presence of H_2O and CO_2. Supported by high temperature these substances undergo dissociation during combustion period modifying both the chemistry of the combustion process and formation of NO_X. Particularly, the flame temperature is reduced by the endothermic dissociation of H_2O (Ghazikhani et al., 2010, Maiboom et al., 2008).

The modification of in-cylinder temperature and composition of the inlet charge (the addition of CO_2 and H_2O) due to the application of EGR also affects the start of ignition. It is generally observed that the ignition delay increases. However, the main problem caused by the EGR application is the significantly increased particulate matter (PM) formation. The reduced in-cylinder temperature and pronounced diffusion combustion are main reasons for decreased oxidation ability of the combustion product. Other adverse effects of the utilisation of EGR include increase in the specific fuel consumption and deterioration of engine durability, lubricant oil quality, while the engine may suffer high cycle-to-cycle variations and power loss (Cadman and Johnson, 1986, Zhao et al., 2000).

2.4.2   Diesel Fuel Injection Timing

One major factor affecting the engine-out emissions is fuel injection timing. Two types of injection timing commonly applied in diesel engines are briefly described below.

Advanced injection timing

Longer ignition delay is a result of the advanced injection timing. Under longer ignition delay the time for air and fuel to mix is increased hence provides a better combustible mixture quality. This is considered as a cause for the increase in the in-cylinder temperature and pressure. The greater heat available at this condition will speed up the chemical reaction within the mixture and thus oxidise well the combustion product decreasing CO and HC emissions. For dual fuel combustion mode, it is generally obtained that the start of combustion is retarded thus increasing the ignition delay. Therefore, advancing fuel injection is one method to minimise the combustion alteration due to the presence of gaseous fuel.

Retarded injection timing

This type of injection is used mainly to reduce NO_X emissions. A late injection causes a short ignition delay. The improper mixing between air and fuel due to less time for mixing leads to non-homogeneous mixture and reduces maximum in-cylinder temperature. This also affects the combustion process rate becoming slower which in turn minimises the capability of combustion product oxidation. As a result HC and CO emissions might increase. The end of combustion is also extended as the process of combustion is shifted to the expansion stroke. The combustion behaviour describes that majority of combustion is located after TDC and hence reducing the effective work cycle. In dual fuel combustion the retarded injection timing is not a proper option due to a retarded start of combustion in the combustion mode.

In addition, the quality and effectiveness of the mixture formation in the combustion chamber is also affected by the fuel injection system. In general, the fuel injection system can be divided into pump-line-nozzle and common-rail system which is discussed briefly below.

Pump-line-nozzle system is a 'classic' fuel injection system technology which has been used for decades. This injection system is categorised as a low pressure injection (injection levels ranging from 140 – 1350 bar) when compared with the common-rail system. The fuel injection pump transfers fuel to the injector through a high-pressure fuel line and then spraying fuel via nozzle into the combustion chamber. Engine load determines the quantity of the injected fuel. The inherent advantage such as high durability and relatively easy maintenance make this injection system still used in many heavy duty truck and marine engines (DieselNet, 2010).

Common-rail system is developed to meet the demand of the diesel engines with has low emissions, low fuel consumption, low combustion noise but more specific engine power output. The injection system has flexibility in injecting fuel therefore it can adapt well to the

engine operating conditions and engine design. Higher injection pressure (about 1500 – 3000 bar) including variable injection pressure in accordance with engine operating conditions, variable injection timing, multiple injection capability including pre and post injection phase are benefits of the injection system (Stone, 1999).

2.5 Hydrogen Production from Fuel Reforming

One of the mechanisms to obtain hydrogen is through reforming of the hydrocarbon fuel. The fuel reforming process for hydrogen production can be performed by either non-catalytic or catalytic processes. However, the hydrogen production catalytically is promising as the process requires less residence time and relatively low operating temperature (Chaniotis and Poulikakos, 2005).

Exhaust gas fuel reforming is an on-board technique for providing the engine with hydrogen-rich gaseous fuel. Hydrogen production is carried out by catalytic interaction of hydrocarbon fuel directly assisted by exhaust gas in a reforming reactor. The reformed gas then is recirculated into the engine. Therefore, the method is also known as reformed EGR (REGR) (Tsolakis et al., 2005b). The production of hydrogen via reforming of hydrocarbon fuels involves all basic reforming processes. Those techniques are explained briefly as follows.

Steam reforming (SR) is a process using high-temperature steam to yield hydrogen and carbon monoxide. The process is highly endothermic requiring high level of heat input (Tsolakis and Megaritis, 2004). To eliminate the CO produced in the reaction, a further water-gas shift reaction (WGSR) may be involved. With this reaction more hydrogen can be produced.

Partial oxidation (POX) is another process to produce hydrogen. In this process hydrocarbon fuel is burned using lower stoichiometric oxygen. The advantages of this process are: is able to be started quickly, is appropriate in a small system and is an exothermic reaction. With this process syngas produced contains less calorific value than that of steam reforming (less hydrogen content in the syngas) (Tsolakis et al., 2003). Complete oxidation may take place depending on the condition of the reactor. This is undesirable as there is no hydrogen produced. If the reaction occurred at relatively high temperature (> 800 ^{o}C) where the availability of steam is limited, the endothermic dry reforming can take place.

Autothermal reforming (ATR) is a process which combines steam reforming and partial oxidation in a reactor. The process requires no external heat (unlike SR) and reaction temperature is lower compared to that of POX. In this process partial oxidation reaction generates heat which is used to drive the steam reforming reaction. Therefore, the production of hydrogen with this process is possible using simple and small reactor with relatively high efficiency. Moreover, the hydrogen yield is higher than that produced by POX (Park et al., 2010). Hydrogen-rich gas production assisted by exhaust gas has an advantage as the source of oxygen (from water and air) is already available abundantly from diesel exhaust thus requires no additional equipment. Furthermore, the liquid fuel in the reactor is evaporated by heat from exhaust while water is already provided in the form of steam.

2.6 Current Method of Alternatives Fuels Utilisation in Dual Fuelled Diesel Engines

Researches of the utilisation of gaseous fuels and other alternative liquid fuels on dual fuel combustion process have been carried out extensively in order to improve its engine out

emissions and performance. Various solutions have been proposed and the researches on the combustion process can be grouped in three main areas as described briefly as follows.

a. *Increasing the initial temperature*. A slight pre-heating of the inlet air in the intake manifold can lead to a higher combustion temperature (Karim and Wierzba, 1992). Under this technique the flammability limits of the gaseous fuels can be extended resulting in a reduction of unreacted gas in the cylinder. Therefore, HC and CO emissions can be significantly reduced. However, engine knock problem can occur when this method is applied at high engine load.

b. *Methods involving the pilot fuel*. Increasing the quantity of pilot fuel in dual fuelled engine gives benefits for better combustion of charge mixture leading to the reduction of engine exhaust emissions. This is due to bigger ignition centres, a larger reaction zone and greater energy release can be created with higher pilot fuel quantity (Karim and Wierzba, 1992, Gatts et al., 2012). Moreover, advancing injection timing increases the residence time and activity of the partial oxidation reactions, increases the charge temperature, and so extends the flammability boundary (Abd Alla et al., 2002). Moreover, various new methods of fuel injection timing have been developed and investigated. Some of them will be discussed briefly in this section.

   PREDIC (Premixed lean diesel combustion). PREDIC is a direct injection dual fuel engine where is achieved by application of various fuel injection strategies. This technique is introduced as an attempt to minimize wall wetting and improves mixture level and homogeneity, power densities, and to produce lean premixed mixture. The fuel injection mechanisms can be three injections (one at the centre and two on the sides) (Takeda et al., 1996), implementation of second fuel injection near TDC injection (Hashizume et al., 1998), and multiple injections (Nishijima et al., 2002).

MULINBUMP (Multi-pulse fuel injection in bump combustion chamber). The fuel injection technique applies multi fuel injection but basically it can be divided into two separate injection timings. The first fuel injection, injected on BTDC, contains a multi-pulse injection where the number of injection, the start of injection, the period of each injection, and the dwell time between the injections are managed. The main fuel injection is injected around TDC (Su et al., 2005). Under the injection strategy, the fuel and air mixing rate is much higher compared to the conventional CI engines.

PREMIER (Premixed Mixture Ignition in the End-gas Region). This combustion process is different from the above mentioned as the combustion involves synthetic gas apart from liquid fuel which acts as a pilot fuel. Rather than two or multi fuel injections, this combustion method is divided in mainly two stages of heat released. The first rate of heat release is generated by the ignition of pilot fuel which is injected on BTDC. The pilot combustion then increases the in-cylinder temperature to initiate the development of synthetic gas flame. The second rate of heat release, higher and faster compared to the first one, is generated by the autoignition of synthetic gas-air mixture where occurs in the compression stroke (Azimov et al., 2011).

c. *The utilisation of hydrogen.* Due to its burning characteristics and better performance drives more interest in hydrogen utilisation in dual fuel combustion process (Saravanan et al., 2008). The use of hydrogen combined with Diethyl Ether as ignition source has shown improvement in carbonaceous emissions and thermal efficiency (Hashimoto et al., 2008). Hydrogen dual fuelled engine using solenoid in-cylinder injection and external fuel injection technique is another method which increases thermal efficiency by about 22% (Lee et al., 2000). Under this injection method, the stability and maximum power could be obtained by direct injection of hydrogen. In addition, an

experiment with an electronic injector for hydrogen has been carried out to be operated under high engine speed conditions in order to eliminate problems such as backfire and pre ignition (Bailey et al., 1997). The addition of hydrogen into other gaseous fuel like natural gas can improve the exhaust gas emissions and combustion characteristics (Akansu et al., 2004). It has been shown that hydrogen addition in a natural gas combustion with turbo-charging and exhaust gas recirculation can improved lean combustion capability and HC, CO, and CO_2 emissions (Bauer and Forest, 2001).

Despite the works have shown that the use of hydrogen can improve thermal efficiency and reduce carbonaceous emissions however, the supply of hydrogen is from a compressed gas from a storage cylinder. This indicates that the utilisation of hydrogen as an energy carrier in motor vehicle still has technical and economical challenges. In this work, the hydrogen is provided from the biogas and propane reforming to produce reformate (H_2 and CO). The reformate then is fed back into the engine and known as reformed exhaust gas recirculation (REGR). In addition, other novelties of this work are the combustion of combination of gaseous and liquid renewable fuels with hydrogen, the measurement of soluble organic material (SOM) and HC species in dual fuelled engine combustion which are less well investigated.

CHAPTER 3

EXPERIMENTAL SETUP

All the equipment used during the experimental research is described in this chapter. It covers the engine test cell, equipment for emission monitoring, and fuels both gaseous and liquid.

3.1 Test Engine

A Lister Petter TR1 experimental diesel engine is used for this research (Figure 10).
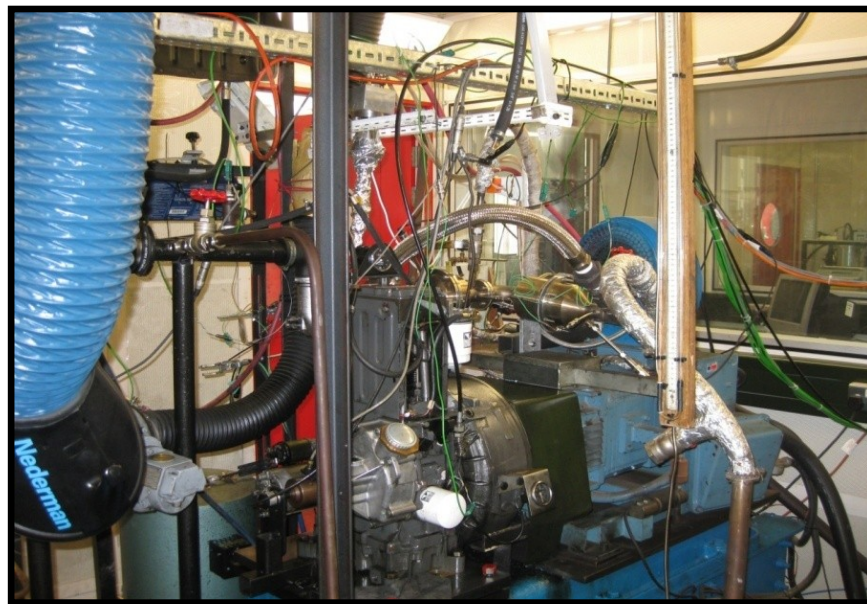
Figure 10. The Lister Petter TR1 diesel engine test cell

It is a single cylinder direct injection and naturally aspirated engine. The engine is coupled with a direct current (DC) electric dynamometer (i.e. Thrige Titan) with a thyristor-controlled Shackleton System Drive and a load cell to motor and load the engine. The fuel

injection timing over the entire tests was maintained at the manufacturer settings at 22 Crank Angle Degree (CAD) Before Top Dead Centre (BTDC) unless otherwise specified (for advanced injection timing testing) and it has the fuel injection pressure of 180 bar. In addition, the system used for fuel injection is a pump-line-nozzle injection. The engine specifications from the manufacturer are shown in Table 2.

Table 2.   Test engine specifications (Theinnoi et al., 2009, Chong et al., 2010)

Engine Specification	Data
Number of cylinders	1
Bore/stroke	98.4 mm/101.6 mm
Connecting rod length	165 mm
Displacement volume	773 cm^3
Compression ratio	15.45:1
Rated power	8.6 kW@2500 rpm
Peak torque	39.2 Nm@1800 rpm
Injection system	Three hole direct injection
Combustion chamber type	Bowl-in-piston

3.2 Dual Fuel System Setup

The intake manifold has been modified to enable fresh air and gaseous fuels mixing flowing into the combustion chamber while the liquid fuel was injected directly into the combustion chamber. In addition, a dedicated flow meter was used to control the inducted gaseous fuels level. The temperature and pressure of the inducted gaseous fuel were at room temperature and ambient pressure. Therefore, it minimizes the temperature and pressure gradient between gaseous fuels and the air in the intake manifold.

An external EGR configuration has also been employed and is controlled manually by a valve. The concentration of gaseous fuels and EGR is expressed as a volumetric percentage of the total intake charge at the particular engine speed being investigated.

Figure 11 shows the experimental layout highlighting the gaseous fuels induction into the inlet manifold and the sampling locations.
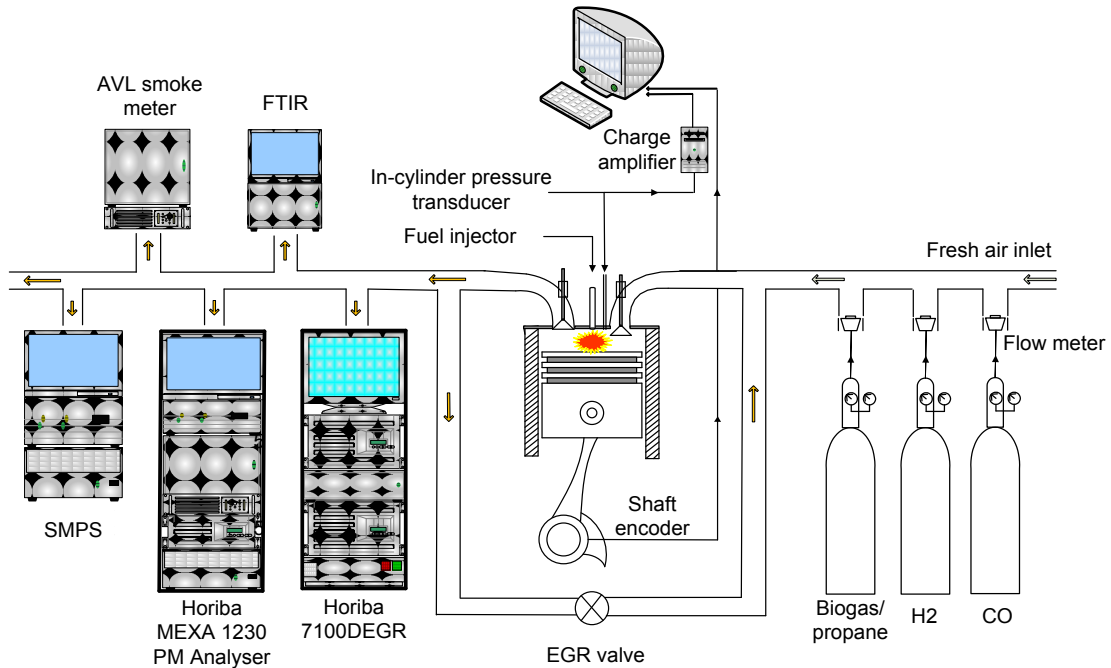
Figure 11. Schematic diagram of experimental setup

3.3   Engine Instrumentation

To measure in-cylinder pressure a pressure transducer (i.e. Kistler 6125B) was used. Mounted flush at the cylinder head it was connected to a National Instruments data acquisition board (National Instruments PCI-MIO-16E-4) via a Kistler 5011 charge amplifier. The position of crankshaft was recorded by a digital shaft encoder. In-house developed LabVIEW-based software was used to carry out data acquisition and combustion analysis.

The test rig was equipped with other standard engine apparatus. Inlet manifold, exhaust, air and oil temperatures were measured using thermocouple. During the tests the atmospheric conditions such as pressure, temperature and humidity were monitored. In addition, safety features of standard engine test bed were also included. Output from the analysis of consecutive engine cycles (from a minimum of 200 cycles) included rate of heat release (ROHR), values of indicated mean effective pressure (IMEP), peak in-cylinder pressure,

average values and percentage of COV of peak cylinder pressure and percentage coefficient of variation of IMEP and other standard combustion parameters.

3.4 Engine-out Emissions Measurement

An Horiba MEXA-7100DEGR emissions analyser was used to measure carbon dioxide and carbon monoxide by Non-Disperse Infrared (NDIR), oxygen using a magneto-pneumatic detection, oxides of nitrogen ($NO_X = NO + NO_2$) by chemiluminescence detection (CLD), and hydrocarbons (HC) by flame ionization detector (FID). The engine-out emissions were sent to the analyser through a temperature controlled heated line (190 ^{o}C) to avoid condensation. Appendix A shows the range of measurement and accuracy of the equipment.

An HORIBA MEXA-1230PM analyser was used to measure soot, SOM, and total PM. With the equipment soot and SOM are measured separately and continuously where soot is measured by a diffusion-charging (DC) detector with a dilution device. The air line for dilution is heated at about 200 ^{o}C to prevent condensation. Two heated flame ionization detectors (HFID) are used for SOM measurement. One of the FID is controlled at 191 ^{o}C and the other one is controlled at 47 ^{o}C. The amount of Hydrocarbons vaporised after passing through the detectors is indicated by the signal from the FIDs and the difference is used to determine SOM component. In this study the dilution ratio was 40 part of air to 1 exhaust.

Smoke was evaluated by an AVL 415SG002 Smoke Meter. The exhaust gas passes through the filter paper and the result was displayed as a filter smoke number (FSN) conforming to ISO 10054. The analyser is equipped with a reflectometer to measure a blackened filter paper which is scaled from 0 to 10 and indicates the soot content (0=low, 10= high smoke). The sampling line is purged by clean air after taking measurement to ensure no

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particles left in the dead volume for next measurement. The dead volume is the volume of lines from sampling point to filter paper (AVL, 2005).

The particle size distribution and concentration was measured using an SMPS (scanning mobility particle sizer) unit by classifying particles based on their electrical mobility which is related to particle size. It consists of a condensation particle number (CPC) series 3775, an electrostatic classifier (EC) series 3080, and a differential mobility analyzer (DMA) series 3081. The sample was diluted using a TSI 379020 thermodiluter (dilution ratio 200:1 and dilution temperature 150 ℃). The equipment has capability to measure particle size distributions in the range of 0.01 μm – 1 μm (Sitshebo, 2010).

A MultiGas 2030, FTIR (Fourier transform infrared spectroscopy) analyser was also used for measurement of different hydrocarbon species. The measurement is performed by passing a beam of infrared through the exhaust gas. Each sample or compound has different wavelength and the amount of energy absorbed from the infrared beam by each sample is measured. The differences in spectral frequencies absorbed and their intensity are resulted from the chemical bond and the strength of the bond of each compound. The spectra are measured at ambient pressure and temperature of 150 ℃. All the emissions measurement equipment was calibrated before taking any data measurements.

3.5 Fuels

The fuels used in this research work are divided into gaseous and liquid diesel fuels. Bottled gaseous fuels are biogas, propane, hydrogen and carbon monoxide which are supplied by BOC (British Oxygen Company). Hydrogen and carbon monoxide are used to form and simulate reformate from stoichiometric biogas and propane reforming. The composition of biogas was 60% methane and 40% carbon dioxide.

The diesel fuels used were ultra low sulphur diesel (ULSD), rapeseed methyl ester (RME) and gas-to-liquid (GTL) provided by Shell Global Solutions UK. The properties for those liquid and gaseous fuels are shown in Table 3 and 4 respectively.

Table 3.   Liquid fuel properties (Abu-Jrai et al., 2009, Rounce et al., 2012)

Property	Method	ULSD	RME	GTL
Cetane Number	ASTM D613	53.9	54.7	80
Density at 15 ^{o}C (kg/m^3)	ASTM D4052	827.1	883.7	784.6
Viscosity at 40 ^{o}C (cSt)	ASTM D455	2.467	4.478	3.497
50% Distillation (^{o}C)	ASTM D86	264	335	295.2
90% Distillation (^{o}C)	ASTM D86	329	342	342.1
LCV (MJ/kg)		42.7	37.4	43.9
Sulphur (mg/kg)	ASTM D2622	46	5	<10
Aromatics (%wt)		24.4	~0	0.3
O (%wt)		~0	10.8	~0
C (%wt)		86.5	77.2	85
H (%wt)		13.5	12.0	15
H/C ratio (molar)		1.88	1.85	2.10

Table 4.   Gaseous fuel properties (Verhelst and Wallner, 2009, Abd Alla et al., 2002, Qi et al., 2007, Sahoo et al., 2012, Reiter and Kong, 2011)

Property	methane	propane	hydrogen	carbon monoxide
Relative density (15.6 ^{o}C, 1 atm)	0.554	1.5	0.07	0.97
Cetane number	~0	~0	~0	~0
Research octane number	120	112	140	~106
Boiling point (^{o}C)	-161.6	-42.1	-252.8	-191.5
Latent heat of vaporisation at 15.6 ^{o}C (kJ/kg)	510	358.2	454.3	214.85
Flammability range (%vol. in air)	5-15	2.2 – 9.5	4-75	12.5-63
Autoignition temperature (^{o}C)	595	470	560	630
LCV (MJ/kg)	50	46.3	120	10.9
Theoretical air requirement (m^3/m^3)	17.1	24	34.2	2.45

3.6 Equations

Below are the equations used to calculate different combustion and performance parameters. Indicated mean effective pressure (IMEP (bar)) is calculated by using the following equation:

$$\rule{3cm}{0.4pt} \qquad \rule{1cm}{0.4pt} \tag{3.1}$$

where p (MPa) is in-cylinder pressure and V_d (cm^3) is displaced cylinder volume.

Exhaust gas recirculation (EGR) applied was flow rate of exhaust in volumetric according to reduction in the volumetric air flow rate. The equation is expressed as follow:

$$\rule{1.5cm}{0.4pt} \tag{3.2}$$

where   and   (m^3/s) are volumetric flow rates of the measured intake air without and with EGR respectively.

The brake power P_b (kW) delivered by the engine was determined by:

$$\rule{2cm}{0.4pt} \tag{3.3}$$

Where ω (rad/s), N (rps), and T_b (Nm) are angular speed, engine speed and engine brake torque respectively.

Brake specific fuel consumption (BSFC (g/kWh)) is fuel mass flow rate per unit power output and defined as:

$$\rule{1.5cm}{0.4pt} \tag{3.4}$$

where   (kg/s) is the fuel mass flow rate. For fuel blend   is expressed as:

$$\tag{3.5}$$

Where   ,   (kg/s) are the ULSD and GTL mass flow rate respectively.

To calculate the engine thermal efficiency (η_{th}) the following equation is used:

$$\overline{\qquad}$$

(3.6)

Where LCV (MJ/kg) is lower calorific value of the fuel used. For fuel blend

is determined by equation:

(3.7)

The rate of heat release $\overline{\qquad}$ (J/CAD) was calculated using the equation below (Heywood, 1998):

$$\overline{\quad} \quad \overline{\quad} \quad \overline{\quad} \quad \overline{\quad} \quad \overline{\quad}$$

(3.8)

Where γ is the ratio of specific heats (c_p/c_v), p (bar) is the instantaneous cylinder pressure, and V (cm^3) is the instantaneous volume of the cylinder. The γ value was calculated for each crank angle degree (CAD) by interpolating between the values of γ_1 for a specific point before the start of combustion in the compression stroke (30 CAD BTDC) and γ_2 for a specific point after the end of combustion in he expansion stroke (50 CAD ATDC) (Tsolakis, 2004).

C H A P T E R 4

COMBUSTION AND EMISSIONS CHARACTERISTICS OF BIOGAS-DIESEL DUAL FUELLED ENGINE

4.1   Introduction

This chapter discusses about combination between a renewable gaseous fuel and alternative liquid fuel. Under dual-fuelled engine operation, the inducted gaseous fuel and injected diesel fuel properties are critical parameters that influence combustion patterns and thus the engine-out emissions. The gaseous fuel used is biogas which contains 60% CH_4 and 40% CO_2. CO_2 in biogas acts as diluents and decreases the flame temperature and thus formation of NO_X. Depending on the engine speed and load conditions (i.e. low in-cylinder temperatures), engine thermal efficiency may be reduced with simultaneous increases in CO and total HC emissions as a result of the incomplete combustion due to CO_2 presence. To avoid the decrease in engine power and severe running engine problems, the amount of CO_2 content in biogas should be limited. Therefore, 40% CO_2 by volume is chosen as the highest acceptable level for smooth running (Bari, 1996). The volumes of the biogas added to the engine intake were 2% and 4% expressed as volumetric percentages of the intake air volumetric flow rate at the particular engine speed being investigated. The discussion of the combustion and emissions characteristics of dual fuelled engine mode run by biogas is presented in first section.

The injected diesel fuels effect is also studied. Ultra Low Sulphur Diesel (ULSD) was used as the base engine fuel. Synthetic gas-to-liquid (GTL) and a blend (v/v%) of 30% of

GTL and 70% ULSD (referred to as GD30) were also examined. The discussion of the effect is presented in the second section.

To improve the limitations of the biogas combustion in diesel engines, H_2 and reformate (H_2 and CO) addition may act as a CH_4 combustion enhancer. Hydrogen combustion properties are supposed to enhance methane combustion and reduce exhaust emissions. Hydrogen and reformate concentrations were selected, assuming complete fuel reforming of biogas to the syngas as shown in the dry reforming equation below. Dry reforming was chosen due to CO_2 amount produced with this process was lower compared to that of steam reforming. In addition, with this process the energy content of biogas can be improved (Lau et al., 2011).

$$(4.1)$$

The CO production can be limited by changing the thermodynamic conditions to help promote the water-gas shift reaction (WGSR), an exothermic reaction as shown in the equation below.

$$(4.2)$$

Third section will discuss the effect of H_2 and reformate addition on biogas-diesel duel fuel engine. The engine operating conditions used are described in Table 5. 30 tests were carried out during the experiment, and the volumetric flow rate of the hydrogen and reformate added are shown in Appendix B. GD30 was chosen because the fuel blend properties such as cetane number and density were improved without any significant different in combustion traces. In addition, the influence of engine speed and low load gave relatively similar affect on the combustion and exhaust emissions among the fuels used. Therefore, the study of engine speed and low load was carried out on ULSD combustion only as the baseline fuel. The

experimental layout highlighting the feed of the gaseous fuels into the inlet manifold and the

sampling locations is shown in Figure 12.

Table 5.   Engine operating conditions (biogas-diesel dual fuelling with reformed biogas)

Speed (rpm)	IMEP (bar)	Fuel	Biogas (%)	Reformed biogas
1200	2	ULSD	0	-
			2	hydrogen and reformate
			4	-
	4	ULSD	0	-
			2	hydrogen and reformate
			4	-
1500	2	ULSD	0	-
			2	hydrogen and reformate
			4	-
	4	ULSD	0	-
			2	hydrogen and reformate
			4	-
	4	GD30	0	-
			2	hydrogen and reformate
			4	-
	4	GTL	0	-
			2	hydrogen and reformate
			4	-
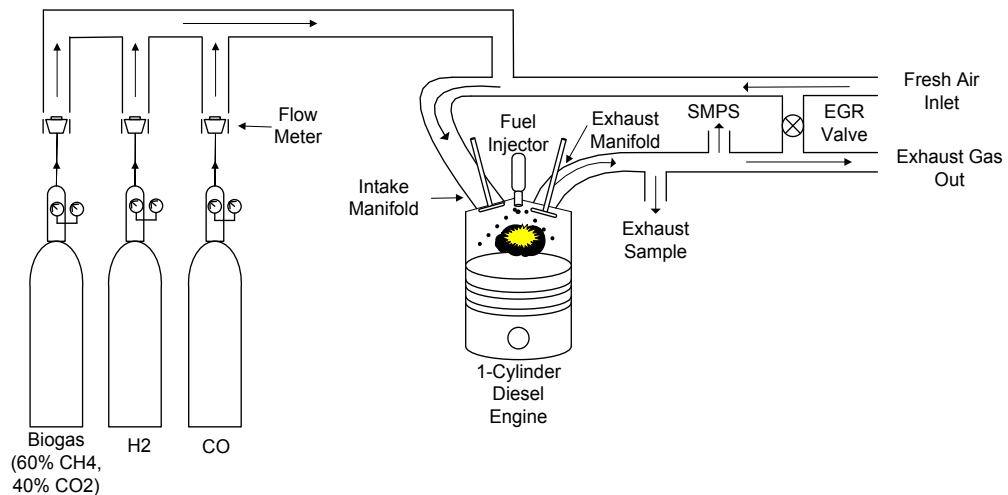
Figure 12. Schematic diagram of experimental setup for biogas-diesel combustion

4.2 Biogas-ULSD Combustion and Emissions

Combustion and engine performance characteristics. Dual-fuelled engine operation was shown to alter the rate of heat release and in-cylinder pressure traces from the baseline standard diesel combustion. In all low load engine conditions (e.g. Figure 13), the pressure rise and peak pressure of dual-fuel mode is lower compared to that of the diesel fuel. This is due to:

i) The lower energy available to efficiently oxidise the gaseous fuel and

ii) The increased diluents in the combustion chamber (i.e. high CO_2 concentration) which increases the ignition delay significantly (Papagiannakis and Hountalas, 2004). The prolonged ignition delay in dual-fuel mode shifts the combustion process closer to top dead centre (TDC).

As the engine load increased to 4 bar IMEP, the combustion of the gaseous fuel was improved due to an increase of in-cylinder temperatures, which in turn promotes combustion.

When biogas was added into the cylinder, the volumetric efficiency was reduced with part of the fresh air being displaced by the biogas. The reduced air or oxygen for combustion initiation inhibited the pre-ignition reaction activity which resulted in longer ignition delay where in turn provided longer time for the air to mix with in-cylinder injected diesel and thus burn in premixed combustion.
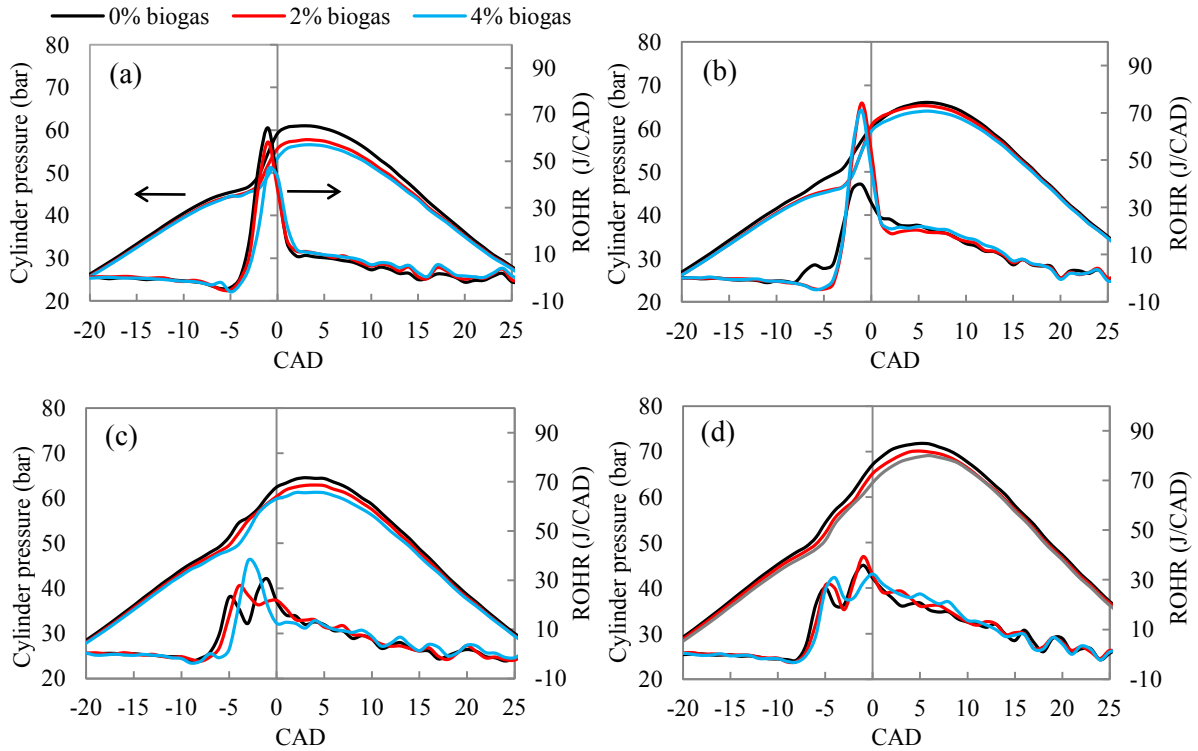
Figure 13. In-cylinder pressure and ROHR for biogas-ULSD combustion. (a) 1200 rpm 2 bar, (b) 1200 rpm 4 bar, (c) 1500 rpm 2 bar, (d) 1500 rpm 4 bar.

The combustion variability, as shown by the COV of both IMEP and peak pressure in Figure 14, is within the acceptable limits of <5% for all the engine operating conditions with 2% biogas addition and high engine load. For the higher biogas concentration of 4%, combustion becomes unstable at low engine loads. This was resulted from the presence of high CO_2 concentration and low in-cylinder temperature. However, for 4 bar IMEP the combustion variability was within the limits. When the engine speed was increased, the COV increased specifically at low load. The low in-cylinder temperature supported by high diluents both from air and biogas deteriorated the combustion stability.
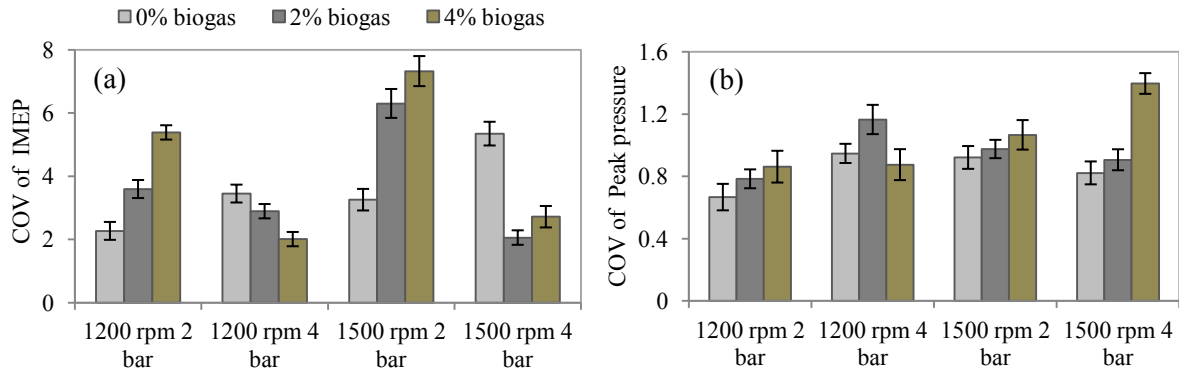
Figure 14. COV for biogas-ULSD combustion. (a) COV of IMEP, (b) COV of peak pressure.

The total liquid fuel reduction (Figure 15a) is defined as the amount of the liquid fuel mass being reduced on a percentage basis injected into the cylinder of dual fuel operation compared to that of diesel fuel operation only.

The engine thermal efficiency (Figure 15b) calculation involves the energy content of gaseous and liquid fuels used. A decrease in engine thermal efficiency of the dual fuelled engine is a result of the incomplete combustion and in particular the oxidation of methane (explained further below). The reduction in thermal efficiency was more significant at low loads where the CH_4 oxidation is less efficient. Likewise, the liquid fuel reduction by biogas addition affects the liquid fuel spray quality, resulting in poor liquid fuel preparation which has adverse effects on the gaseous fuel combustion process (Kim et al., 2005). This was also supported by the combustion stability (COV) graphs shown in Figure 14, where dual-fuel operation is more suitable for higher engine load conditions. A reduction in engine thermal efficiency was obtained when the engine speed was increased specifically at low load, while it was relatively not affected at high load. Lean combustion occurred at high engine speed can lead to a slow combustion rate which resulted in deterioration of fuel conversion efficiency decreasing the engine thermal efficiency.
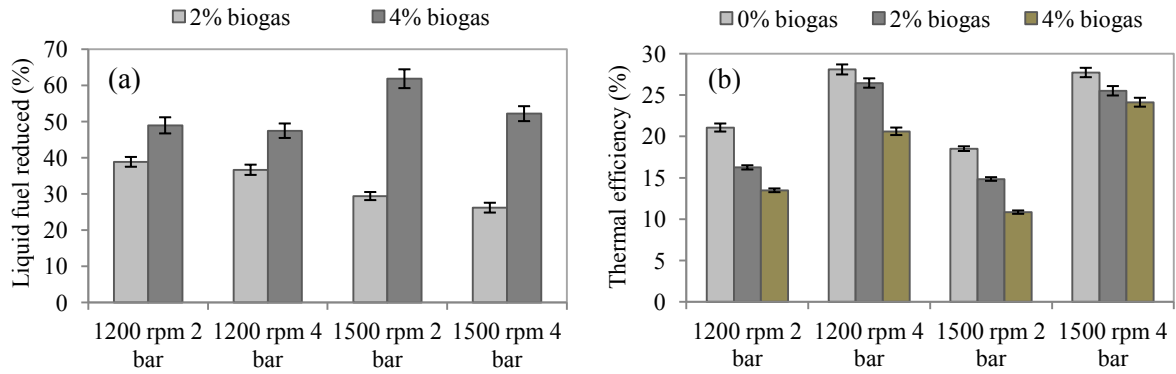
Figure 15. Liquid fuel replacement (%Wt) and thermal efficiency for biogas-ULSD combustion.

Emissions. Figure 16 shows the emissions results. For all operating conditions shown, both CO and HC emissions were sharply increased under dual-fuelling (Figures 16a and 16b). Some factors such as the air-fuel ratio, in-cylinder temperatures, fuel distribution, low cetane number of methane, and mixing quality are all influential in affecting the rate of formation and oxidation of CO and HC (Kim et al., 2005, Houseman and Hoehn, 1974). CO and HC emissions increased with a 4% biogas addition and were more pronounced at the lower engine load due to lower in-cylinder temperature which is caused by the longer ignition delay. These emissions were also higher at higher engine speeds (at the same load). This was the result of there being less time available for the biogas-diesel mixture in the cylinder to combust and reduced laminar flame speed of methane at high air-fuel ratio and also the presence of CO_2 (Stone et al., 1998).

NO_X and smoke emissions were reduced as described in Figures 16c and 16d. The mechanism of NO_X formation is predominantly dependant on the combustion characteristics (in-cylinder temperature and combustion duration), fuel properties, engine load, air-fuel ratio, oxygen availability, and residence time in the cylinder (Samuel et al., 2010, Duc and Wattanavichien, 2007, Tsolakis et al., 2005b). In this study, the reduction of NO_X emissions is also associated to the reduced in-cylinder temperatures because of the increased heat capacity

of CO_2 and the reduction in the combustion performance. Smoke emissions (filter smoke number) were also reduced as the biogas ratio increased, especially at the low engine load, through the reduction in particulate size (Figure 17).

CO_2 emission increased with the addition of biogas as shown in Figure 16e. It is suggested that CO_2, as a constituent compound of biogas, leaves the combustion chamber without get involved in the combustion process. A decrease in thermal efficiency also indicates that the CO_2 emission being deteriorated. When engine load was concerned, CO_2 was higher at high load compared to that of low load. This was mainly due to the presence of high amount of fuel in the combustion process and more complete combustion because of high temperature. Therefore, the CO_2 emission might come from biogas and liquid fuel. However, the emission was less affected by the engine speed. High air-fuel ratio compensated the low in-cylinder temperature for biogas combustion.
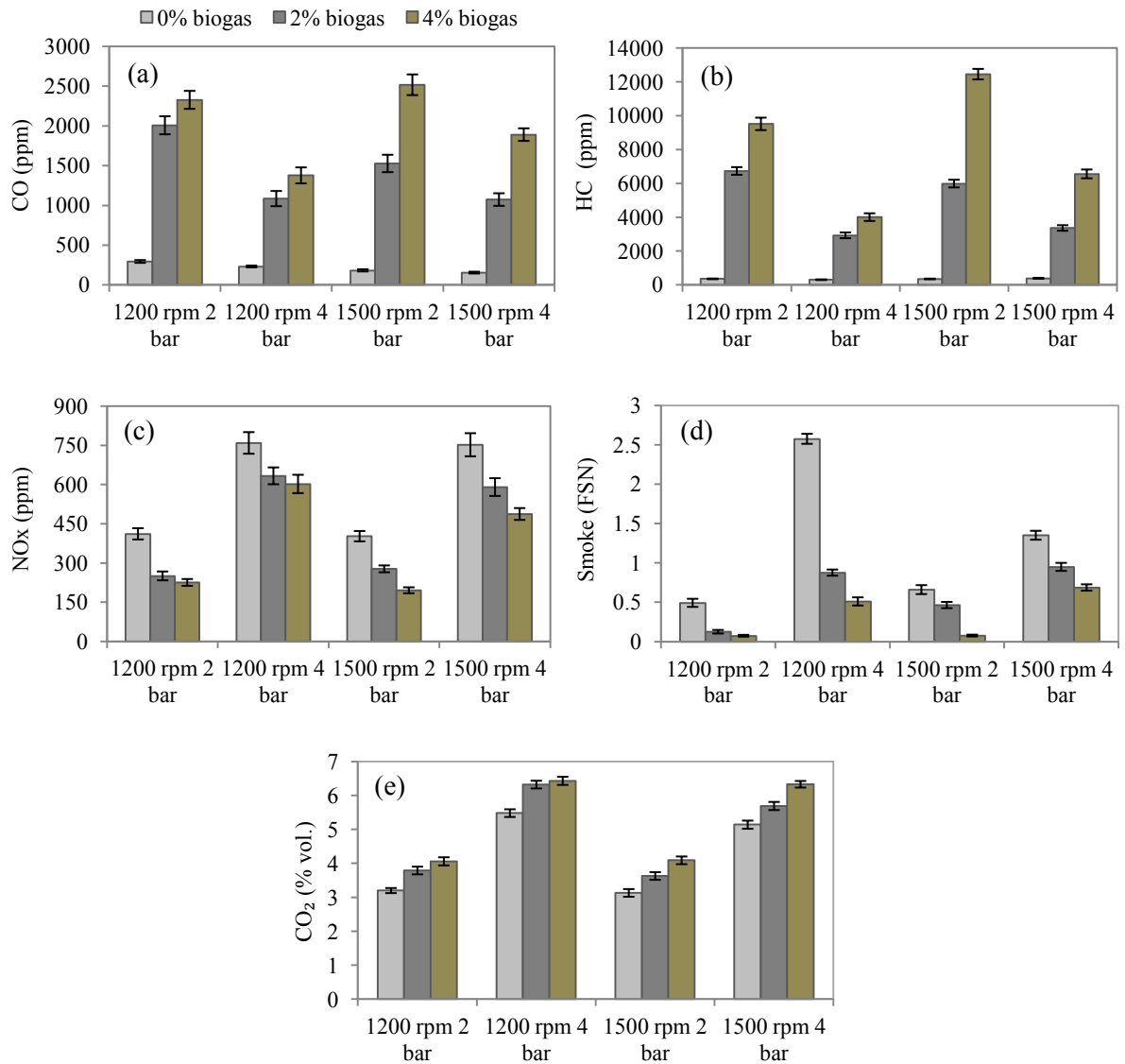
Figure 16. Emissions for biogas-ULSD combustion. (a) CO, (b) HC, (c) NO_X, (d) smoke, (e) CO_2

The biogas addition into the cylinder reduced the accumulation mode (soot) of particulate matter distribution and promoted the nuclei mode (hydrocarbon nucleation) as seen in Figure 17. The majority of the particles of diesel fuelling are ultrafine (diameter below 0.1 μm) and those from a dual fuel mode mainly consist of nanoparticles (diameter less than 0.05 μm). The reduction of the injected liquid fuel and the increase in the injected biogas amount promoted the reduction of the number of bigger diameter particles. With the reduction in soot particles, the surface area available for the hydrocarbons to adsorb onto them is reduced,

being possible to self nucleate (Figures 17b and 17c). Moreover when methane, which contained no C-C bonds, was added, the liquid fuel was reduced so the number of C-C bonds (and aromatic species) in the cylinder was reduced, which was likely to cause a reduction in particulate emissions (Tree and Svensson, 2007). For mass distribution, the majority of the particulates (i.e. the particulate mass) are located in the accumulation mode while most particulate number distributions are in the nucleation mode (Mustafi and Raine, 2008). The biogas combustion resulted in the reduction of the total particulate number as seen in Figure 18. In addition, the total particulate mass decreased with biogas percentage because of the small contribution in mass of the nucleation mode.
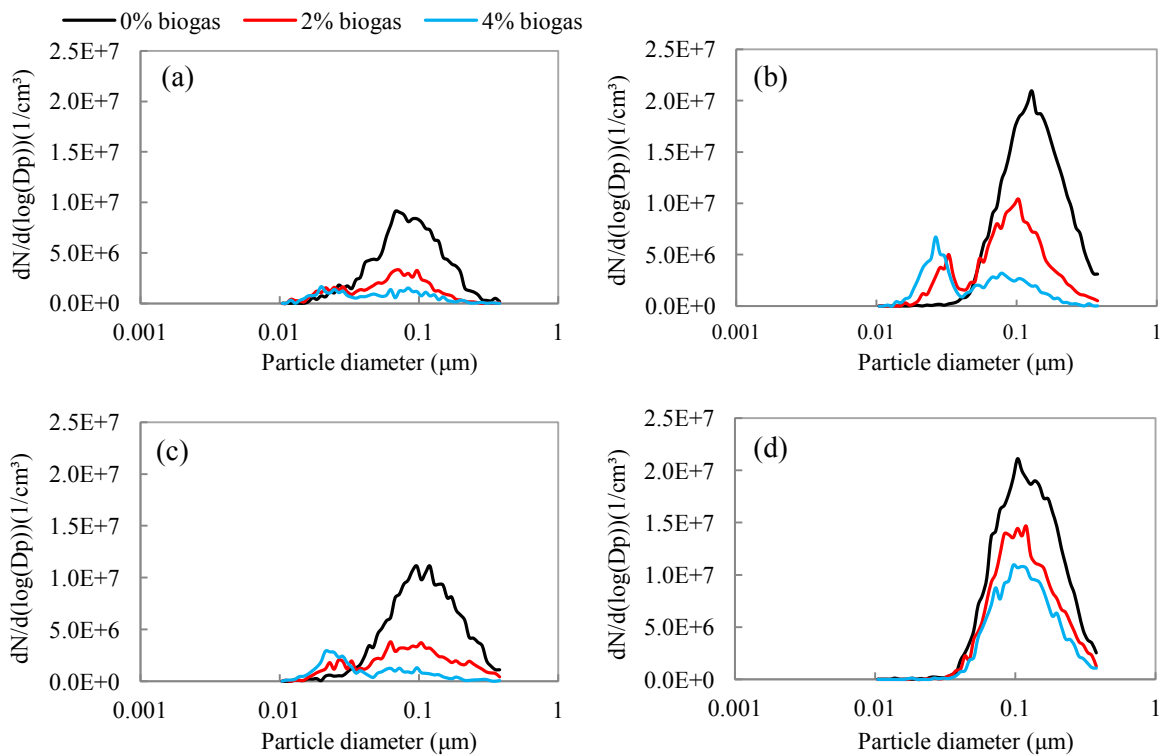
Figure 17. Particulate size distribution for biogas-ULSD combustion. (a) 1200 rpm 2 bar, (b) 1200 rpm 4 bar, (c) 1500 rpm 2 bar, (d) 1500 rpm 4 bar.
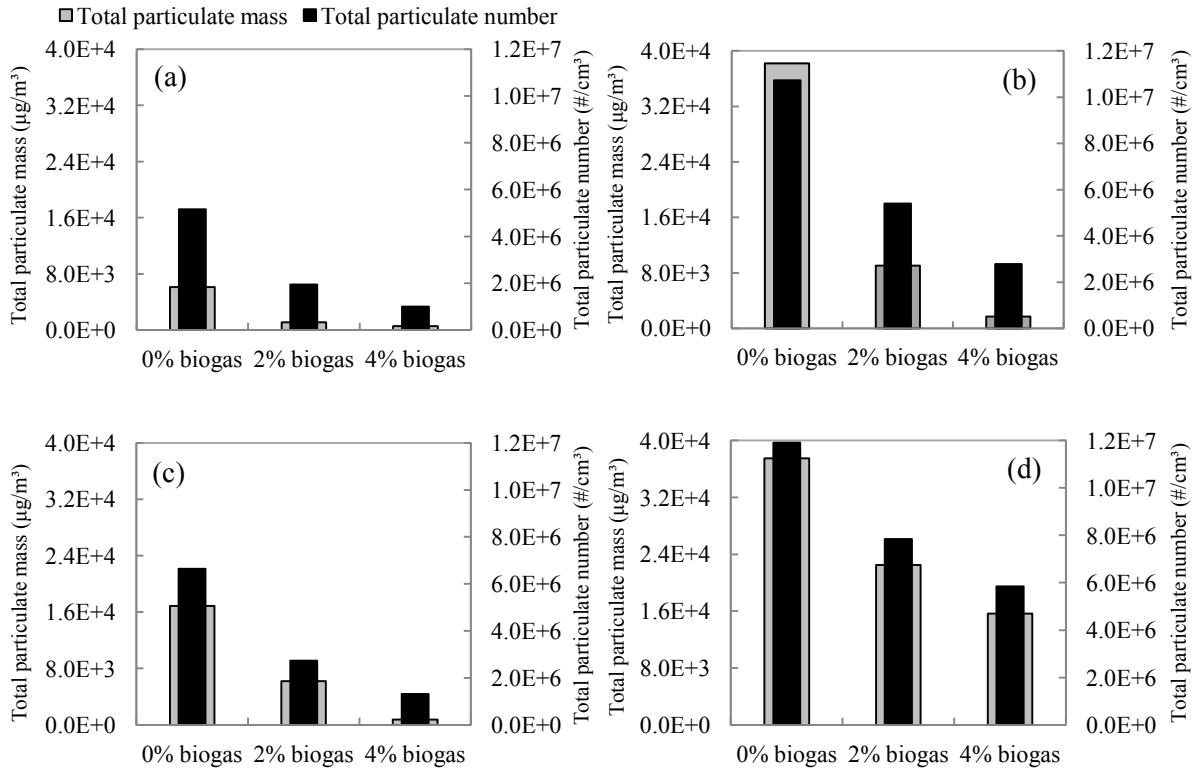
Figure 18.   Total particulate mass and number biogas-ULSD combustion. (a) 1200 rpm 2 bar, (b) 1200 rpm 4 bar, (c) 1500 rpm 2 bar, (d) 1500 rpm 4 bar.

4.3   Effects of Diesel Fuel Properties (ULSD, GD30 and GTL) on Biogas-Diesel Combustion

Combustion and engine performance characteristics. The high cetane number of GTL reduced ignition delay, but its lower density contributed to the retarded start of injection, while the presence of biogas retarded the start of ignition. Therefore, it was observed that the most retarded start of combustion was on the biogas-GTL fuelled engine operation with 4% biogas concentration (Figure 19) and resulted in a reduction in peak in-cylinder pressure. GD30 combustion has an almost identical combustion trace like that of ULSD as the change in cetane number and density. However, the combustion duration of the biogas-GTL mixture was longer than both GD30 and ULSD mixtures. The late start of combustion because of the retarded fuel injection resulted in high peak of the premixed combustion phase and shifting it

to the top dead centre region. This also caused a delay in the fuel burnt in the diffusion combustion phase hence the end of combustion was delayed.
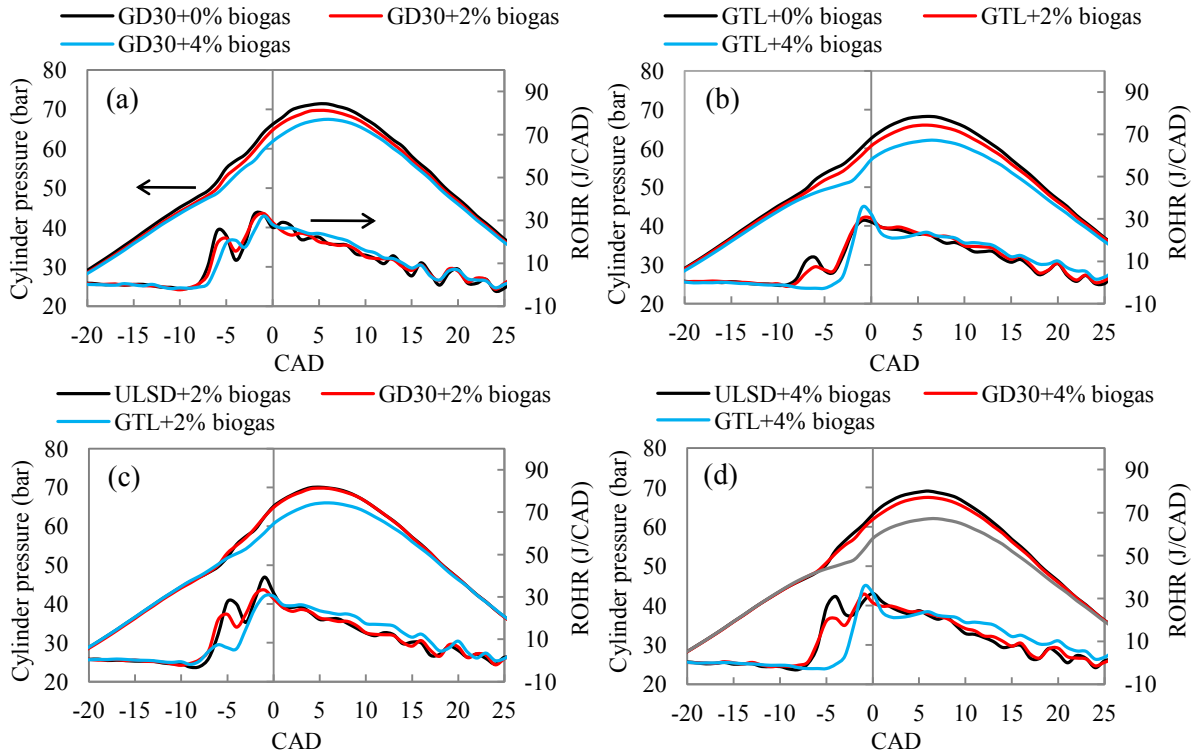
Figure 19. In-cylinder pressure and ROHR for biogas-Diesel (ULSD, GD30, GTL) at 1500 rpm 4 bar. (a) GD30, (b) GTL, (c) ULSD, GD30 and GTL at 2% biogas addition, (d) ULSD, GD30 and GTL at 4% biogas addition.

At the same inducted biogas proportions (2 and 4%), the combustion stability was relatively similar for all diesel fuels as can be seen by the cycle-by-cycle combustion variability indicator, COV of IMEP and peak pressure, as shown in Figure 20.
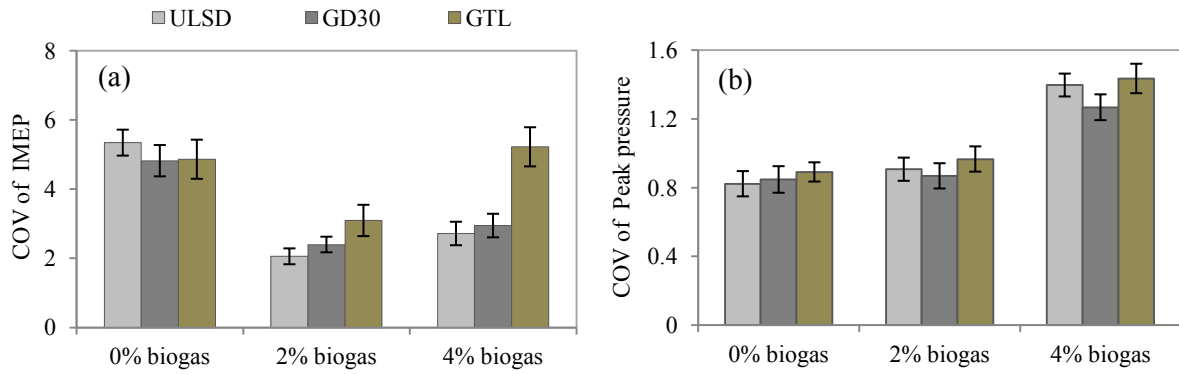
Figure 20. COV for biogas-Diesel (ULSD, GD30, GTL) combustion at 1500 rpm 4 bar. (a) COV of IMEP, (b) COV of peak pressure.

The in-cylinder injected liquid fuel quantity, the injection parameters, and fuel properties, are amongst the most influential parameters in controlling engine performance and emissions (Sahoo et al., 2009). For the same biogas percentages, 2 and 4%, the reduced in-cylinder liquid fuel (Figure 21a) was similar for all the three diesel type fuels (i.e. ULSD, GD30 and GTL). Although for GD30 and GTL fuelling the engine thermal efficiency was slightly improved (Figure 21b), under dual fuelled engine operation (2%), the engine thermal efficiency was reduced for all the three diesel fuels, as a result of the retarded start of combustion (Figure 19). Furthermore, the reduction in pilot fuel mass affected the initial flame volume which influence the capability to burn the charge mixture.

In addition, high biogas concentrations lead to highly CO_2 diluted combustion and thus this reduces the flame speed and can also lead to incomplete combustion, as explained below in the emissions section.

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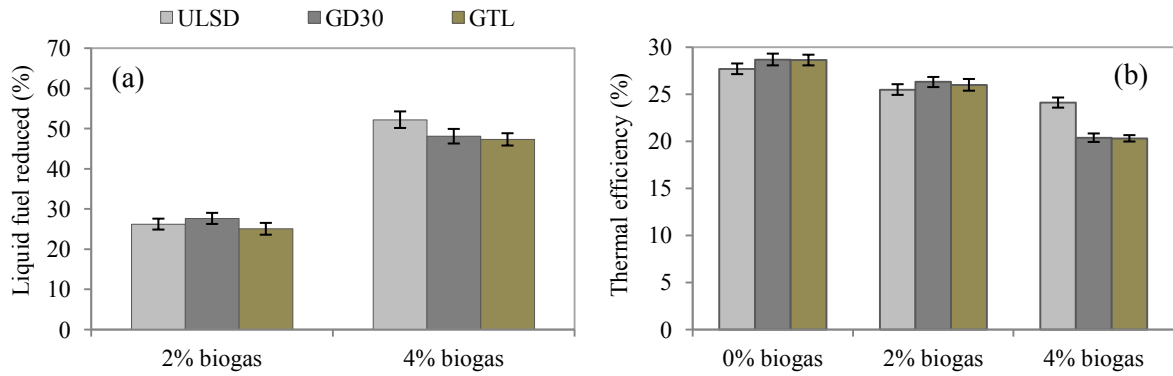
Figure 21. Liquid fuel replacement (%Wt) and thermal efficiency for biogas-Diesel (ULSD, GD30, GTL) at 1500 rpm 4 bar.

Emissions. The increased cetane number of GTL and GD30 fuels reduced both CO and HC engine out emissions. However, under dual fuelling engine, the reduced in-cylinder pressure and thus temperature because of the late start of combustion, diluted inlet charge from increased CO_2, and possibly non optimum fuel (gaseous/liquid)/air mixing (Heywood, 1988, Papagiannakis et al., 2010) increased CO and HC engine emissions (Figure 22).

NO_X and smoke engine-out emissions were associated to the fuel type and the amount of biogas inducted. The combustion of paraffinic, high cetane number fuels such as GTL and its blend GD30 reduces the premixed combustion while providing improved diffusion controlled combustion quality, leading to reduced smoke and NO_X emissions.

GTL combustion showed lower CO_2 emissions compared to that of ULSD (Figure 22e). C/H ratio and the quantity of liquid fuel in the combustion chamber are the parameters which play important role in CO_2 formation. Therefore, GTL exhibited low CO_2 emission due to its low C/H ratio. However, a deterioration in thermal efficiency for GTL in 4% biogas led to more GTL injected into the combustion chamber (Figure 21a) thus slightly increase CO_2.
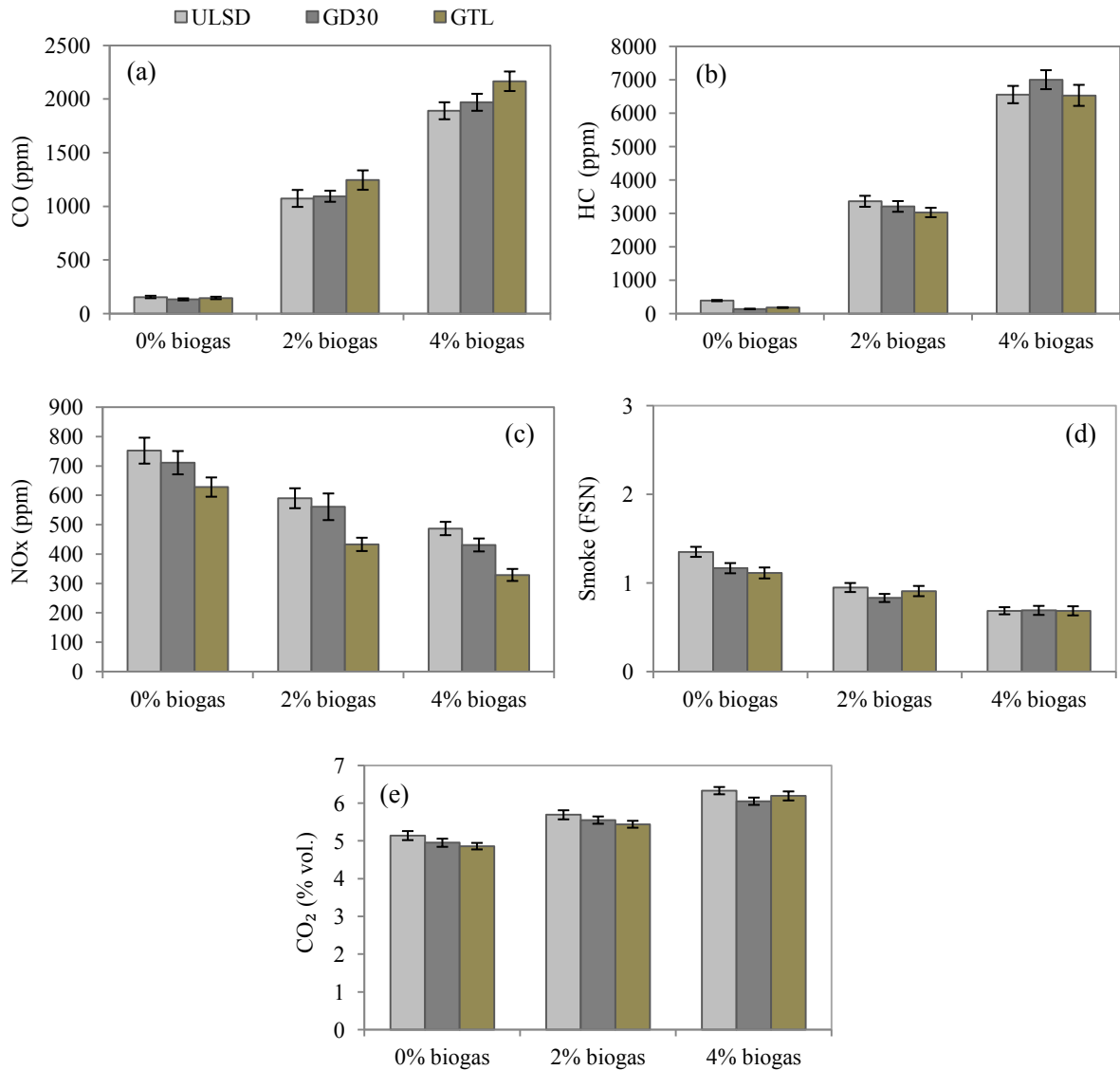
Figure 22. Emissions for biogas-Diesel (ULSD, GD30, GTL) combustion at 1500 rpm 4 bar. (a) CO, (b) HC, (c) NO_X, (d) smoke, (e) CO_2.

From Figure 23, biogas-ULSD fuelling showed that most of the particulates are located in the accumulation mode because of higher aromatic content of ULSD which promoted the PM formation. For GD30 fuelling, the start of combustion was not significantly affected but the premixed combustion phase was reduced and the diffusion combustion phase relatively similar to ULSD. This resulted in a decrease in the total particulate number and mass (Figures 24c and 24d). For GTL fuelling, it was observed that the reduction in aromatics is likely to lead a significant reduction in large particles because aromatics are known as a soot

precursors (Tree and Svensson, 2007). The sulphur content in the fuel may also affect the particulate size and thus the particulate mass. Apart from hydrocarbons, the sulphuric acid from fuel (sulphur content of ULSD is higher than that of GTL) may condense to agglomerated soot rather than forming a stand-alone particles producing relatively bigger and heavier particulates (Khalek, 2006). With a decrease in soot just a little fraction of hydrocarbon adsorbed/condensed onto the soot particle.
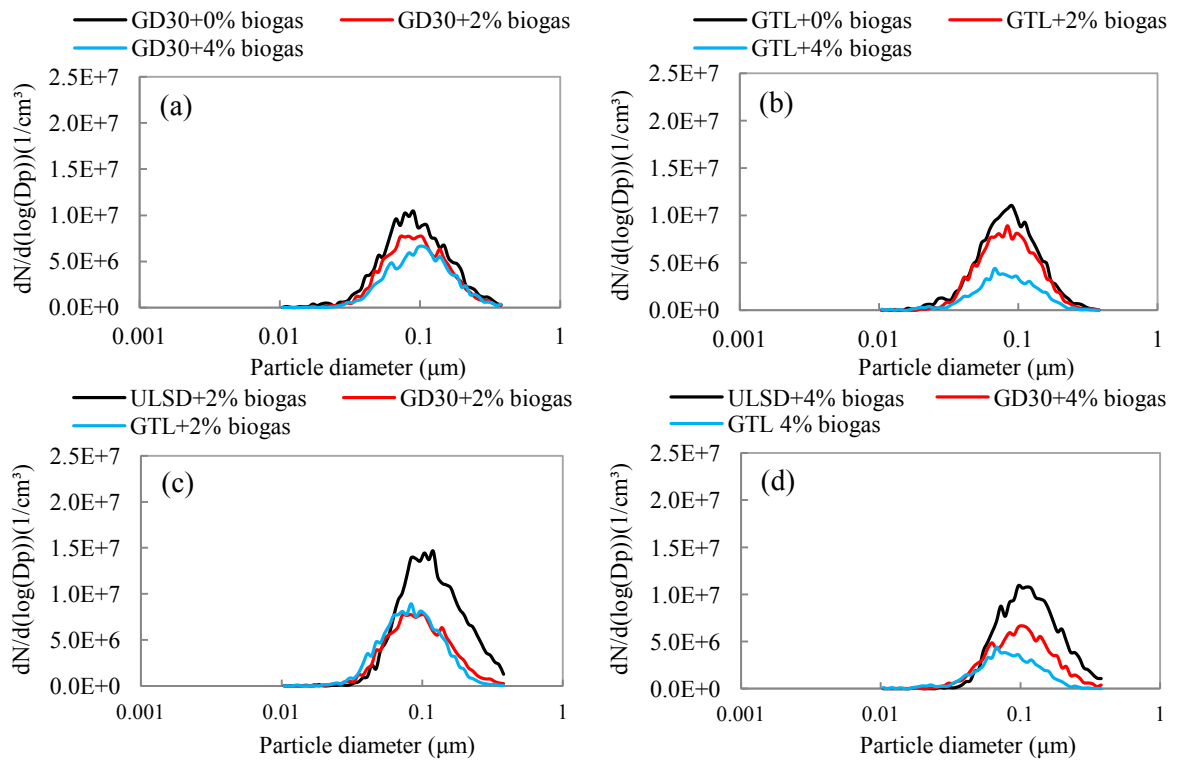
Figure 23. Particulate size distribution for biogas-Diesel (ULSD, GD30, GTL) combustion at 1500 rpm 4 bar. (a) GD30, (b) GTL, (c) ULSD, GD30 and GTL at 2% biogas addition (d) ULSD, GD30 and GTL at 4% biogas addition.
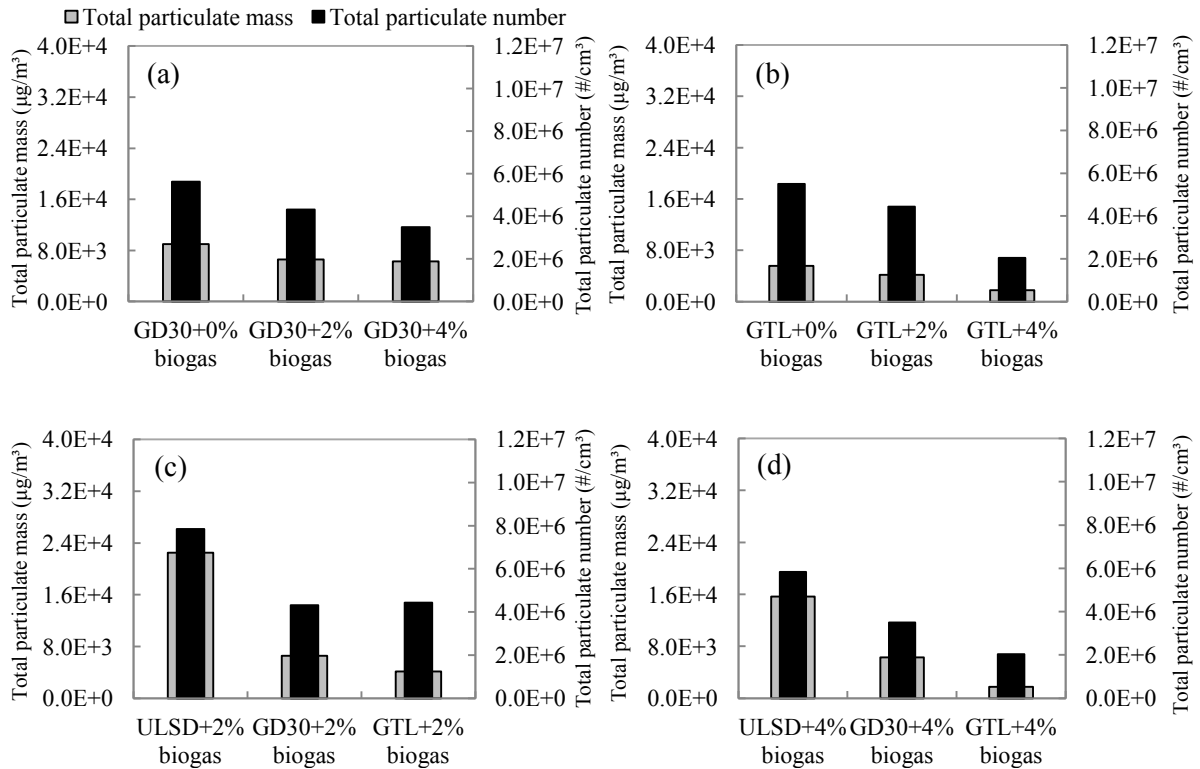
Figure 24. Total particulate mass and number for biogas-Diesel (ULSD, GD30, GTL) combustion at 1500 rpm 4 bar. (a) GD30, (b) GTL, (c) ULSD, GD30 and GTL at 2% biogas addition, (d) ULSD, GD30 and GTL at 4% biogas addition.

4.4 Effects of Hydrogen and Reformate on Biogas-Diesel Combustion

Combustion and engine performance characteristics. In the case of hydrogen and reformate addition along with biogas (Figure 25), the peak in-cylinder pressure of the dual fuelled engine combustion was a bit higher compared to that of biogas-diesel dual fuelled engine conditions due to decreased amount of CO_2 from biogas and the presence of hydrogen. The in-cylinder pressure increased up to 1 bar in the case of biogas-GD30 dual fuelling while it increased of about 0.5 bar in the case of ULSD and biogas-GTL dual fuelling respectively. Reduced air-fuel ratio with the introduction of more gaseous fuel like hydrogen and reformate apart from biogas also affected the pressure traces. However, the start of combustion was not affected in case of the ULSD and GD30, but was slightly retarded in case of the GTL fuelling.

Although hydrogen has higher flame speed and wide flammability limit which can improve the biogas combustion, the lower density and bulk modulus of GTL affected the initial heat release which is lower compared to that of ULSD and GD30.
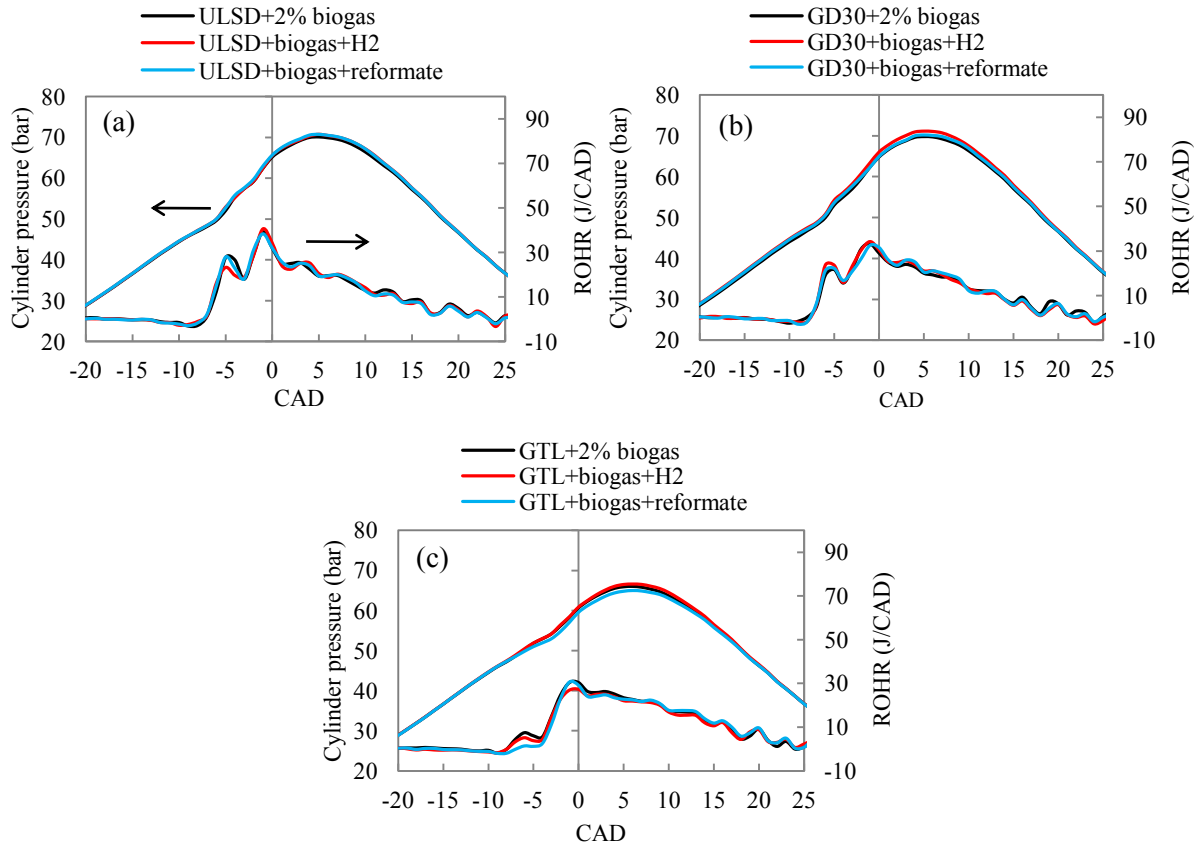
Figure 25. In-cylinder pressure and ROHR for biogas-Diesel (ULSD, GD30, GTL) with hydrogen and reformate addition at 1500 rpm 4 bar. (a) ULSD, (b) GD30, (c) GTL.

The addition of H_2 or reformate resulted in an improvement in combustion stability as shown by the COV of IMEP values in Figure 26. An improvement of about 20% in COV of IMEP was achieved in the case of biogas-ULSD dual fuelling when part of biogas was converted to hydrogen. However, the COV of peak pressure was less affected. The addition demonstrated better combustion stability as the amount of flammable mixture was increased

and caused better flame propagation leading to improved biogas combustion which reduced the unburned zone (Verhelst and Wallner, 2009).

Figure 26. COV for biogas-Diesel (ULSD, GD30, GTL) combustion with hydrogen and reformate addition at 1500 rpm 4 bar. (a) COV of IMEP, (b) COV of peak pressure.

The liquid fuel reduction (Figure 27a) was not as great as when H_2 or reformate was added, as compared to the same engine operating conditions without any addition. The amount of inducted hydrogen and reformate represents the amount (theoretically) produced by reforming half of the delivered biogas.

From Figure 27b, it was noted that the addition of H_2/reformate on biogas combustion mode caused a slight improvement in engine thermal efficiency. The brake thermal efficiency of the biogas-ULSD dual fuelling showed an increase of about 7% and 4.1% with hydrogen and reformate addition respectively. In addition, for biogas-GD30 dual fuelling, the thermal efficiency increased by 1.8% and 0.2% while in the case of biogas-GTL dual fuelling the thermal efficiency increased by 1.9% and 0.3% with hydrogen and reformate addition respectively. It was resulted from the presence of hydrogen in the cylinder which improved the biogas combustion slightly due to its high mass diffusivity and high heating value, causing the reduced heterogeneous mixture and a higher flame speed thus led to combust the fuel mixtures in the cylinder effectively (Verhelst and Wallner, 2009). Therefore, engine thermal

efficiency of biogas-diesel dual fuelled combustion was improved with hydrogen and reformate addition (Figure 21b). For example, in ULSD operation with 2% biogas the engine efficiency is 26% compared with 27.8% and 27.1% in biogas plus H_2 and biogas plus reformate respectively. This indicates that the engine efficiency could be improved further with the addition of more reformate. However, the reforming efficiency (heating value of reformate compared to heating value of biogas) would need to be considered to ascertain if there is an efficiency improvement to the whole system.
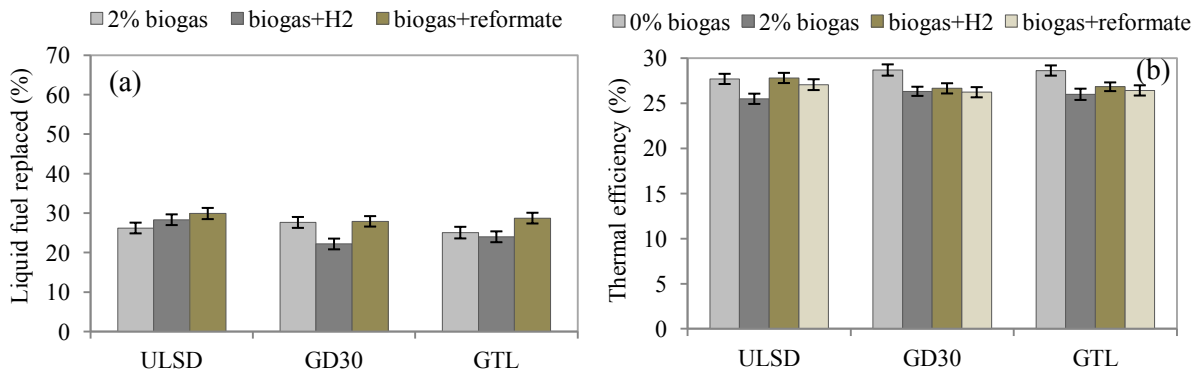
Figure 27. Liquid fuel replacement (%Wt) and thermal efficiency for biogas-Diesel (ULSD, GD30, GTL) combustion with hydrogen and reformate addition at 1500 rpm 4 bar.

Emissions. When the hydrogen and reformate were added into the engine, the CO and HC concentration increased compared to the diesel fuelling (Figures 28a and 28b). The reduction in CO and HC emissions of 46% and 50% respectively was achieved when the combustion was enriched by hydrogen in the biogas-ULSD dual fuel combustion process. For GD30 dual fuelling, CO and HC emissions decreased by 46.8% and 54.2% while in the case of GTL dual fuelling, CO and HC emissions decreased by 49.7% and 53.4% respectively under the combustion of hydrogen-enriched charge mixture. Adding gaseous fuels into the cylinder reduced the amount of liquid fuel used to maintain the energy input at the same engine load. Additionally, some of the intake air was displaced by gaseous fuels reducing the

cylinder average air-fuel ratio. This condition favoured slower and incomplete combustion and increased the engine exhaust hydrocarbon. However, hydrogen and reformate addition improved the emissions achieved on the operation with biogas alone, and this improvement was also obtained with GD30 and GTL. The improvement was resulted from the presence of hydrogen and reformate which had high turbulent burning velocities, and hence promoted higher burning intensity and better biogas-diesel fuel mixture combustion, and it was also caused by the reduction in delivered biogas which contained CO_2. On the other hand, engine operation that contained reformate resulted in significant increase of CO emissions due to CO addition in the intake manifold which resulted in reduced combustion efficiency, leading to reduced in-cylinder temperature and hence CO oxidation rates.

On the other side, hydrogen and reformate addition increased the NO_X emission due to the increased in-cylinder temperature while smoke level did not change significantly compared to biogas alone (Figures 28c and 28d). Lower minimum ignition energy, and the higher adiabatic flame temperature of hydrogen compared to biogas which tended to accelerate the development of flame point to high NO_X emission but keeps the smoke levels constant (Verhelst and Wallner, 2009, Rakopoulos et al., 2009).

As shown in Figure 28e, CO_2 reduced significantly with the hydrogen addition even lower compared to that of baseline condition (0% biogas). The reduction of 3.7%, 2.2%, and 2% was achieved for ULSD, GD30, and GTL respectively. The replacement of biogas and ULSD with hydrogen is the main reason for the reduction. This is because hydrogen is a non carbon compound. However, CO_2 increased as CO is present in the reformate. Apart from the deterioration in the combustion process as CO suppresses the benefit characteristics of hydrogen, it also might be attributed to the reaction of CO with oxygen to produce CO_2 according to the chemical reaction $CO + 1/2O_2 \rightarrow CO_2$.
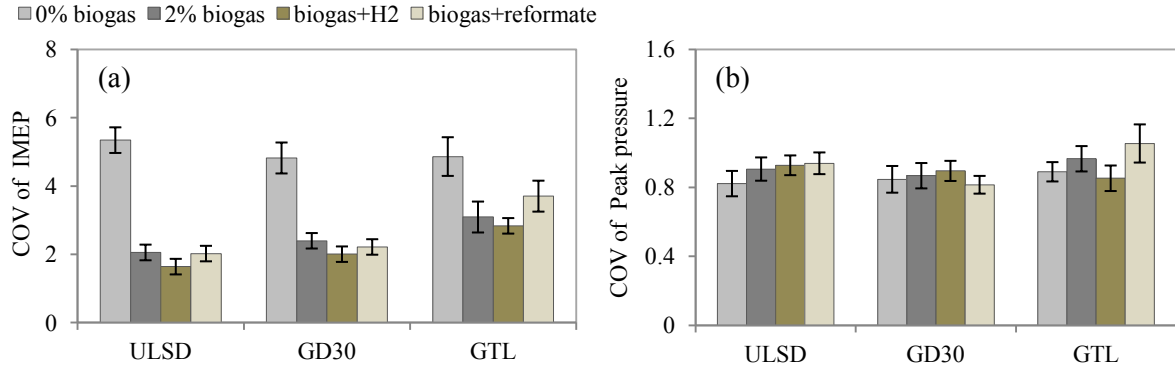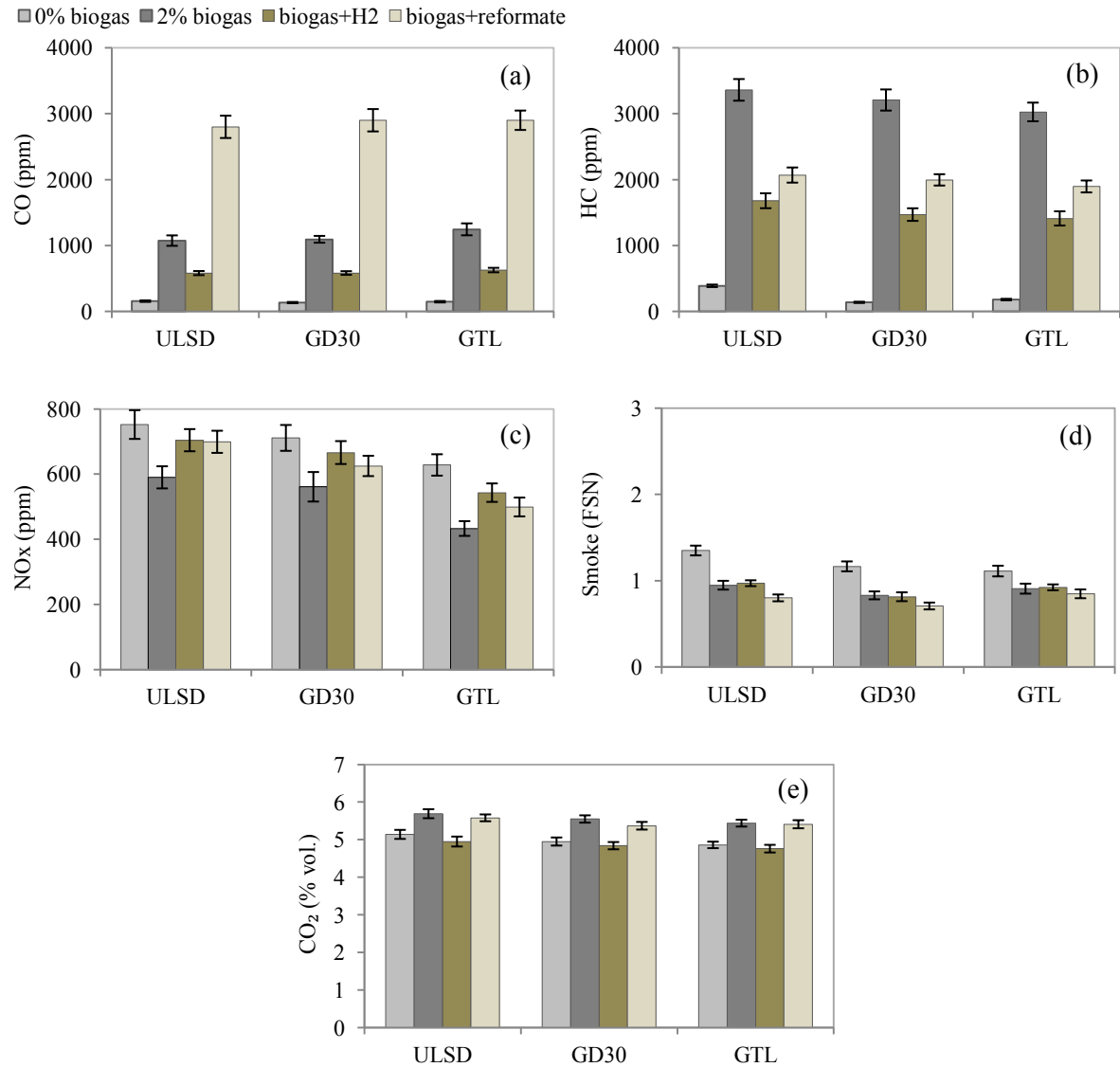
Figure 28. Emissions for biogas-Diesel (ULSD, GD30, GTL) combustion with hydrogen and reformate addition at 1500 rpm 4 bar. (a) CO, (b) HC, (c) NO_X, (d) smoke, (e) CO_2.

The concentration of the particulates is reduced when the hydrogen and reformate was inducted into the cylinder (Figure 29). It was obvious that the particulate size growth was not attributed to the hydrogen and reformate, but liquid fuel thus produced fewer particulates concentration. In addition, relatively low C/H ratio of methane was more likely to produce less soot. While hydrogen is not going to form particulates itself, it will affect the in-cylinder combustion chemistry and hence affect particulate formation and oxidation. Figure 30 shows

that the total particle mass and number concentrations were reduced when H_2 or reformate was added for all liquid fuels investigated. The addition of hydrogen and reformate to the biogas-diesel dual fuelled engine was expected to reduce particulate emissions because of two reasons. The first is that the hydrogen is expected to improve combustion performance through its increased flammability limit and expansion speed of flame front (Verhelst and Wallner, 2009). The second reason is that hydrogen is a carbon-free fuel thus may not contribute to the formation of soot (solid carbon particle) (Tsolakis et al., 2005a). However, very small diameter particles (< 2.5 µm) can enter the lungs through respiration causing adverse health effects in humans. Therefore, reducing the particulate number concentration (specifically for smaller diameter particles) is as important as reducing the particulate mass concentration (Tsolakis et al., 2009).
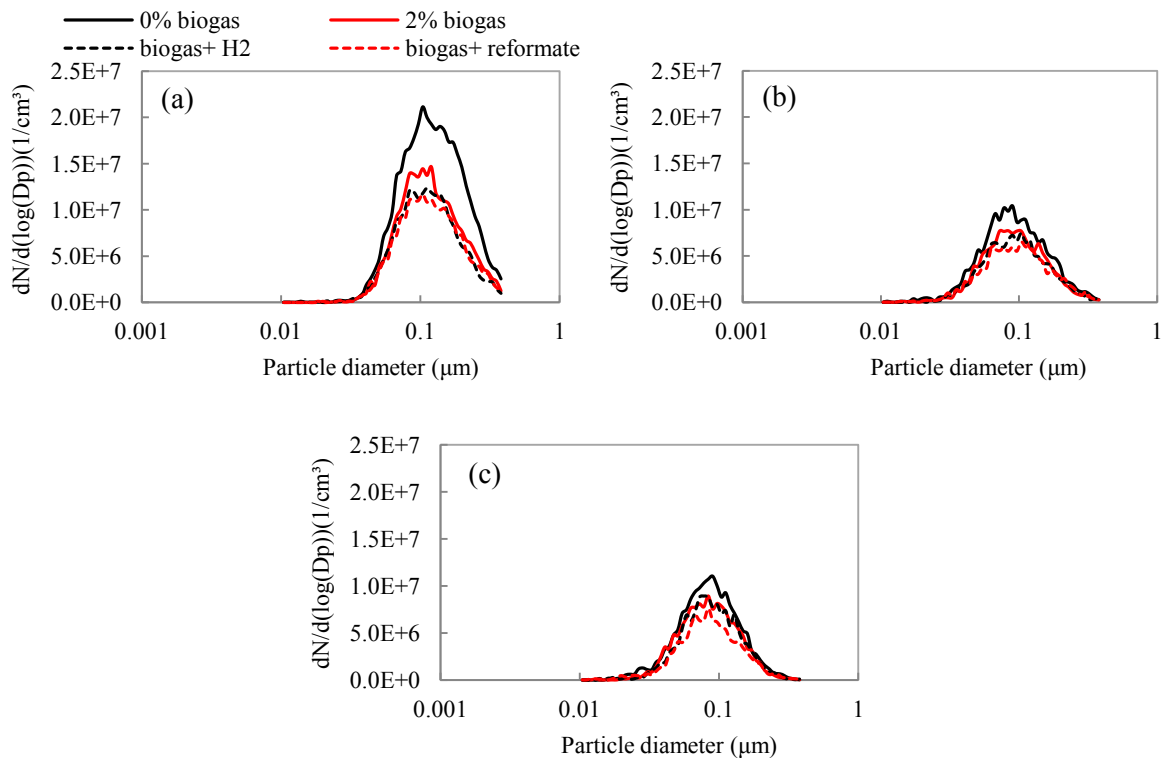
Figure 29. Particulate size distribution for biogas-Diesel (ULSD, GD30, GTL) combustion with hydrogen and reformate addition at 1500 rpm 4 bar. (a) ULSD, (b) GD30, (c) GTL.
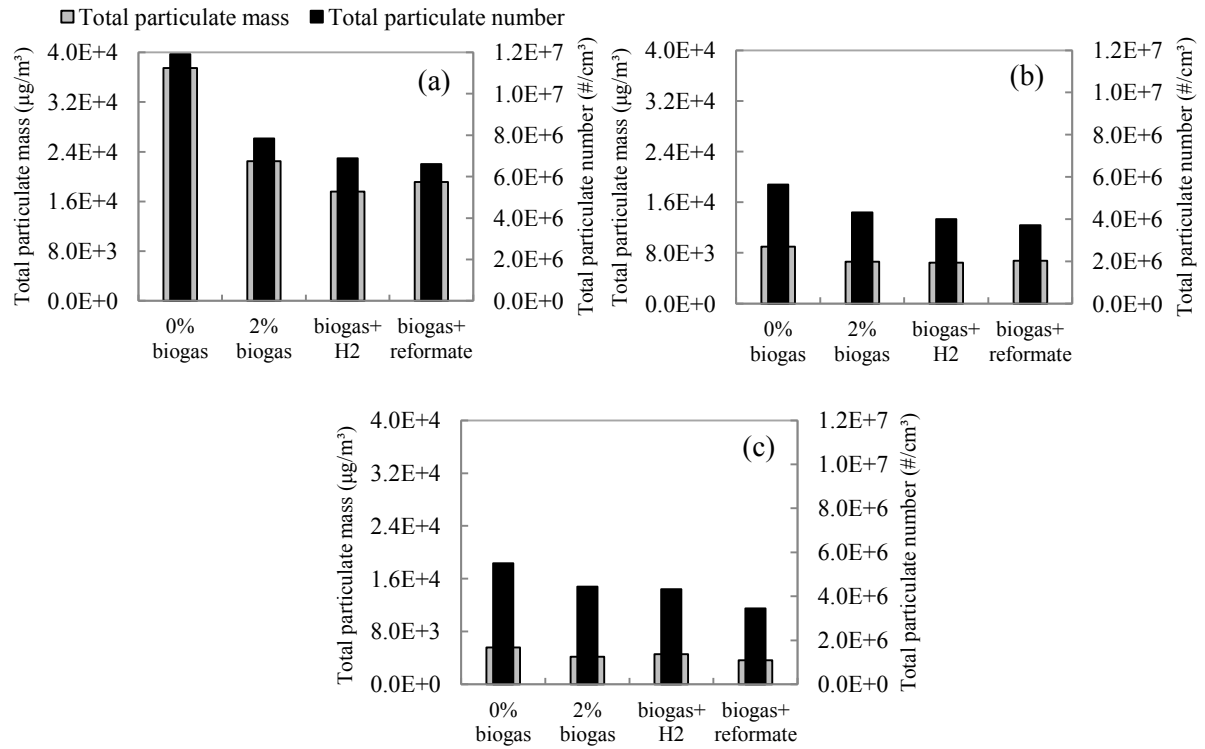
Figure 30. Total particulate mass and number for biogas-Diesel (ULSD, GD30, GTL) combustion with hydrogen and reformate addition at 1500 rpm 4 bar. (a) ULSD, (b) GD30, (c) GTL.

4.5 Summary

The thermal efficiency, combustion stability, and emissions of diesel engine to biogas addition under dual fuelling is dependent on the properties of the directly injected diesel fuel, engine operating conditions (e.g. load), and the settings of the diesel injection system. Low in-cylinder temperatures, conditions that are associated with the engine operation at low loads or at high biogas concentrations, reduce combustion efficiency. This can be observed from the increased CO, HC, and CO_2 emissions. However, under these conditions and similarly with cool combustion, both PM and NO_X emissions were simultaneously reduced. As the in-cylinder temperature was increased (through, for example, a change of engine load), combustion efficiency of the gaseous fuel was significantly improved and thus were combustion variability and emissions of CO and HC.

Under dual fuelling, the physical (e.g. density) and chemical (e.g. cetane number) properties of the directly injected diesel fuel significantly altered the combustion patterns, including the start of injection and ignition of diesel fuel, rate of heat release, and in-cylinder pressure. Fuel injection setting adjustments (e.g. timing, injection pressure and rate) are required in order to further explore the full potential of biogas-diesel fuelled combustion systems. The addition of biogas caused a decrease in the thermal efficiency of diesel fuelling due to an oxygen reduction but reformed biogas slightly increased the efficiency.

Hydrogen addition in biogas-diesel fuelling or substituting biogas with reformed biogas (e.g. simulated H_2 and CO gas, in this case) makes a small improvement in CO, HC, and CO_2 emissions compared to a biogas-diesel dual fuelled engine. The lower combustion efficiency and engine thermal efficiency of biogas-diesel dual fuelling was improved with the application of reformed biogas. Apart from high hydrogen flame speed, the thermal efficiency improvement was also attributed to the high diffusivity of hydrogen which allowed for a more homogeneous air-fuel mixture.

C H A P T E R 5

CHARACTERISTICS OF LPG-DIESEL DUAL FUELLED ENGINE OPERATED WITH RAPESEED METHYL ESTER AND GAS-TO-LIQUID DIESEL FUELS

5.1   Introduction

This chapter presents the results of dual fuelled engine combustion running on liquefied petroleum gas (LPG). LPG has been considered as a promising alternative fuel and has been widely used in transportation due to its environmental and economical benefits. The benefits come from its high octane number therefore, makes it suitable for spark ignition engines. However, because of its advantages the utilisation is extended to be used in diesel engines. In this work, the LPG used contains 100% propane and is provided in a gas cylinder.

To study the effect of biodiesel and synthetic fuel characteristics in propane–diesel dual fuelled combustion RME and GTL were used as injected diesel fuels.

Table 6 shows the experimental conditions. The experiment was performed with induction of three different LPG substitution levels, 0.2, 0.5 and 1%. They are expressed as percentages of the total volumetric intake charge air flow rate at the engine inlet. Two different engine loads operated represent the conditions at low and high engine load where the engine speed was 1500 rpm. There were 16 tests carried out in this experiment. In addition, In order to get a better understanding of the effect of the higher in-cylinder temperature to the dual fuelled combustion process while maintaining the benefits of low load operation, the operated engine loads were increased to 3 and 5 bar IMEP which represented ≈42% and

≈71% of maximum load respectively. The experiment also was carried out to study the effect of EGR (20% EGR). In addition, to study the change in fuel injection point, an advanced fuel injection by 2 CAD of standard injection timing (22 CAD) was performed. Apart from soot, SOM is also measured and the correlation with HC emission is evaluated.

Table 6.   Engine operating conditions (LPG-diesel dual fuelling)

IMEP (bar)	EGR (%)	LPG concentration (%)
3	0	0, 0.2, 0.5 and 1
	20	0, 0.2, 0.5 and 1
5	0	0, 0.2, 0.5 and 1
	20	0, 0.2, 0.5 and 1

5.2   Effect of LPG and EGR for ULSD

Combustion. Figure 31 shows the in-cylinder pressure and rate of heat release traces of LPG-ULSD combustion for different percentages of LPG. As the LPG percentage was increased, the start of combustion (SOC) was slightly delayed. The reasons for justifying this delay include the low CN of LPG, the higher heat capacity of the mixture, and the lack of oxygen, leading to a longer ignition delay (Sahoo et al., 2009). Moreover, the more LPG concentration in the cylinder the more pronounced was the premixed combustion phase. As LPG is inducted along with the air in the induction stroke, there is sufficient time to mix LPG with air in the cylinder. This leads to the formation of a ready-combustible charge mixture, which is burned in the premixed combustion phase. At low engine load, the premixed combustion phase was dominant in dual fuel engine operation (Figure 31a). In addition, the unburned LPG at this condition resulted in lower in-cylinder temperature. However, at high engine load the ignition delay was shortened and the liquid fuel injection was extended compared to the low engine load. The higher in-cylinder temperature at high engine load

promotes LPG combustion. In addition, the high calorific value of LPG contributes to a higher pressure rise rate and hence in-cylinder pressure with respect to ULSD. Additionally, the diffusion combustion phasing was extended (Figure 31b).
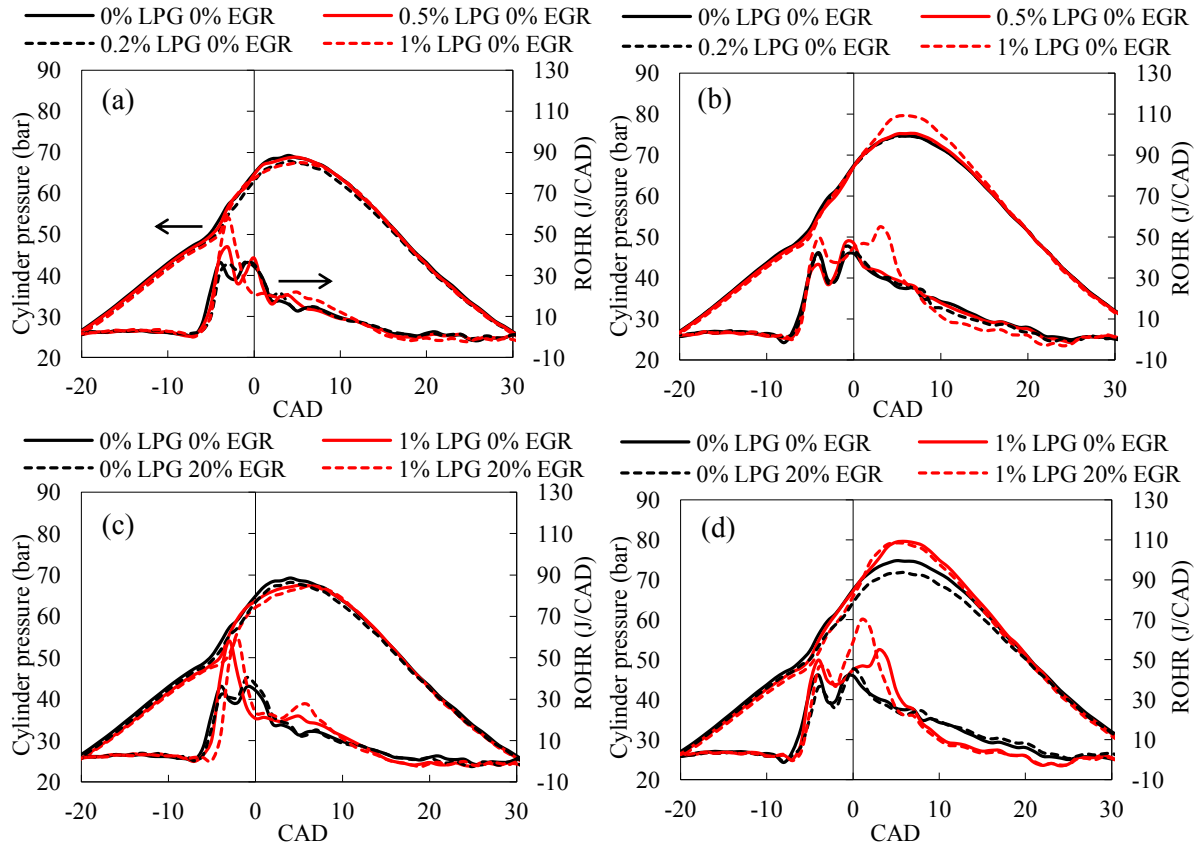
Figure 31. In-cylinder pressure and ROHR for ULSD-LPG combustion. (a) 3 bar, (b) 5 bar, (c) effect of EGR at 3 bar, (d) effect of EGR at 5 bar.

It was found that the in-cylinder pressure of LPG-diesel dual fuelling was decreased as the EGR took part in the combustion process (Figure 31c). However, the in-cylinder pressure was not affected in the case of high load under 1% LPG (Figure 31d). The preparation of pre-ignition activity was also influenced by the presence of EGR as the oxygen from fresh air inlet was replaced by EGR (dilution effect) (Hountalas et al., 2008, Ishida et al., 2010). This resulted in a longer ignition delay and hence further retarded SOC, lowering the in-cylinder temperature. These were caused by the water vapour as a constituent of EGR which have high

specific heat capacity thus acting as a heat-absorbing agent (thermal effect) (Zheng et al., 2004, Choi et al., 2011). In addition, deterioration in combustion air availability in EGR combined with low CN of LPG even led to longer ignition delay.

Figure 32a shows that the liquid fuel replacement increased linearly with the increase of the inducted LPG. At low engine load and 1% LPG concentration, the amount of diesel substituted was 60% on a mass basis. The maximum diesel substitution was achieved at low load because the concentration of the inducted LPG was kept for the different engine loads while the amount of injected liquid fuel was low. However, the high LPG and EGR addition potentially raises the combustion variability and misfire as consequence of insufficient oxidant and low CN of LPG, therefore, the concentration should be limited.

Combustion stability, which is indicated by the coefficient of variation (COV) of indicated mean effective pressure (IMEP), was in the acceptable range (lower than 5%) in all the tested conditions (Figure 32b) (Heywood, 1988). An increasing trend is observed with the increase in LPG quantity, limiting the use of LPG-diesel dual fuel operation. A non-uniform mixture may lead to unstable combustion under a high LPG fraction. A higher quantity of LPG reduces the amount of combustion air and the in-cylinder injected diesel fuel, leading to misfire which can produce relatively high cycle-by-cycle variation (Qi et al., 2007, Peng et al., 2008b).
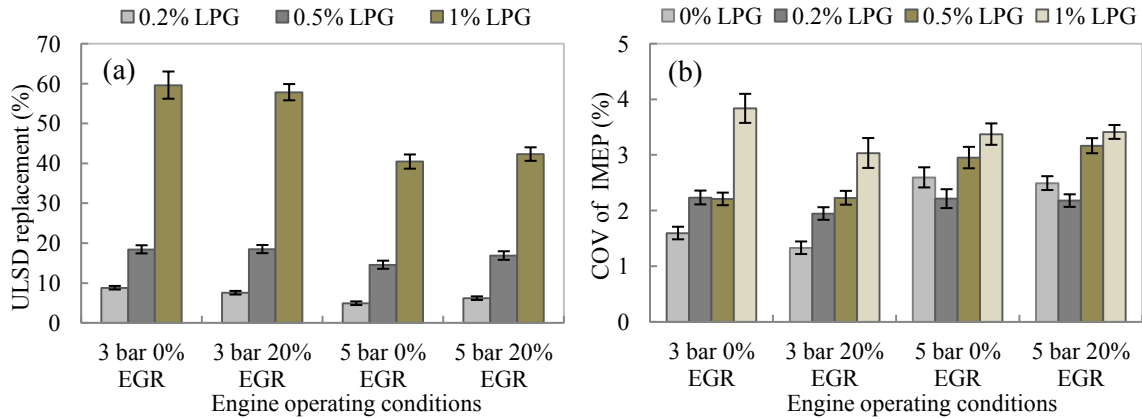
Figure 32.   Liquid fuel replacement (%Wt) and COV of IMEP for ULSD-LPG combustion.

The reasons to explain the decreased brake thermal efficiency (Figure 33) in LPG-diesel dual fuelled engine operation mode can be the reduction in volumetric efficiency, incomplete combustion, reduced flame propagation, and an abundant presence of residual gases (Saleh, 2008, Qi et al., 2007, Miller Jothi et al., 2008). Furthermore, the reduction in the amount of liquid fuel used to initiate the combustion has adverse effects on the quality of liquid fuel spray. This produces poor liquid fuel preparation and atomisation due to a slow development of fine droplets which affects the mixture combustion process (Heywood, 1988). These factors shifted the combustion process to the expansion stroke and thus producing less useful work (Sahoo et al., 2009). However, when EGR was employed the thermal efficiency was not further deteriorated. As the EGR used in the experiment was not fully cooled EGR, the 20% EGR rate increased slightly the intake temperature enriching the inducted LPG-air charge mixture leading to the enhanced LPG combustion (Saleh, 2008, Miller Jothi et al., 2008).
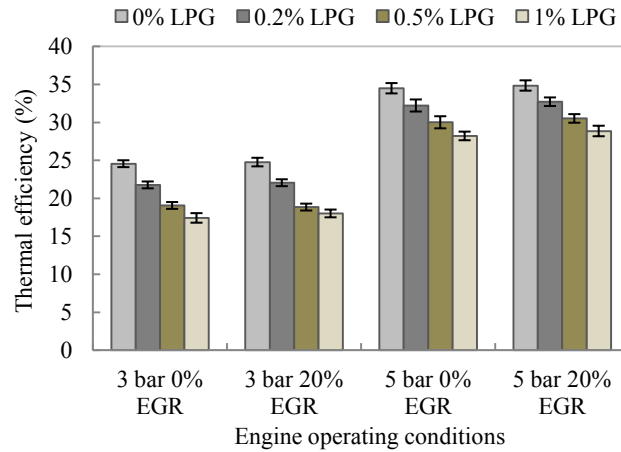
Figure 33. Thermal efficiency for ULSD-LPG combustion.

Emissions. It is shown that the HC and CO emissions increased with the increase of LPG in the LPG-diesel dual fuelling (Figures 34a and b). Engine load has an important role in the emission formation and oxidation. At low engine load, some parameters such as poor mixing quality, rich premixed mixture, and flame quenching at dual fuelling resulted in incomplete combustion (Saleh, 2008, Heywood, 1988). High auto-ignition temperature of LPG (Table 4) also hampered its oxidation due to low combustion temperature. At these conditions, the slow combustion velocity resulted in the flame cannot propagate to the entire mixture leaving the unburned mixture in the combustion chamber (Miller Jothi et al., 2008). In addition, the other reason for the emissions deterioration was influenced by the reduction of the overall lambda (λ). It was obtained that in the low engine load operating condition the overall lambda reduced from 3.5 (0% LG) to 2.6 (1% LPG). At high engine load the trend was similar to low engine load, but the HC and CO penalty was lower because of the higher combustion temperature, which promotes a better rate of mixture decomposition and oxidation. Therefore, a relatively constant NO_X emission in LPG-diesel dual fuelling was observed compared to diesel only combustion (Figure 35).

Figure 34c shows that the CO_2 emission decreased with the LPG addition. Liquid fuel replacement from high C/H ratio fuel (diesel fuel) to the lower one (propane) gives an impact to the decreased emission. In addition, it might be associated to the production of HC and CO rather than the production of CO_2 as a result of incomplete combustion. With EGR, CO_2 increased because of CO_2, unburned HC are recycled from exhaust into combustion chamber.
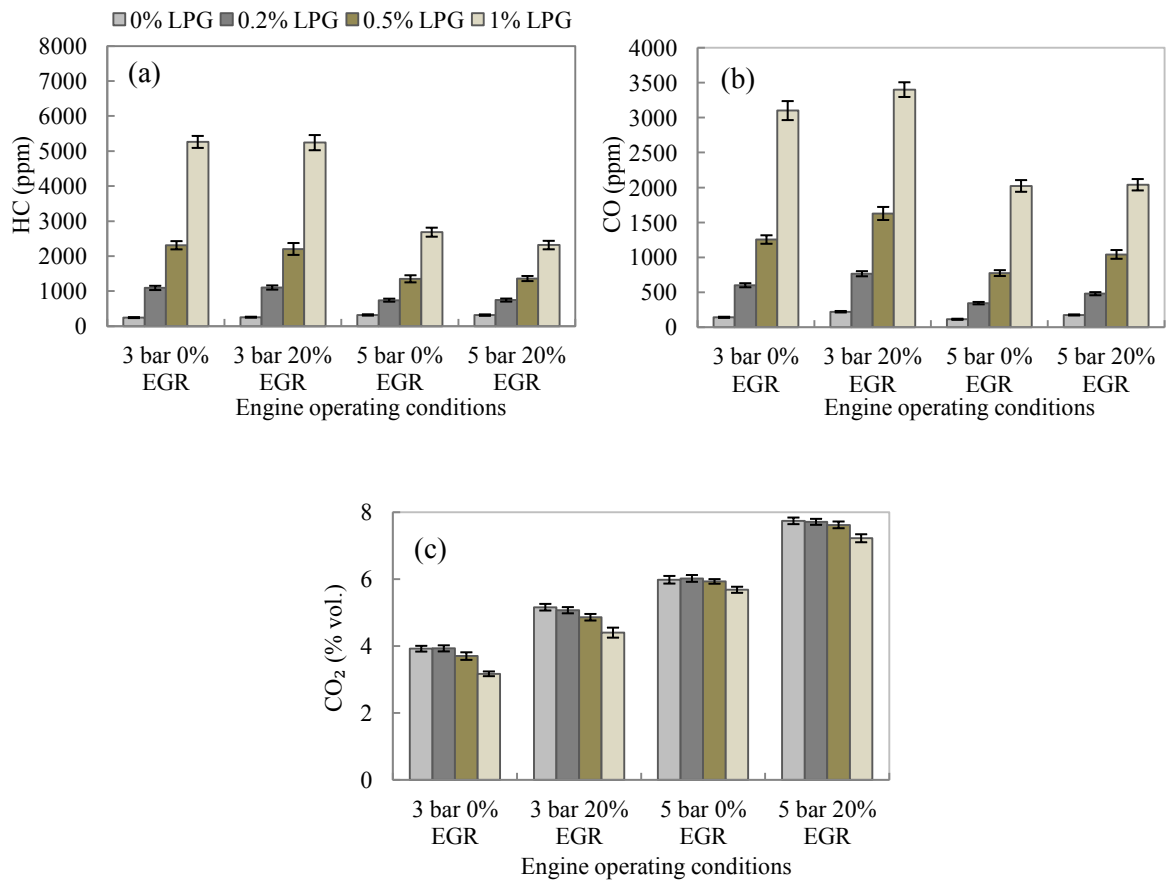
Figure 34. Emissions for ULSD-LPG combustion. (a) HC, (b) CO, (c) CO_2.

The NO_X emissions show different trend between low and high engine load as can be seen in Figure 35. At low engine load, a retarded SOC due to LPG and EGR addition decreased the in-cylinder temperature. This contributed to the inhibition of NO_X formation thus reducing the level in line with the increase of LPG even though in the premixed combustion phase the energy released was relatively high (Maiboom et al., 2008, Miller Jothi

et al., 2008, Hountalas et al., 2008, Zheng et al., 2004). When EGR takes part in the combustion process, the oxygen availability reduces and hence decelerating the mixing rate between fuel and oxygen. Therefore, in order to access more oxygen the flame region grows to a bigger size which in turn it absorbs heat from its surrounding and hence lowering the flame temperature (Maiboom et al., 2008). The low in-cylinder temperature which is indicated by low pressure (Figure 31c) is the result of thermal and dilution effect of EGR employment suppresses the NO_X formation.

At high engine load, the higher in-cylinder temperature favours NO_X emissions formation (Zheng et al., 2004). In addition, when 1% LPG was inducted, NO_X emissions were higher than those obtained with ULSD only combustion. It was obtained that NO_X increased by 0.2% when high LPG concentration (1% LPG addition) was added at high engine load. This suggests that fuel injection modification and a limitation on LPG addition are required to avoid this NO_X penalty at high engine load.

A significant reduction in soot was seen in dual fuelled diesel engine at all engine operating conditions (Figure 35). Increasing the fraction of LPG will be followed by the increase in liquid fuel replacement. As soot is mainly produced in the locally liquid fuel rich regions (Mueller et al., 2003, Tree and Svensson, 2007), the presence of LPG reduced the number of the available regions hence producing less soot. This replacement also provided less carbon-contained fuel in the combustion chamber, as LPG has less carbon compared to that of diesel, suppressed the soot formation propensity. An advantage was obtained in the case of LPG and EGR combination where NO_X emissions were further improved while soot was kept at low level especially at 1% LPG addition low engine load. It is suggested that at this condition the local in-cylinder temperature is considerably reduced, hence inhibiting soot

formation. Lean-liquid fuel regions and low air entrainment because of the presence of gaseous fuel also hampered the formation of soot precursor (Tree and Svensson, 2007).
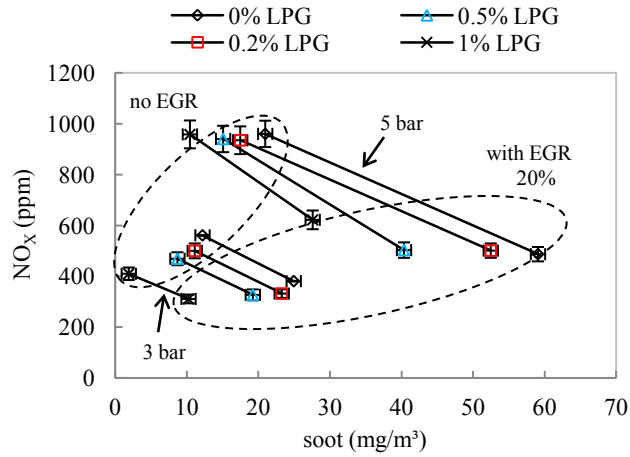
Figure 35.   Soot-NO_X trade-off for ULSD-LPG combustion.

Soluble organic material (SOM) is one of the constituents of PM apart from soot. Its proportion in the total PM can be defined as soluble organic fraction (SOF) and is expressed as follows:

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (5.1)$$

Unburned or partially oxidised hydrocarbons of lubricating oil and parent fuels contributed to the formation of SOM. Those hydrocarbons were then adsorbed/condensed onto soot particles (Zhu et al., 2011a).

From Figure 36a, it was obtained that as LPG addition was increased, SOM reduced, even though unburned total hydrocarbons emissions were higher (Figure 36b). The significant reduction of soot with LPG limits the soot surface area in which organic material can be adsorbed/condensed, hence reducing SOM. However, in the case of low load with 20% EGR, the SOM was relatively similar or even increased with the addition of LPG compared to that of baseline condition. Low combustion temperature and the increased soot concentration due

to EGR addition resulted in the propensity of hydrocarbon to be adsorbed onto the soot surface increased leading to formation of SOM. However, the high concentration of hydrocarbons with LPG addition promotes their adsorption and condensation onto this limited soot, slightly increasing SOF (Figure 37). This SOF increment is limited as most of the engine-out gaseous hydrocarbons in LPG combustion might be unburned LPG and other light hydrocarbons. These hydrocarbons have a low dew point restricting their adsorption/condensation onto soot particles.
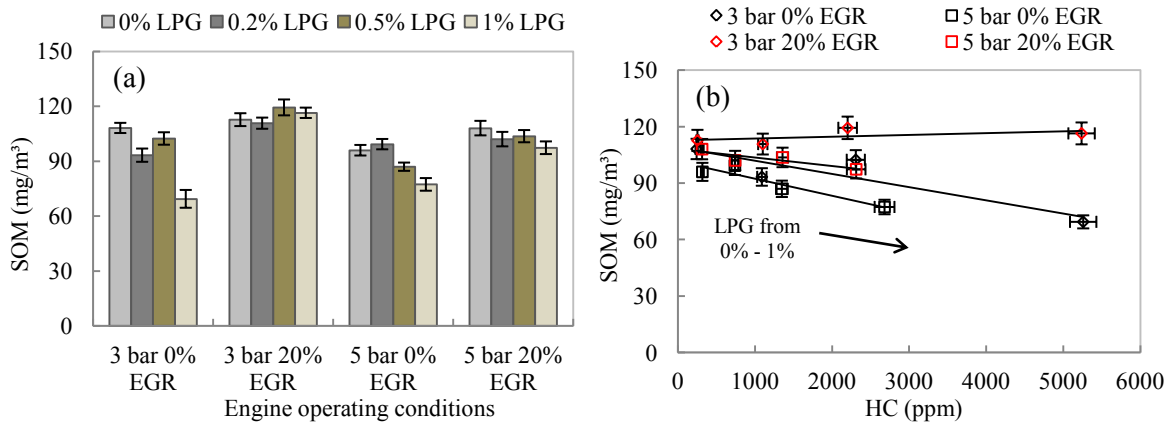
Figure 36.   SOM emission and HC-SOM correlation for ULSD-LPG combustion.

The engine operating conditions also affect the quantity of SOM. In the case of high engine load where lambda was lower, the in-cylinder temperature was high and hydrocarbons emissions were lower compared to low engine load hence the SOM was reduced (Furuhata et al., 2007). In the case of EGR application, the SOM was higher compared to the case without EGR, while the SOF was lower. When EGR was added, soot concentration significantly deteriorated, while hydrocarbon emissions were similar with respect to operation without EGR (Figure 34a). As a consequence, there is more available soot surface in which hydrocarbons could be adsorbed or condensed, increasing the total SOM. However, the

organic material per particle was reduced, as there were more soot particles while the hydrocarbons concentration remained similar.
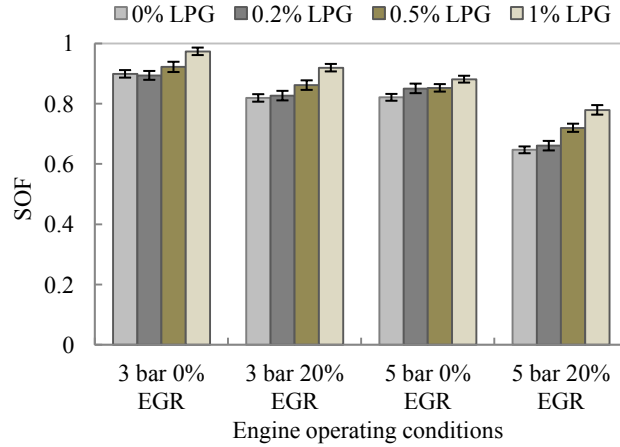
Figure 37. SOF emission for ULSD-LPG combustion.

5.3 Effect of Liquid Fuels

Combustion. The effect of different properties of diesel fuels on the combustion characteristics of LPG-diesel dual fuelling is shown in Figure 38. Because the trend of combustion patterns for 0.2 and 0.5% LPG concentrations was relatively similar for all fuels used in this work, only the 0 and 1% LPG are shown.

The premixed combustion phase with GTL was low because of the reduction in ignition delay derived from its high CN (Table 3). Therefore, most of the GTL was burned in the diffusion combustion phase, extending the combustion duration. However, the SOC of GTL was comparable to that obtained with ULSD. This similar SOC, despite the shorter ignition delay of GTL, is due to the delay in the start of injection (SOI). This delay comes from the low density and high compressibility of GTL (Table 3). These GTL combustion characteristics resulted in lower in-cylinder pressure. On the other hand, higher density and bulk modulus of RME make it less compressible so that the pressure in the injector can

develop faster to reach the required injection pressure (Lapuerta et al., 2008a, Tan et al., 2012). This resulted in the fuel being injected earlier and the start of combustion as well, increasing the in-cylinder pressure.
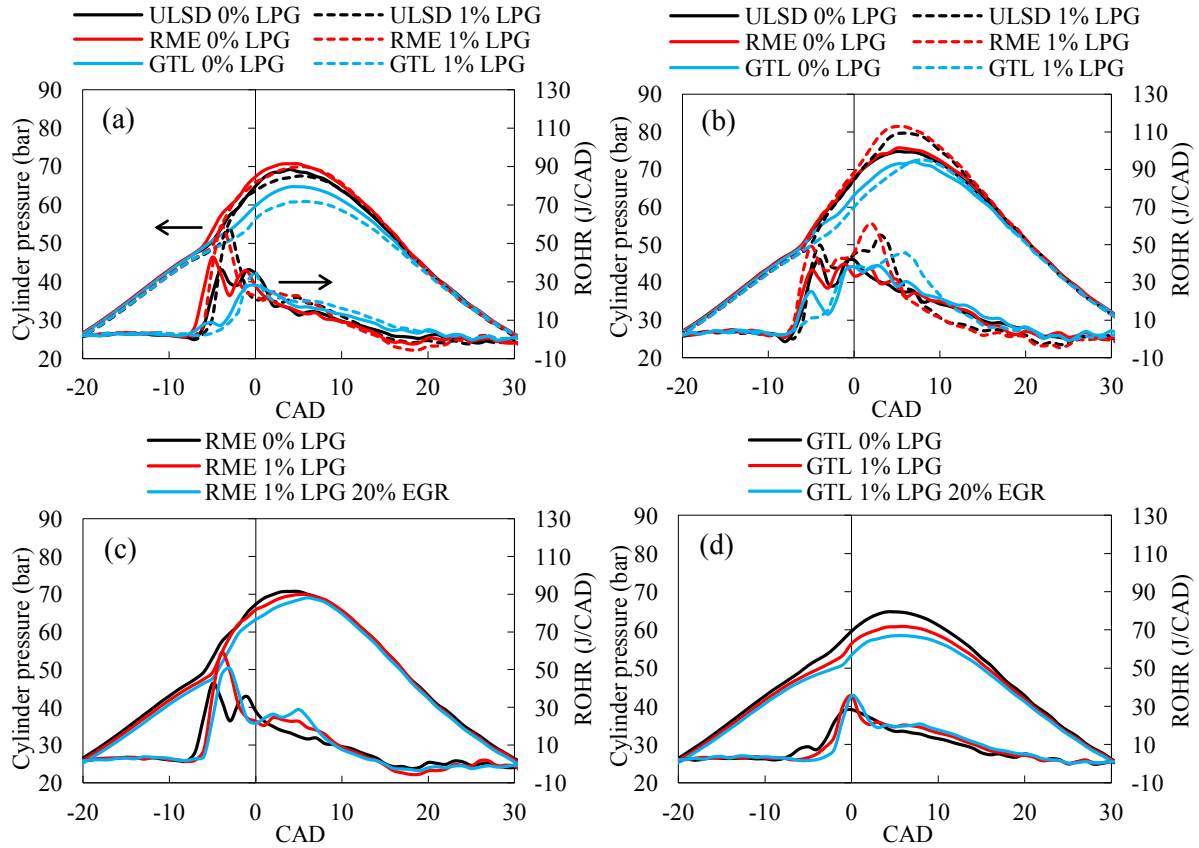
Figure 38. In-cylinder pressure and ROHR for Diesel (ULSD, RME, GTL)-LPG combustion. (a) effect of different liquid fuels at 3 bar, (b) effect of different liquid fuels at 5 bar, (c) effect of EGR on RME-LPG combustion, (d) effect of EGR on GTL-LPG combustion.

The addition of LPG and EGR changed the combustion patterns with respect to the original ones (e.g. LPG-diesel). When 1% LPG was inducted in GTL dual fuel combustion, the low quantity of GTL (i.e. reduction in the auto-ignition properties of the mixture) cannot compensate the injection delay, producing a retard at the start of ignition. With EGR the SOC for the three fuels was retarded. The higher heat capacity of the mixture and lower oxygen

availability are the barriers for early ignition. The delay in the SOC was more noticeable in the case of GTL, as it was explained previously in 1% LPG.

Figure 39 shows the liquid fuel replacement and combustion variability from cycle-by cycle from different diesel fuels used. The amount of liquid fuel replaced has correlation with the brake thermal efficiency as shown in Figure 40. It is shown that ULSD and RME have relatively comparable brake thermal efficiency. However, RME has lower calorific value compared to that of ULSD (Table 3). Therefore, a higher amount of the fuel was required to reach the similar brake thermal efficiency, hence there was lower liquid fuel replacement.

On the other hand, GTL has slightly higher calorific value than that of ULSD. It is expected to burn a slightly smaller quantity of GTL as well to attain the same output engine power. Therefore, in this case the fraction of liquid fuel was smaller than that of ULSD. However, the brake thermal efficiency of LPG-GTL dual fuelling was deteriorated at low load resulted in more liquid fuel required leading to a lower liquid fuel replacement. However, at high load the LPG-air mixture combustion efficiency was improved thus increasing the thermal efficiency which then reducing the utilisation of liquid fuel (higher liquid fuels replacement).

The use of LPG affected the COV of IMEP for both low and high load (Figure 39b). The COV was increased and it was further pronounced at low load. The deterioration was caused by more diluted in-cylinder charge which led to less effective combustion. Considering the effect of different liquid fuels to the COV, GTL showed the most susceptible change to the COV. However, in all cases COV was maintained in the acceptable range. According to Heywood, the driveability problems are likely to occur when the value COV of IMEP is more than 10% (Heywood, 1988).
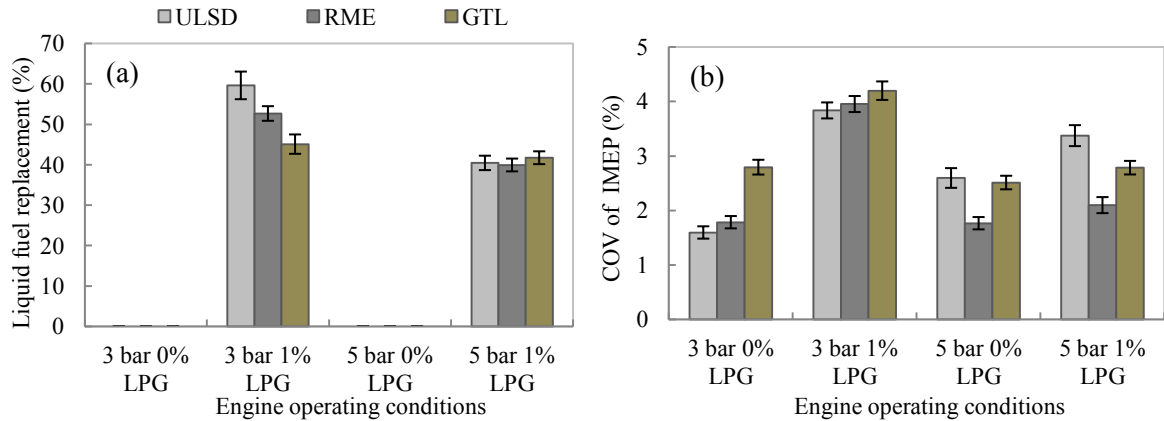
Figure 39. Liquid fuel replacement (%Wt) and COV of IMEP at different liquid fuels for Diesel-LPG combustion.

It is widely reported that the brake thermal efficiency between ULSD and RME does not show a significant difference (Tsolakis, 2006, Senatore et al., 2000, Lapuerta et al., 2008b, Monyem and H. Van Gerpen, 2001). In the LPG-diesel dual fuel mode, the trend of the thermal efficiency was kept similar to the baseline conditions. For GTL case, it shows that its thermal efficiency was better than those of ULSD and RME. This gain is due to the improved fuel atomisation and the high CN of GTL which led to shorter ignition delay (Kitano et al., 2005). In addition, enhanced complete fuel oxidation reduces fuel consumption and improves thermal efficiency (Theinnoi et al., 2009). However, it is shown that in dual fuel (LPG-GTL) mode at 1% LPG and low load the thermal efficiency was reduced. The GTL physical characteristics such as low density and high compressibility are associated to the retarded SOC which contributed to lower in-cylinder pressure hence reducing the indicated work.
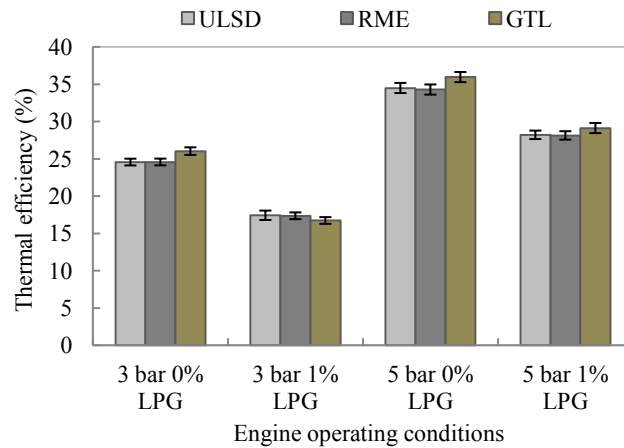
Figure 40. Thermal efficiency at different liquid fuels for Diesel-LPG combustion.

Emissions. Considering the various liquid fuels used, the HC and CO emissions under RME and GTL operation were lower compared to that of ULSD at no LPG engine operation (Figure 41). HC and CO emissions of RME were 28% and 16% respectively lower than that of ULSD while for GTL the emissions were 17% and 5% lower than that of ULSD. The oxidation and formation of the emissions were attributed to several factors specifically the properties of the fuels. It is well known that oxygen content in RME accompanied by higher in-cylinder temperature (Figure 38) can enhance the HC and CO oxidation (Saanum et al., 2008). Similarly, the benefits in high CN and H/C ratio for GTL improved the oxidation of hydrocarbon fuel. However, in the case of GTL at 1% LPG for both engine loads (specifically low load), there was considerably increase in the HC emission. Low combustion temperature and less energy released are some of the main reasons for a poor charge mixture oxidation.

CO_2 emission of RME combustion is the highest than those of ULSD and GTL over the engine conditions. The calorific value of each fuel influences the amount of the injected fuel at the same engine torque output conditions. RME with the lowest calorific value of the fuels examined was injected more compared with ULSD and GTL and conversely to GTL. This resulted in more CO_2 formed in the case of RME (Figure 41c).
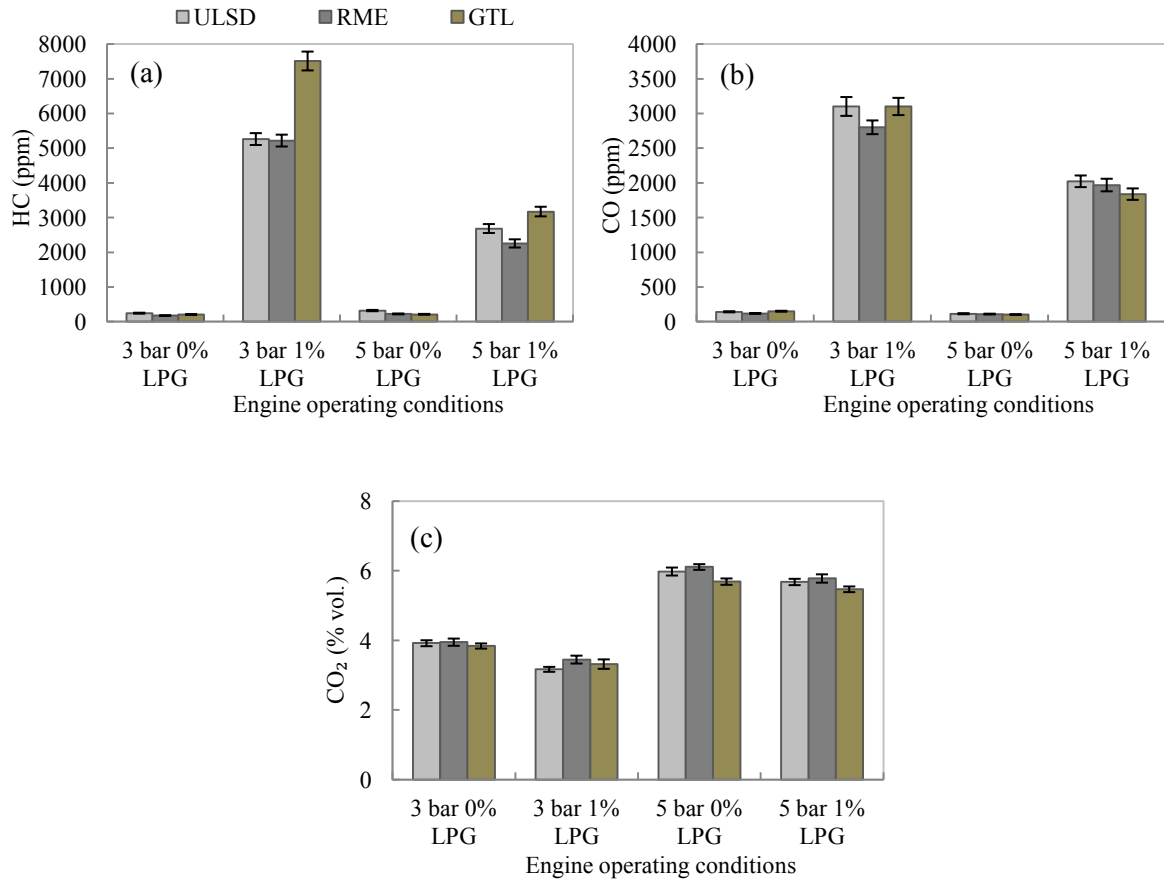
Figure 41. Emission at different liquid fuels for Diesel-LPG combustion. (a) HC, (b) CO, (c) CO_2.

The advantage of LPG addition in reducing soot concentration was not only obtained in ULSD but also in RME and GTL at all engine operating conditions. This was achieved mainly due to the reduction in number of liquid fuel rich regions. High LPG concentration in the combustion chamber resulted in less rich regions (less fuel droplets) leading to soot reduction.

At low engine load and 0% EGR, NO_X emissions also decreased when LPG was inducted, breaking the soot-NO_X trade-off for all the liquid fuels combustion (Figure 42a). In 20% EGR, a simultaneous soot and NO_X reduction with LPG application was also obtained (Figure 42b). GTL showed better soot-NO_X trade-off lines with the application of EGR than in the case of ULSD (i.e. lower NO_X and comparable soot emissions) at each percentage of LPG

addition. The lower NO_X emissions in the case of GTL (paraffinic fuel) are the result of a slower rate of premixed combustion (see Figure 38) and lower in-cylinder temperature, a consequence of its high CN. On the other hand, the large proportion of fuel which is burned in the diffusion combustion phase enhances soot formation. However, its free-aromatic composition balances soot formation and hence produces similar soot emission to ULSD. Therefore, LPG-GTL dual fuelled engine mode is a good combination as the high CN of GTL can partially compensate the poor auto-ignition properties of LPG.

In the case of RME, the oxygen-assisted and slightly advanced combustion caused a faster combustion rate in the premixed combustion phase (Figure 38). These increased the in-cylinder pressure and temperature and consequently engine-out NO_X emissions compared with ULSD and GTL. Soot emission for RME was the lowest mainly due to the oxygen content which reduces soot formation and enhances soot oxidation (Rounce et al., 2009, Makareviciene and Janulis, 2003, Tsolakis, 2006, Lapuerta et al., 2008b, Benajes et al., 2011). Meanwhile, the effect of EGR addition on 1% LPG did not increase soot emission significantly even reduced NO_X. Based exclusively on NO_X and soot emissions (without taking into account the engine thermal efficiency, HC and CO penalties), 0% and 20% EGR for GTL and 20% EGR for RME with 1% LPG are the optimal combinations.

At high engine load and 0% EGR, a simultaneous soot and NO_X reduction was only seen with GTL dual fuelling. In the case of RME, NO_X gradually increased with LPG addition, limiting the use of LPG-diesel dual fuel combustion at high engine load without EGR. However, at 20% EGR a simultaneous reduction in soot and NO_X were obtained for GTL and RME. Comparing fuels, GTL evidenced a better EGR tolerance at each LPG concentration than RME. In the case of 1% LPG and RME, the implementation of EGR

reduced NO_X emissions without any soot penalty. Therefore for RME, it is suggested a combination of EGR and LPG addition to optimise LPG-diesel dual fuel combustion.
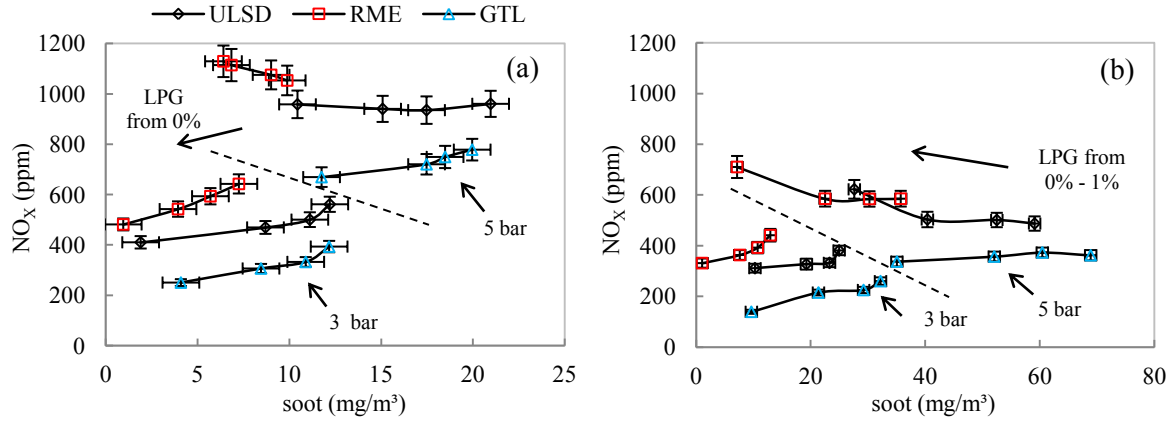
Figure 42. Soot-NO_X trade-off at different liquid fuels for Diesel-LPG combustion. (a) 0% EGR, (b) 20% EGR

As shown in Figure 43a, the addition of LPG in RME and GTL decreased the SOM level, lower than that of baseline condition, although HC emission was very high (Figure 43b). The reduction in SOM with 1% LPG addition occurred both at low and high engine load conditions. In the case of RME, SOM level was 26.4% and 27.7% lower than that of ULSD for low and high engine load respectively. In addition, a decrease of 17% (low load) and 23% (high load) was obtained in the case of GTL. As in the case of ULSD, the decrease in soot which leading to reduction in soot surface area and the lower dew point of the emitted unburned hydrocarbons are the reasons for the emission reduction.
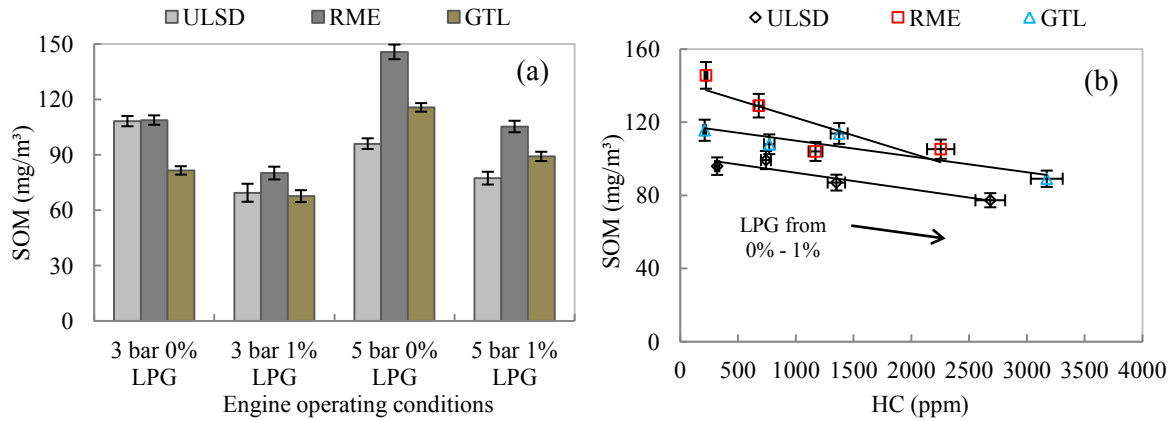
Figure 43. SOM emission and HC-SOM correlation at different liquid fuels for Diesel-LPG combustion.

RME produced higher SOM emissions than in the case of ULSD with and without LPG addition (Figure 43a). At high engine load, the SOM of RME was 26.6% and 34.1% higher than that of ULSD with LPG and without LPG respectively. This trend can be justified by the lower volatility of the hydrocarbons emitted using RME (Lapuerta et al., 2008a). In addition, the SOM emission also could be affected by fuel viscosity and density where they are relatively high in the case of RME. This led to slower evaporation rate and bigger fuel size droplets which could raise the SOM level (Saanum et al., 2008). The low soot emission (Figure 42) but high SOM for RME resulted in higher SOF compared with ULSD and GTL (Figure 44). A significant difference occurred at high engine load without LPG addition which SOF of RME was 12.4% and 9% higher compared to those of ULSD and GTL respectively. Generally, SOM emission with GTL is higher than that of ULSD specifically at high engine load. This is due to the higher T90 (distillation temperature at 90ºC) of GTL and a lower in-cylinder pressure and temperature compared with ULSD (see Figure 38) (Hori and Narusawa, 1998). On the other hand, the absence of aromatic compounds in GTL reduces soot formation, resulting in a higher SOF compared with ULSD. At high load, the SOF of GTL was 3.7% and 2.7% higher compared to that of ULSD both for 0% and 1% LPG addition

respectively. As in the case of ULSD, SOF increased for RME and GTL at low engine load compared with high engine load, as it was previously explained.
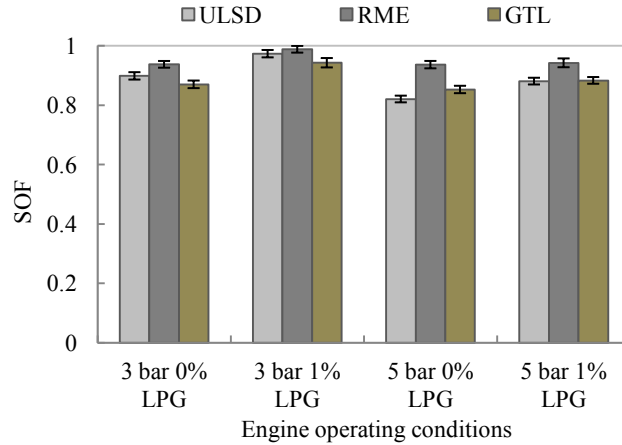
Figure 44. SOF emission at different liquid fuels for Diesel-LPG combustion.

5.4   Effect of Advanced Injection Timing

This section specifically discusses the effect of the advanced fuel injection timing which is applied to GTL. It has been explained in the previous section that dual fuel system on GTL gave longer delay in SOC specifically at low load compared to those of ULSD and RME. Therefore, the fuel injection was advanced as an effort to minimise the adverse effects caused by retarded SOC. The engine has the original injection timing of 22 CAD (as set by manufacturer) and for the experiment the injection was advanced by 2 CAD.

Figure 45 depicts the in-cylinder pressure and rate of heat release of LPG–GTL dual fuel combustion at 3 and 5 bar IMEP with advanced injection timing. At 3 bar, advancing the fuel injection timing did not show a significant impact on SOC because it still occurred later. At low load, the in-cylinder environment could not trigger the initiation of combustion effectively as the self ignition temperature of charge mixture cannot be reached even though GTL relatively has high CN. However, the premixed combustion phase is pronounced as a

result from more available time for charge mixing leading to high in-cylinder pressure. At high engine load without LPG addition, due to high temperature the SOC was clearly advanced about 2 CAD. In addition, the premixed combustion phase tended to be similar although it was slightly lower compared to that of the normal injection timing as the temperature at the time fuel injected was low. However, in the case of LPG addition advancing the injection of pilot fuel cannot trigger earlier ignition. It has been shown that advanced pilot fuel injection would lead to pronounce the pressure rise rate. It is associated to the changes in charge mixture temperature and chemical reaction with related to pre-ignition energy release (Selim, 2004, Selim, 2005). In addition, the longer ignition delay resulted in high premixed combustion leading to high in-cylinder pressure and hence high temperature. When the end of combustion is considered, the combustion finished earlier in the case of advanced injection timing. In addition, high premixed and diffusion combustion phase indicates that more in-cylinder charge was combusted and hence shifted the combustion process near TDC.
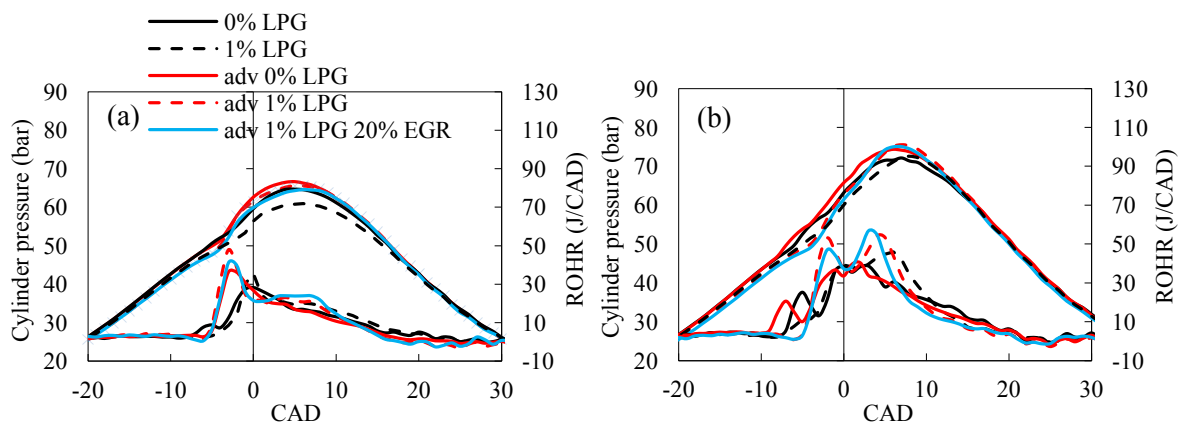
Figure 45. In-cylinder pressure and ROHR with advanced injection timing for GTL-LPG combustion. (a) 3 bar, (b) 5 bar.

Figure 46 depicts the COV for normal and advanced injection timing. A high COV is avoided as it leads to driveability problems. High diluted operation, engine load, lean mixture

and imperfect mixing of cylinder charge are some of the reasons for COV variability (Ozdor et al., 1994). In the case of advanced injection timing, the value of COV tended to increase compared to that of standard one. It was recorded that there was an increase in COV of about 17% and 12.8% for 0% and 1% LPG addition respectively at low load when the advanced injection timing was applied. Although the temperature was relatively high in the cylinder which can promote better combustion, it shows that the change in the standard injection timing as recommended by the manufacturer (22 CAD BTDC) can impact the cyclic variability. The increase in pressure rise rate which is associated to the increased combustion noise might impact to the COV.
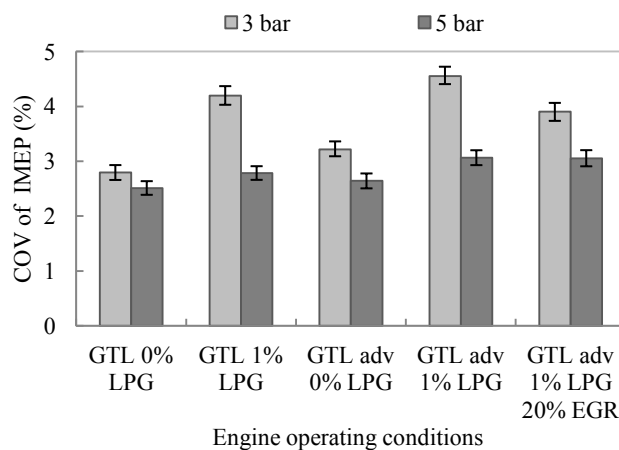
Figure 46. COV of IMEP with advanced injection timing for GTL-LPG combustion.

The comparison of brake thermal efficiency of LPG–GTL dual fuel for standard and advanced injection timing is shown in Figure 47. Under the advanced injection timing, the thermal efficiency was improved both with and without LPG addition. An increase of 3.6% and 4% at low load and 3.3% and 0.1% at high load was obtained with and without LPG addition respectively. High in-cylinder pressure due to advanced injection timing promoted better combustion and fuel consumption. In addition, low viscosity of GTL gave advantage in better fuel atomisation and vaporisation and hence improving the charge mixing led to more

complete combustion. High total energy released which is characterised by high premixed and diffusion phase (Figure 45) also contributed to an efficient combustion for the fuel mixture resulting in high efficiency of fuel conversion and hence improving thermal efficiency (Papagiannakis et al., 2007).
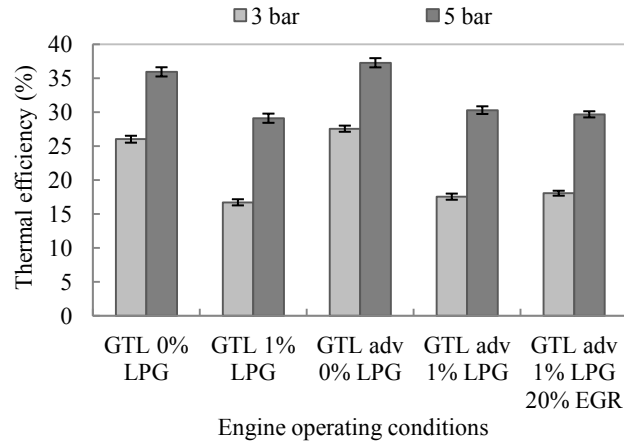
Figure 47. Thermal efficiency with advanced injection timing for GTL-LPG combustion.

HC and CO emissions are the products of the incomplete combustion of hydrocarbon fuel where their concentrations are very influenced by air-fuel ratio. In addition, CO is an intermediate product and highly produced either in the too rich or too lean mixture (Zhu et al., 2012). The results show that when injection timing was advanced, the emissions concentrations were reduced (Figure 48). As it is shown in the combustion traces figure, the in-cylinder pressure increased when fuel was injected earlier. This was a result of more pronounced premixed combustion phase as more liquid fuel was combusted before the TDC. Under higher in-cylinder temperature, the charge mixture oxidation was improved and accelerating the chemical reaction speed occurred in the combustion chamber. Low viscosity of GTL was also considered to contribute the emissions reduction. Better atomisation and vaporisation due to low GTL viscosity and supported by high temperature due to the advanced injection timing led to high burning rate. This provided a better LPG combustion

and the rest of pilot fuel producing less incomplete combustion products (Papagiannakis et al., 2007).

Under advanced injection timing, the CO_2 emission was decreased. A reduction of 4.1% and 2.1% at low load and 1.4% and 1.6% at high load was obtained with and without LPG addition respectively. An improvement in thermal efficiency has led to the low emission.
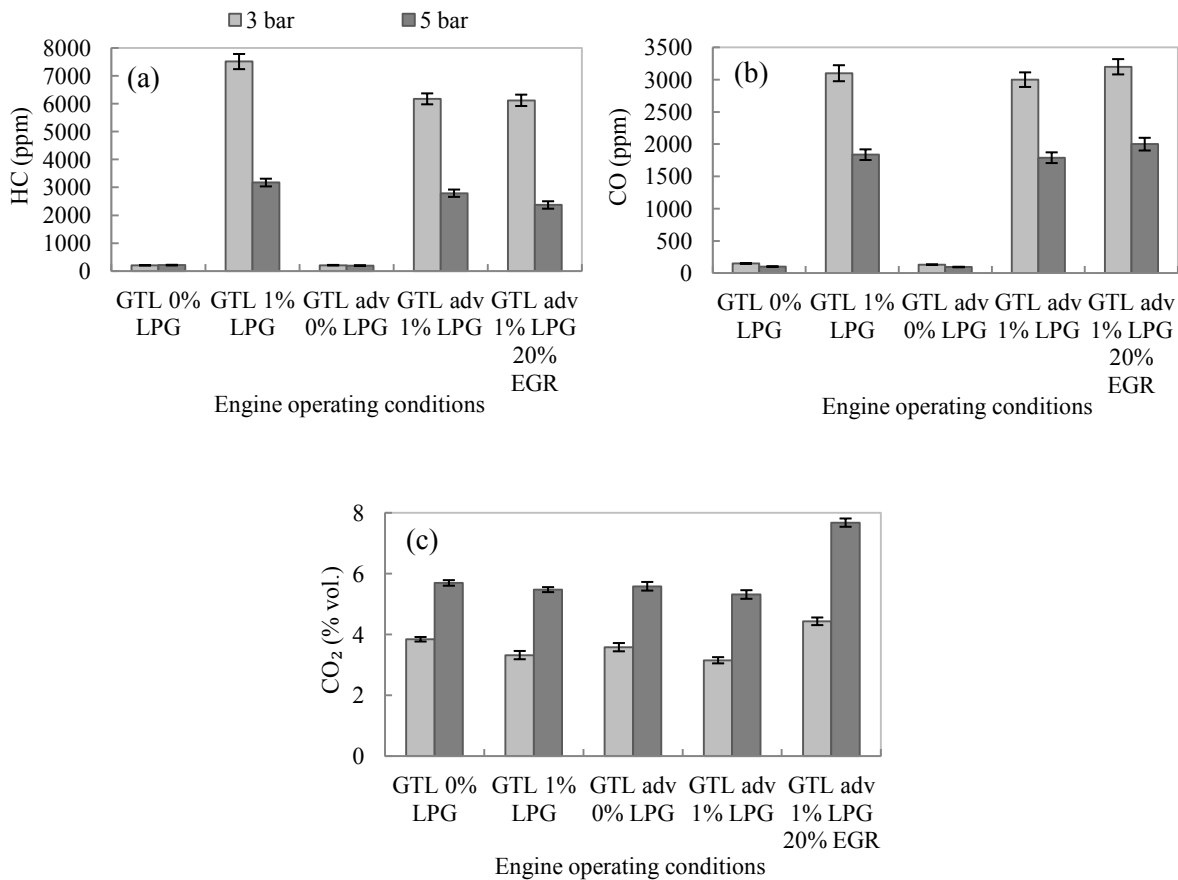
Figure 48. Emission with effect of advanced injection timing for GTL-LPG combustion. (a). HC, (b) CO, (c) CO_2.

NO_X emissions were increased with the advanced injection timing due to the increase in in-cylinder temperature as it is shown in Figure 45. Therefore, this becomes the main factor for the NO_X formation in dual fuel with advance injection timing. Apart from high combustion temperature, the increase in NO_X might also be caused by an increased in

residence time of charge mixture in high temperature which can be observed in wider (in CAD) premixed combustion phase.

Soot and other materials either liquid or solid phase are the constituents of particulates, the undesirable combustion product (Stanmore et al., 2001). The formation of soot is initiated from unburned hydrocarbon fuel which is located in the fuel-rich region at high temperature then nucleates from gaseous phase to solid phase. It contains more carbon atoms and less hydrogen atoms (Tree and Svensson, 2007). The concentration of soot decreased in the case of advanced injection timing for both with and without LPG addition even though the difference is not too much (Figure 49b). The improved combustion process due to the alteration of injection timing contributes to the soot oxidation. The soot oxidation is affected by the OH and O_2 compounds involved in the combustion process. However, in dual fuel combustion the availability of O_2 is reduced. Therefore, in this case OH is the most likely to the significant factor for the soot reduction as OH is produced at high temperature.
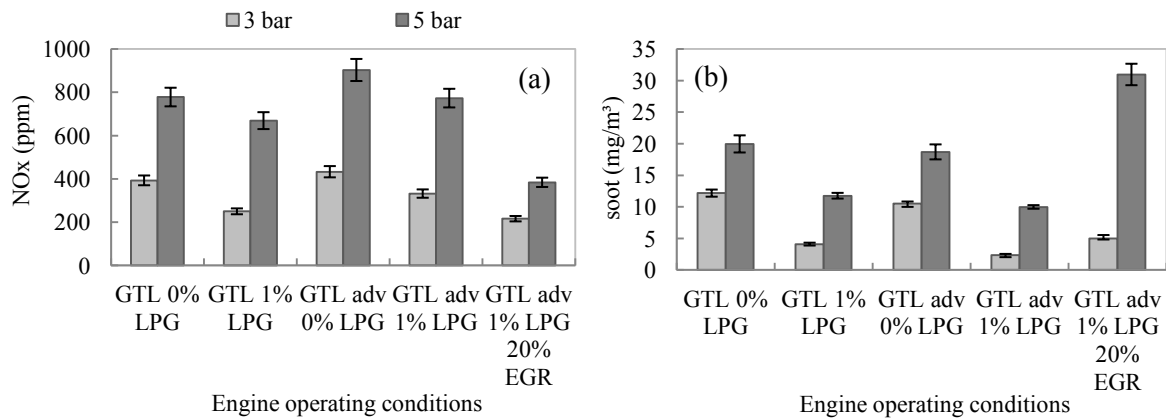
Figure 49. NO_X and soot emission with effect of advanced injection timing for GTL-LPG combustion

The advanced injection timing caused a decrease in SOM as shown in Figure 50a. The pyrolysis of SOM was attributed by the high in-cylinder temperature which tended to increase the in-cylinder wall temperature as well. Warmer in-cylinder wall might effectively reduce the

concentration of unburned fuel and lubricating oil, the sources of SOM. In addition, it is suggested that the concentration of SOM is mainly originated from liquid fuel rather than gaseous fuel. Therefore, a limited liquid fuel availability in dual fuel operation and supported by high premixed combustion phase resulted in a decrease in SOM. SOF for advanced injection timing was comparable to the normal injection timing (Figure 50b). Comparable values of SOM and soot between standard and advanced injection conditions result in a small difference in SOF.
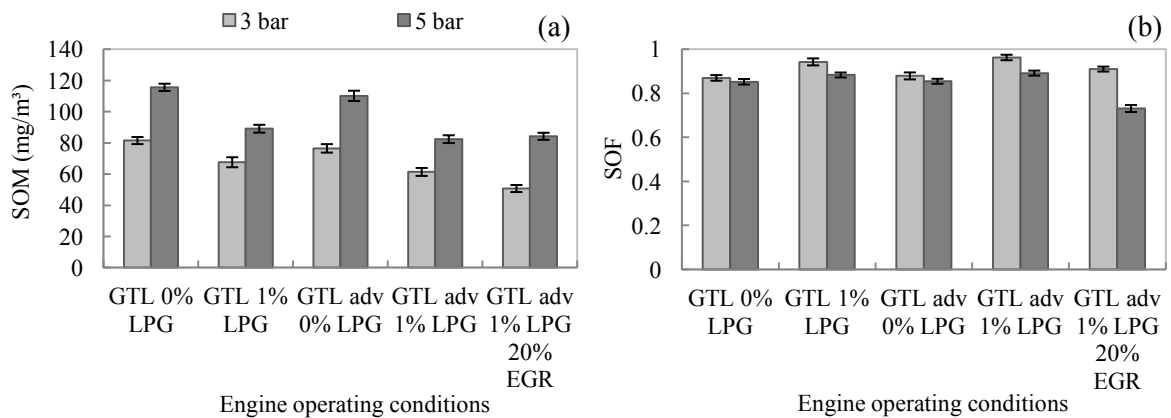
Figure 50. SOM and SOF emissions with effect of advanced injection timing for GTL-LPG combustion.

5.5   Summary

The combustion of inducted LPG to diesel combustion significantly increases the gaseous HC and CO emissions as a result of its low CN, replacement of the oxygen concentration, and possibly due to problems associated with mixing air and gaseous fuel. Increased LPG concentration led to a simultaneous reduction in soot and NO_X and also CO_2 emissions.

Different types of diesel fuels used have shown to have no influence on gaseous HC and CO emissions trends but the substitution of the diesel fuel with RME or GTL resulted in

significantly reduced NO_X–Soot emissions trade-off line to lower values, with the reduction following the order of GTL > RME > ULSD.

The results of the LPG–RME dual fuelling have shown that EGR would be beneficial at high engine load conditions while in the LPG–GTL dual fuelling optimisation of the GTL fuel injection characteristics can enhance further low engine load to keep the engine emission benefits.

The readjustment of the fuel injection setting by advanced injection timing in the dual fuel system has shown as one of the means for improvements in thermal efficiency and engine-out emissions.

Overall, the study confirms that diesel fuel properties need to be optimised for the different LPG additions in order to obtain the improved engine out emissions of LPG-diesel dual fuelling.

C H A P T E R 6

UNDERSTANDING THE INFLUENCE OF THE REFORMATE AND THE PROPERTIES OF DIESEL FUEL IN LPG-DIESEL DUAL FUELLED COMBUSTION

6.1 Introduction

This chapter is an extended study from the previous chapter on LPG-dual fuelled combustion. It has been proven that soot and NO_X (at low engine load) were reduced but HC, CO and engine thermal efficiency were deteriorated. It was observed also that there was an ignition delay and potentially can produce a high proportion of unburned mixture in the exhaust. Therefore, an approach to improve the above mentioned problems is required. The use of hydrogen addition can be one of the solutions. Apart from CO, the hydrogen used in the system can be produced from reformed exhaust gas recirculation (REGR) technique. Hydrogen and carbon monoxide concentrations were selected, assuming complete fuel reforming of half of the different flow rates of propane to the syngas by partial oxidation and then followed by steam reforming reaction. The product then is called reformate (Ref.: H_2 and CO). The other half of the propane is also fed to the engine with the reformate (LPG+Ref.). The combination of the reactions called auto-thermal reforming can be expressed as follows. The exothermic reaction of partial oxidation that produces heat can be used to drive the steam reforming that requires heat. Therefore, the reforming process can be carried out on a small and compact reactor.

$$ \text{—} \qquad \text{—} \qquad \text{—} \qquad\qquad\qquad (6.1) $$

The hydrogen content can be boosted by changing the thermodynamic conditions to promote the exothermic water-gas shift reaction (WGSR) which converts the entire CO to H_2.

$$(6.2)$$

Bottled gaseous fuels (i.e. LPG, H_2, and CO) were used to simulate the LPG-reformed gas. The experiment was performed at a constant engine speed (1500 rpm) and engine loads of 3 and 5 bar IMEP. The concentration of LPG fed into the combustion chamber through the intake manifold was 0.2, 0.5 and 1% of the total volumetric intake charge air flow rate. 60 tests were carried out during the experiment and the volumetric flow rate of the hydrogen and reformate added are shown in the Appendix B. At this experiment, the tests on the baseline fuel (USLD) were repeated (tests performed at chapter 5) and were compared to RME and GTL. The engine operating conditions used are described in Table 7.

Table 7.   Engine operating conditions (LPG-diesel dual fuelling with reformed LPG)

Speed (rpm)	IMEP (bar)	Fuel	LPG (%)	Reformed LPG
1500	3	ULSD, RME, GTL	0	-
			0.2	hydrogen and reformate
			0.5	hydrogen and reformate
			1	hydrogen and reformate
	5	ULSD, RME, GTL	0	-
			0.2	hydrogen and reformate
			0.5	hydrogen and reformate
			1	hydrogen and reformate

In order to obtain a better understanding of HC emission compounds emitted from LPG-diesel dual fuel combustion, HC emissions have been speciated using an FTIR. This measurement can give valuable insight into the organic compounds in the HC emission. Figure 51 depicts the schematic diagram of the experimental setup.
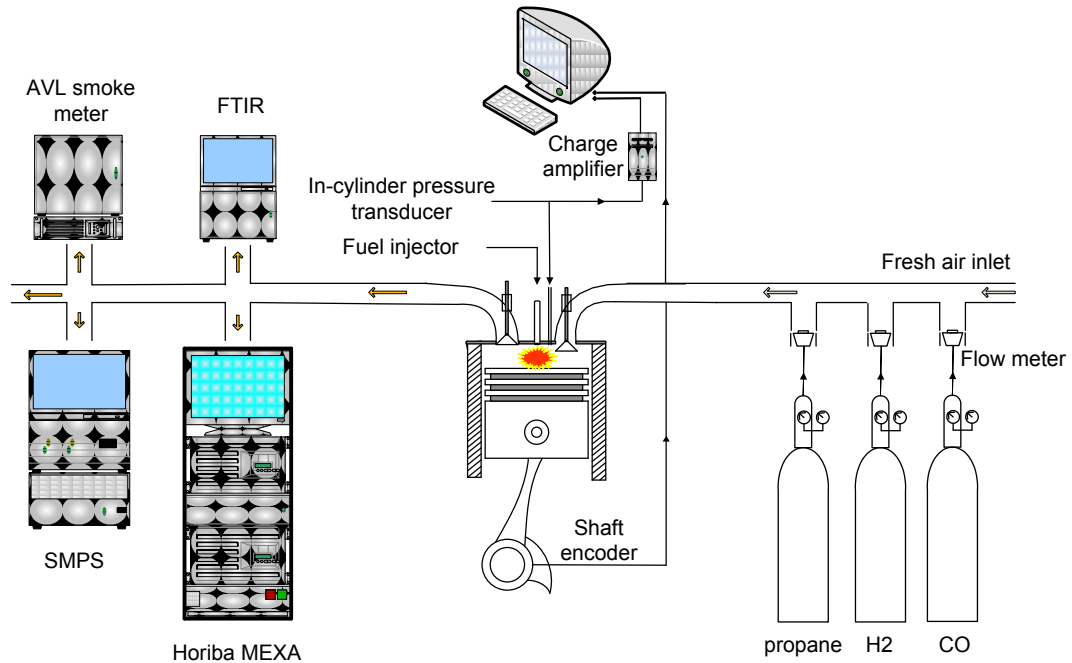
Figure 51.   Schematic diagram of experimental setup for LPG-diesel combustion.

6.2   Effect of Reformate and Hydrogen

Combustion and engine performance characteristics.

The combustion studies with 1% LPG only are shown as the effects of both reformate and H_2 are more significant than in the rest of the ratios while the combustion traces of 0.2% and 0.5% LPG are shown in Appendix C. At low load the LPG addition retarded the start of the combustion (SOC) with respect to the baseline diesel only combustion, and the combustion duration was significantly reduced (Figure 52). At high engine load the relatively high in-cylinder temperature conditions facilitated the injected diesel fuel vaporisation and atomisation, creating good ignition centre area for the improvement in combustion and fuel oxidation (Karim, 2003). In addition, the reformate and H_2 addition reduced the ignition delay, promoted faster combustion of the mixture and increased the in-cylinder pressure.

Combustion duration results were obtained from 10-90% mass fraction burnt and is depicted in Figure 53. The reduction in the amount of the injected liquid fuel when gaseous

fuels were inducted (Figure 54) resulted in shorter liquid fuel injection duration and hence shorter combustion duration (e.g. reduced diffusion combustion phase). Furthermore, it became slightly shorter with the H_2 presence, although there was less liquid fuel replacement compared to LPG (Figure 54). High flame speed of H_2 contributed to faster combustion leading to more gaseous fuels-air mixture ignited spontaneously (Lata and Misra, 2010, Verhelst and Wallner, 2009).
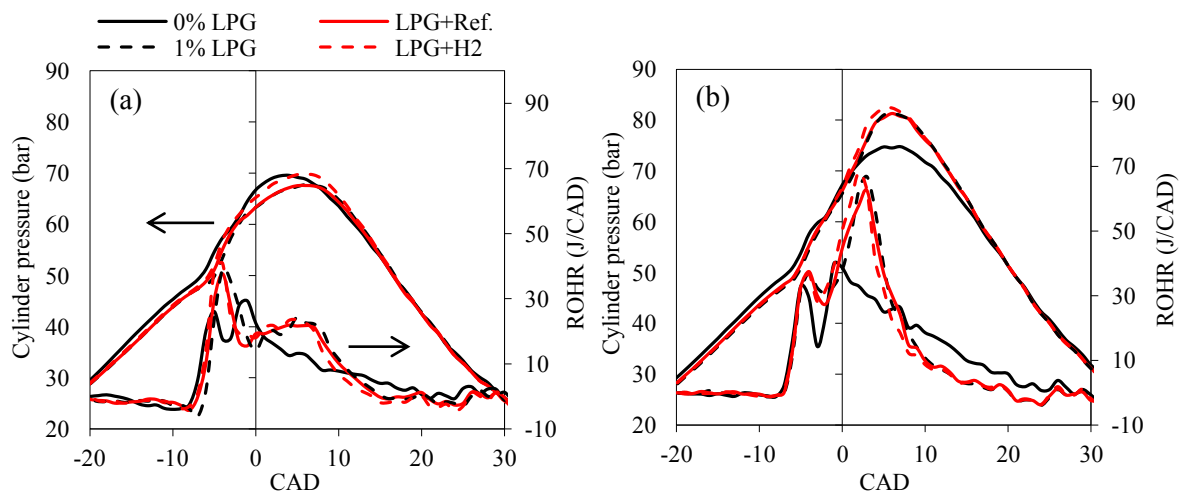
Figure 52. In-cylinder pressure and ROHR for ULSD-LPG combustion with hydrogen and reformate addition. (a) 3 bar, (b) 5 bar.
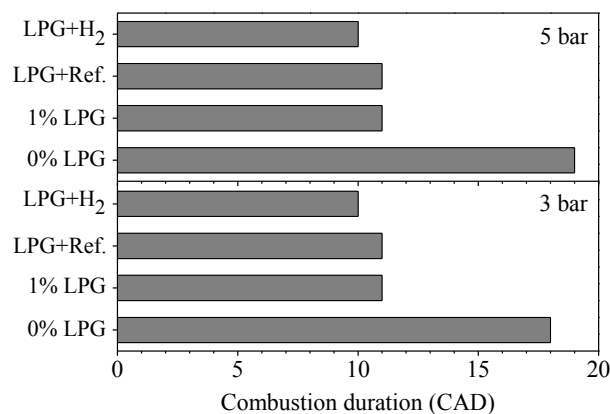
Figure 53. Combustion duration according to 10-90% mass fraction burnt for ULSD-LPG combustion with hydrogen and reformate addition.

At low load, up to 60% liquid fuel replacement in mass basis (Figure 54) was reached at the maximum fraction of LPG addition with acceptable cycle-to-cycle combustion variability (i.e. COV of IMEP <5%). The lower liquid fuel replacement obtained in the case of reformate and H_2 additions than in the case of LPG was due to the low H_2 and CO volume energy densities.
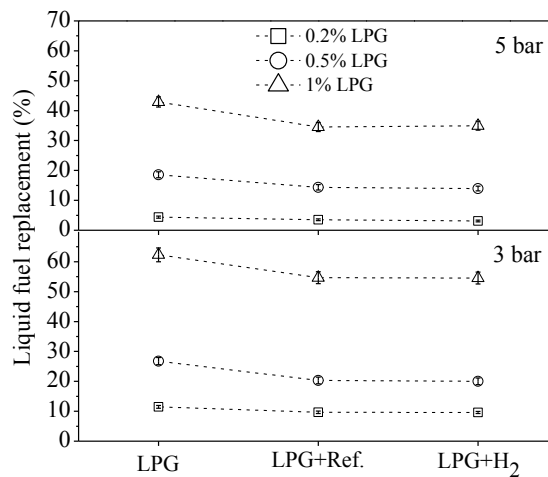
Figure 54. Liquid fuel replacement (%Wt) for ULSD-LPG combustion with hydrogen and reformate addition.

The brake thermal efficiency of LPG-diesel dual fuel combustion was improved for the two different engine loads with utilising the LPG-reformed gas (Figure 55). At 1% LPG addition, an increase of 11.5% and 15% at low and high load conditions respectively was obtained when reformate was added into the combustion chamber. In addition, the improvement even further increased when the hydrogen was added which an increase of 12.2% and 16.7% at low and high load respectively was obtained. The low cetane number (CN) and narrow flammability limit of propane (LPG) might cause unstable combustion of the premixed air-fuel mixture that was ignited by the pilot diesel fuel leading to incomplete combustion of LPG, thus decreasing engine thermal efficiency. However, with the presence of the LPG-reformed gas the mixture was easier to ignite, and intensified thermal diffusion

extending combustion zone. It also contributed in consuming most of the in-cylinder charge because of increased flame stretch area and laminar flame thickness and hence improving thermal efficiency (Szwaja and Grab-Rogalinski, 2009, Tang et al., 2008). Shorter combustion duration also resulted in reduced time available for heat transfer to the cylinder wall thus could reduce heat loss which increased the thermal efficiency (Lata and Misra, 2010). These improvements of the combustion reaction intensity mainly in the expansion stroke, allowed more of the chemical energy of the combustible mixture to be converted to useful work. Augmenting the inducted H_2 fraction, in the case of LPG+H_2, slightly further enhanced the thermal efficiency.

Considering that the quantity of LPG in the intake for 0.5% LPG, 1% LPG+Ref. and 1% LPG+H_2 is the same, it can be stated that the use of LPG-reformed gas resulted in higher liquid fuel replacement and thermal efficiency with the same concentration of LPG (Figure 54 and Figure 55). Therefore, reformate and H_2 can compensate for the thermal efficiency penalty seen with LPG.
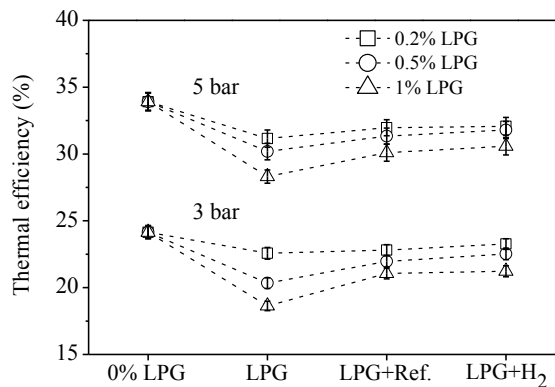
Figure 55. Thermal efficiency for ULSD-LPG combustion with hydrogen and reformate addition

Regulated engine-out gaseous emissions.

The emissions of total HC and CO with LPG increased compared with the baseline condition for all tested engine conditions (Figure 56). This could be resulted from non-homogeneity in the in-cylinder mixture, the delay in the combustion, low temperature combustion and insufficient oxygen which can lead to unburned propane and other gaseous emissions formation (Goto et al., 1999, Jian et al., 2001).

However, the application of reformate and H_2 as additional fuels to LPG-diesel improved these emissions. Under reformate addition, HC and CO emissions respectively were reduced up to 32.6% and 48% at high load while the emissions were reduced of about 34.2% and 44.7% for HC and CO respectively at low load. This maximum improvement was achieved at 1% LPG condition. With the H_2 addition the H/C ratio of the mixture increased and also enhanced the homogeneity of the mixture due to the high mass diffusivity of H_2 leading to reduced HC and CO emissions (Verhelst and Wallner, 2009). The improved combustion characteristics seen with the H_2 presence as a result of it created in-cylinder conditions (i.e. higher temperature) that enhanced the LPG combustion efficiency (Szwaja and Grab-Rogalinski, 2009). However, the increase of CO emissions seen in the case of reformate addition is due to the un-combusted CO part of the added reformate.
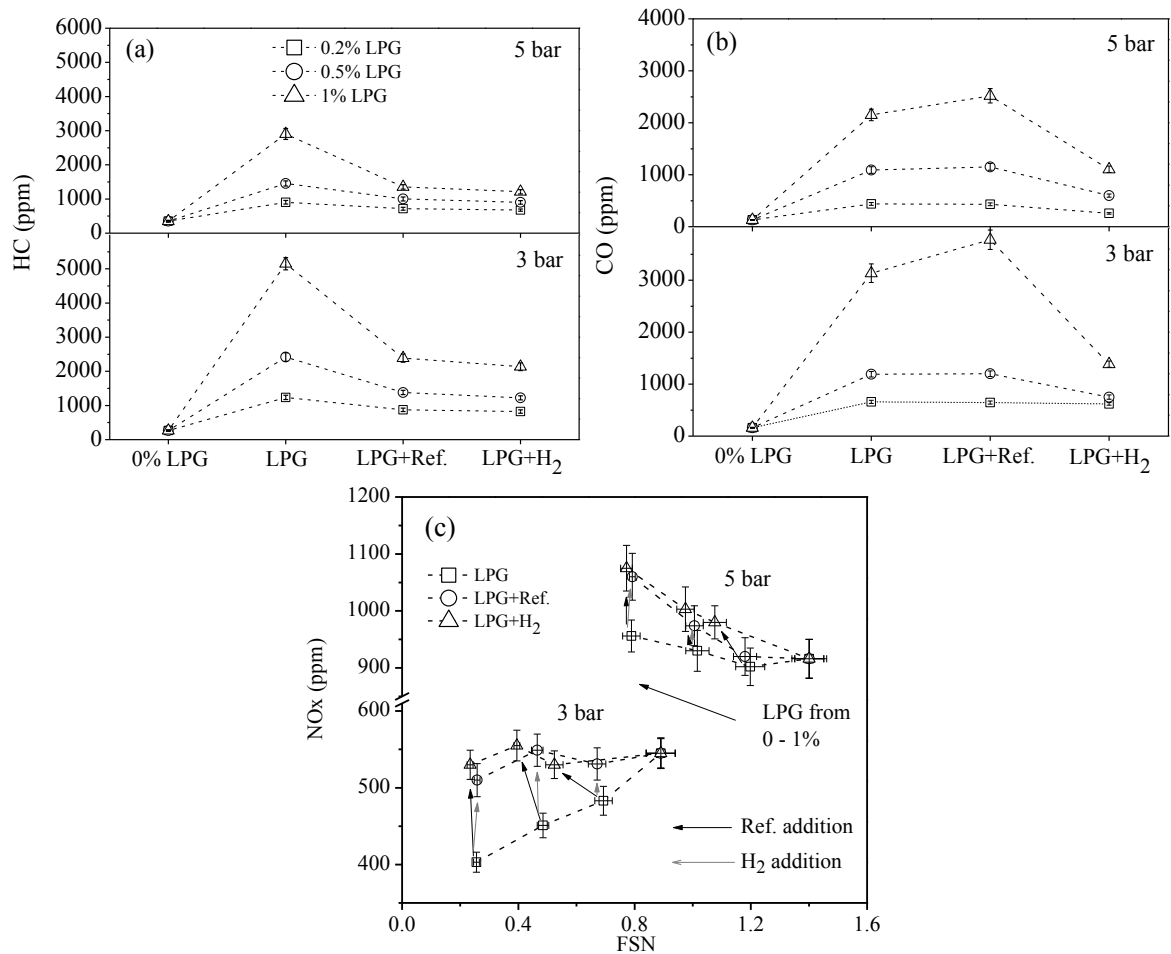
Figure 56. Regulated gaseous emissions and FSN for ULSD-LPG combustion with hydrogen and reformate addition. (a) HC, (b) CO, (c) FSN-NO_X trade-off.

With the LPG-reformed gas addition the increase in the in-cylinder pressure was evident as a result of both high premixed combustion and H_2 combustion characteristics thus increasing the flame temperature and hence increasing NO_X emissions as can be seen in Figure 56c (Verhelst and Wallner, 2009). However, CO dilution could reduce the flame temperature in the entire mixture (Karim et al., 1985) thus NO_X in this case is lower compared with H_2 addition.

Unregulated engine-out hydrocarbon species.

The HC species produced during dual fuelling are derived from incomplete combustion or thermal cracking of propane and they will contain three or less carbon atoms in their molecule. Therefore, the studied species here are volatile hydrocarbons with three or less atoms of carbon and those which have extensively been studied in standard diesel operation such as olefin (ethylene, propylene), acetylene, and other short-chain paraffin (methane and ethane) (Figure 57) (Zervas, 2008, Payri et al., 2009).

The concentration of all of these HC species increased with propane addition especially at low load. At high load the rates of propane oxidation were improved and the HC species concentration in the engine exhaust was reduced. This clearly indicates that the emissions are heavily related to the in-cylinder temperature (thermal pyrolysis) (Flynn et al., 1999).

Among these species, propylene was studied because of its high tendency to generate ozone (MIR: 11.66). Also, it is one of the first and most abundant compound produced during the combustion of propane (Lindgren et al., 2011). As it is shown in Figure 57 the propylene increasing rate in LPG-diesel dual fuel combustion is higher than other hydrocarbons species with respect to the baseline condition. However, the concentration of these species was reduced with the addition of the LPG-reformed gas. Beneficial effects of the hydrogen-enriched gas addition to the emission improvement was more obvious at low load which a reduction of 33% and 36.1% was achieved due to the reformate and hydrogen addition respectively. The presence of H_2 in the combustion chamber is associated with the improved oxidation rates of propane due to higher in-cylinder temperatures (e.g. increases cylinder pressure) compared with LPG addition only. However, the reduction of propylene, acetylene, ethylene, ethane, and methane species was not proportional to the reduction seen with the total HC. This could be attributed to the fact that with reformate and H_2 propane was involved

in the combustion process leading to the increase of smaller HC species such as propylene. Formaldehyde (CH_2O) (MIR: 9.46) as a member of carbonyl compound strongly pollutes the atmosphere as it acts as a source of free radical for tropospheric photochemistry. It may also affect the human health through eyes and lung irritation (Carlier et al., 1986). Formaldehyde concentration measured in the engine exhaust is higher under the LPG-diesel combustion compared to the baseline diesel combustion only (Figure 57b). The addition of reformate and H_2 assisted the straight-chain aliphatic hydrocarbon oxidation, like propane, and reduced formaldehyde, as an intermediate product of hydrocarbon fuel combustion, with respect to LPG-diesel combustion only. Under hydrogen addition the emission reduced by 38.3% and 36.6% at low and high load respectively. In addition, under reformate addition the emission reduced up to 32.3% and 29.6% at low and high load respectively.
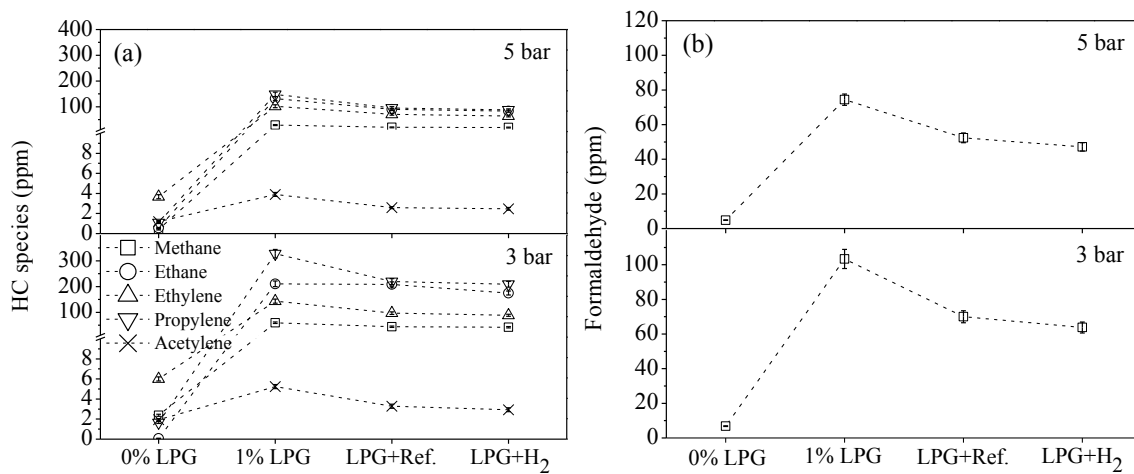
Figure 57. Hydrocarbons species and formaldehyde emissions for ULSD-LPG combustion with hydrogen and reformate addition.

Smoke and particulate emissions.

The addition of LPG clearly reduced smoke emissions (Figure 56c). When half of the LPG is firstly reformed (reformate composed of H_2 and CO) the smoke level was relatively similar to only LPG (indicated with full black arrow), while soot was clearly reduced by

complete hydrogen production via the WGSR. This net effect of reformate and hydrogen is the result of different factors which have been isolated.

- *Dilution effect (overall lambda)*. The induction of gaseous fuels replaced liquid fuel and oxygen in the intake and modified the mixture oxygen stoichiometric requirements. These effects resulted in a different overall lambda. In all the conditions the overall lambda for reformate and hydrogen additions are higher than in the case of LPG leading to lower soot emissions.

- *Local rich regions effect*. It is suggested that the liquid fuel replacement influences not only the overall lambda but also the local lambda. Gaseous fuels replaced part of the liquid fuel reducing the formation of locally liquid fuel rich regions in the combustion chamber, the region where for the most part of soot is produced. The replacement of liquid fuel with reformate and hydrogen was lower than in the case of LPG (Figure 54). Therefore, higher soot levels are expected in the case of hydrogen and reformate compared to LPG due to this effect.

- Chemical effects.

  Inhibition of soot formation. According to Frenklach and Wang (Frenklach and Wang, 1991) it is suggested that soot formation increases with the increased H/H_2 ratio. Therefore, H_2 addition will decrease this ratio and as a result will decrease soot formation. In addition, it has been suggested that after certain hydrogen concentrations, further hydrogen addition does not result in further soot reductions when the H/H_2 reaches the saturation value (Schefer, 2001, Pandey et al., 2007). In contrast, the effect of CO is opposite to the hydrogen. CO is oxidised by OH forming atomic hydrogen thorough the reaction $OH + CO = CO_2 + H$. This results in an increase of the atomic hydrogen and as a consequence in an enhancement of soot growth.

Enhancement of soot oxidation. Hydrogen addition promotes the formation of OH, through the reactions $H_2 + O = OH + H$ and $O_2 + H = OH + O$ (Saxena and Williams, 2006). As the OH radical plays a significant role in the soot precursors and soot oxidation processing, this could cause a decrease in the number of soot nuclei and the particle surface area (Pandey et al., 2007). However, when the hydrogen concentration is higher than the saturation level, there is no further OH promotion (Pandey et al., 2007). Opposite with the addition of CO the concentration of oxygen and OH radical are reduced and this could result in a reduction in the soot precursors and soot oxidation rate.

- *Thermal effect*. The OH production heavily depends on in-cylinder temperature (Dec and Coy, 1996). As it was shown in the combustion plots, hydrogen increases in-cylinder temperature and as a result, this could lead to a higher OH concentration resulting in an enhancement in soot oxidation.

Therefore, it can be concluded that the soot benefit of the hydrogen contained in the reformate was slowed down by the presence of CO. Coherently, when CO was substituted by hydrogen a clear reduction in smoke was obtained as an overall result of the different factors previously discussed. Considering different hydrogen additions, the soot benefits obtained with hydrogen are lower in 1% LPG addition with respect to 0.2 and 0.5% approaching to the hydrogen saturation value limit.

Particulate size distribution results are focused on 0.2 and 1% LPG addition as 0.5% LPG gave an intermediate tendency in both engine loads (Figure 58). The addition of LPG and the reformate made the concentration for every diameter decreased gradually with the increase in the gaseous fuels concentration. Further hydrogen addition reduces more the particle number concentration for each diameter. This trend is coincident to the obtained in

smoke emissions and the reasons previously commented in the soot section can be applied here. As a consequence, most of the carbon of the parent fuel (i.e. ULSD and LPG) is converted to gaseous products (i.e. HC, CO, CO_2) and there is no further conversion to soot.
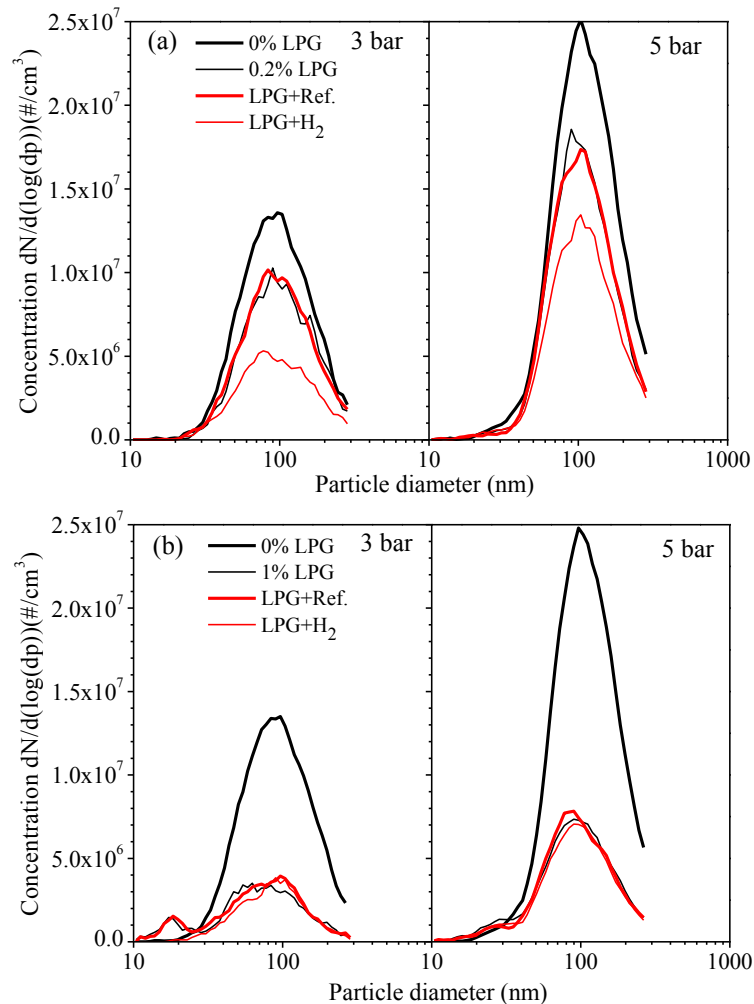
Figure 58. Particulate size distributions for ULSD-LPG combustion with hydrogen and reformate addition. (a) 0.2% LPG, (b) 1% LPG.

A small nucleation mode was obtained in the case of 1% LPG at both low and high engine loads as depicted in Figure 58b. These nucleation particles consist of droplets of hydrocarbons which underwent nucleation rather than adsorption or condensation onto soot particle surface. The nucleation of gaseous hydrocarbons depends on gaseous hydrocarbon concentration and volatility, soot concentration, and exhaust temperature (Kittelson et al.,

1999). Nucleation appears when the engine output hydrocarbon emissions are higher while soot concentration is limited (low load and high LPG addition) (Figure 56a and c). As a result, some of the gaseous HC cannot be adsorbed or condensed onto the soot particles (reduced soot surface availability) and hence they self nucleate forming new particles of small size.

6.3 Effect of Liquid Fuels

Combustion and engine performance characteristics.

In LPG-RME dual fuelling, the SOC was slightly advanced when H_2 was introduced but was not affected in the case of LPG-GTL fuelling (Figure 59). The variations on the SOC are influenced by some factors such as the quantity and quality of pilot fuel and pre-ignition reaction activity. In the case of RME fuelling, apart from oxygen availability the SOC was also affected by the high pilot fuel quantity available in the combustion chamber. It was due to the relatively low calorific value of RME thus more in-cylinder injected fuel mass was needed per cycle to reach the required engine load. Higher pilot fuel quantity could lead to larger pilot fuel flame area and reaction zones which provided better hydrogen-containing charge mixture combustion and increased burned fraction. Therefore, they could contribute to the earlier SOC. For GTL fuelling case, the GTL's retarded injection and delayed SOC under dual fuelling (i.e. LPG-GTL) mode lowered the in-cylinder temperature. Although GTL has relatively high CN, its lower density and bulk modulus significantly influenced the start of injection and the SOC in dual fuelling. These combustion characteristics and low in-cylinder temperature condition affected the pre-ignition reaction activity of the hydrogen-contained mixture which affected the engine-out emissions (explained later).

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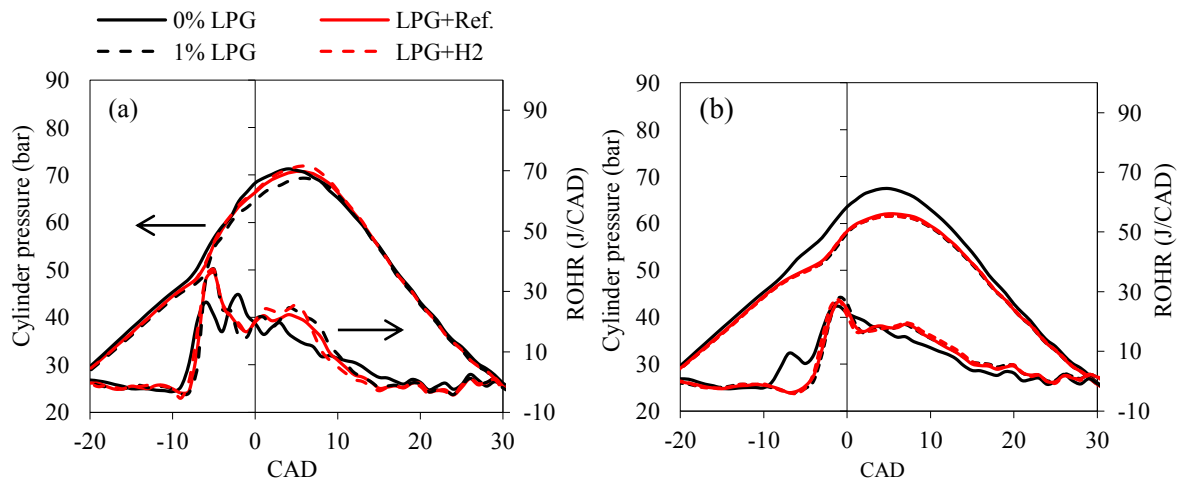
Figure 59. In-cylinder pressure and ROHR for different liquid fuels with hydrogen and reformate addition. (a) RME-LPG combustion, (b) GTL-LPG combustion.

Figure 60 shows that the thermal efficiency of RME and GTL was fairly comparable to that of conventional diesel fuel in baseline condition. However, in dual fuel operation, GTL and 1% LPG and with reformate and H_2 addition exhibited the greatest decline compared to other fuels. Although the thermal efficiency increased in the case of reformate and H_2 addition (compared with LPG addition only) but the LPG-GTL dual fuelling combustion characteristics (i.e. low in-cylinder temperature) were likely to be the significant factor for the thermal efficiency deterioration. The low in-cylinder pressure because of retarded combustion initiation was an influential effect which could lead to low adiabatic flame temperature, low effective combustion, and heat loss to the cylinder wall. On the other hand, a positive effect in thermal efficiency through the combination of RME fuelling with hydrogen at high load was observed. The improved ignition ability seen in the dual fuelling with RME as a result from high in-cylinder temperature and lower stoichiometric air requirement (high oxygen content in RME), supported by faster H_2 combustion improved combustion efficiency.
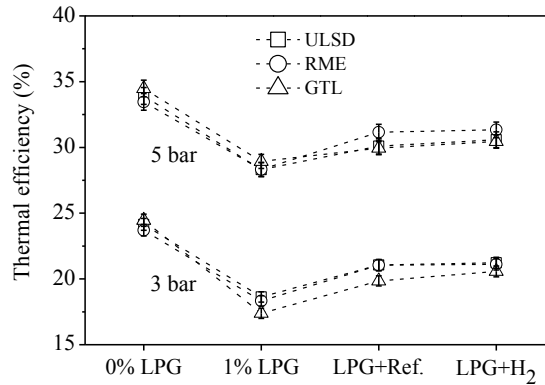
Figure 60. Thermal efficiency for different liquid fuels with hydrogen and reformate addition.

Regulated engine-out gaseous emissions.

RME exhibited the lowest total HC and CO emission over all the engine operating conditions (Figure 61). With the use of oxygenated fuel like RME, the oxygen availability in the fuel spray improved the mixture oxidation. This can compensate the reduced oxygen concentration in dual fuelling system and improved H_2 combustion. In addition, the higher density of RME also contributed in better in-cylinder charge mixing through better fuel penetration associated in a non-common rail fuel system and hence released greater energy in the premixed combustion stage, leading to reduced HC and CO emissions (Rounce et al., 2010, Sun et al., 2010). It has also been suggested that a fuel with high density has larger cone-shape spray (Yamane et al., 2001). Therefore, with these better fuel spray characteristics of RME and diffusivity of H_2 could improve mixture homogeneity, flame propagation, and lead to increased oxidation rates. The low in-cylinder pressure as a result of the late SOC seen with LPG-GTL fuelling directly impacted the HC and CO emission (Figure 59b). It has been shown that GTL has advantages in reducing the regulated emissions as a result of its physical and chemical characteristics. Its high H/C ratio and more volatile combined with H_2 addition were likely to enhance the mixture homogeneity which can result in the reduction in carbon-

contained emissions. In addition, it was thought that the emissions reduction also supported by its high ignitability due to GTL's high CN. However, low in-cylinder temperature as seen in the LPG-GTL dual fuel combustion characteristics significantly inhibited the HC and CO oxidation rates. Under low in-cylinder temperature, the charge mixture cannot be completely burned. Therefore, there was a possibility that part of H_2 was not involved in the combustion as a result of its high autoignition temperature.

NO_X emissions were higher with RME and lower with GTL fuelling. It has been suggested that in mechanical injection system, the high bulk modulus and speed of sound of biodiesel advanced the start of injection (SOI) leading to advanced combustion pronounced premixed combustion phase (Schönborn et al., 2009). As a result, an increase in the in-cylinder temperature elevated the thermal NO_X formation. Additionally, another theory concludes that the low soot produced (explained later) with RME resulted in low soot radiative heat transfer from flames hence increasing NO_X (Schönborn et al., 2009). (Boehman et al., 2004).

Meanwhile, the low bulk modulus of compressibility and high CN of GTL reduced the peak of the premixed combustion rate thus hampered the NO_X formation rate (Song et al., 2002). In addition, the relatively lower C/H ratio of GTL than those of other fuels tended to reduce the adiabatic flame temperature and thus the propensity to produce NO_X (Miyamoto et al., 1998). Under dual fuel mode, the trend of the NO_X emissions was kept similar obtaining the lowest NO_X emissions for GTL. In all cases, NO_X decreased with LPG addition but slightly increased with the reformate and H_2 addition as it was explained in the previous section. However, GTL shows better trend where the increasing rate is lower compared to other fuels and the emission levels are below to those in baseline condition even at high load.
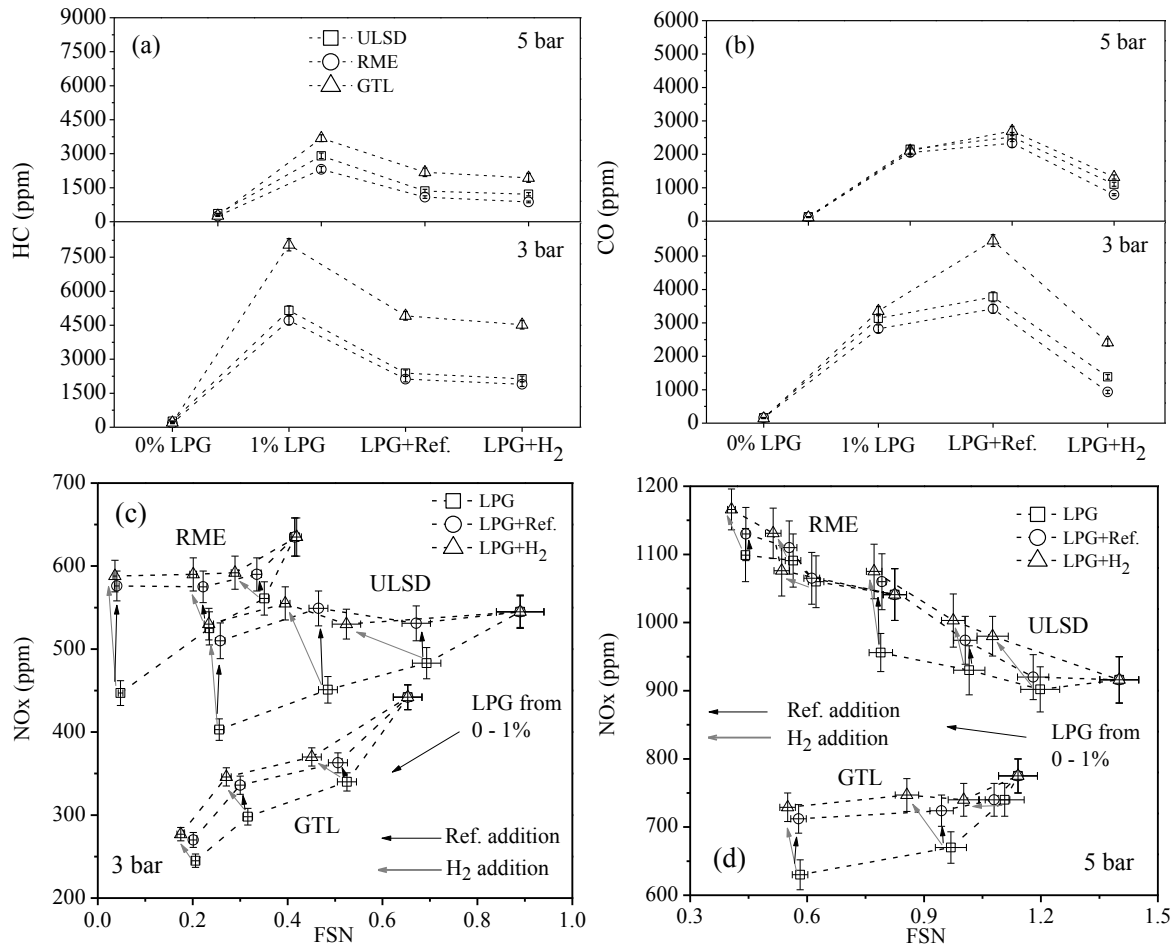
Figure 61. Regulated gaseous emissions and FSN for different liquid fuels with hydrogen and reformate addition. (a) HC, (b) CO, (c) FSN-NO$_X$ trade-off at 3 bar, (d) FSN-NO$_X$ trade-off at 5 bar.

Unregulated engine-out hydrocarbon species.

Hydrocarbon species emissions were lower for the RME and GTL combustion compared to that of ULSD at baseline condition. At low load, the emissions of methane, ethane, ethylene, propylene, and acetylene with RME reduced up to 46.6%, 100%, 19.9%, 45.7%, and 20.5%, respectively compared to that of ULSD while for GTL the emissions above reduced up to 20.2%, 6.2%, 20.2%, 25.2%, and 7.4% respectively. The reduction of the total HC and some of the species examined here including formaldehyde (Figure 62) was

mainly because of oxygen content for the RME and the high CN and H/C ratio for GTL (Efthimios, 2008).
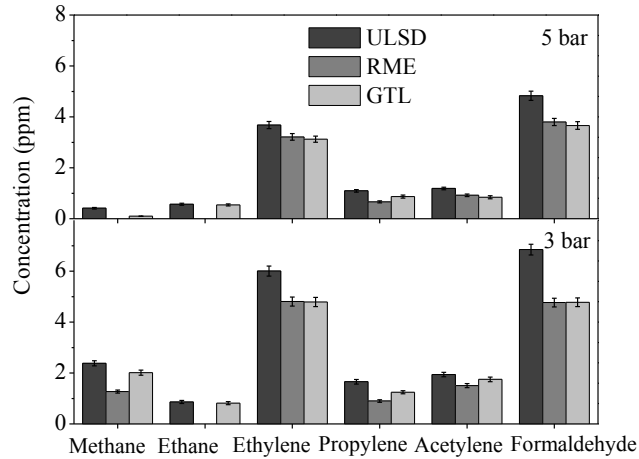
Figure 62. HC species and formaldehyde at baseline condition for different liquid fuels.

However in dual fuel operation, HC species emissions level with RME was relatively similar to that of ULSD (Figure 63). It has been shown that the oxygen content in RME and high in-cylinder temperature which is seen in the combustion characteristics were associated to the reduction in HC species in RME dual fuelling. However, its slightly high equivalence ratio (results of liquid fuel replacement are not shown) was likely to increase the emission as has been shown by Zhu et al. (Zhu et al., 2011b). Therefore, these parameters contributed to the relatively similar results in RME and ULSD. In dual fuel mode, GTL showed the highest HC species emissions. This mainly was attributed to low in-cylinder temperature results in a reduction in the fuel oxidation capability.

It is observed at baseline condition that formaldehyde level in the case of RME and GTL is lower compared to that of ULSD. It was obtained that for RME the formaldehyde emission showed a reduction of 30.4% and 21.3% for low and high load respectively. In addition, for GTL it showed up to 32.2% and 24.2% reduction at low and high load respectively. It is thought that the carboxyl group from biodiesel were removed under high

temperature, decarboxylation, reducing the propensity to form oxygenated compounds (Lapuerta et al., 2008a). The decrease of formaldehyde also can be linked to the increased H/C ratio hence we would expect a decrease of the emission with GTL fuelling (Zervas et al., 2002). As in the case of the other HC species, the formaldehyde emission tends to increase in dual fuel operation. It indicates that formaldehyde emissions not always associated to initial pilot fuel composition but from multiple sources (like unburned propane) and species in the combustion chamber (Zervas et al., 2002). However, the LPG-reformed gas addition reduced the studied hydrocarbon species. The hydrogen combustion facilitated the thermal cracking process of propane as a saturated hydrocarbon by removing the hydrogen and carbon atoms from molecular structure became short-chain hydrocarbon molecules.
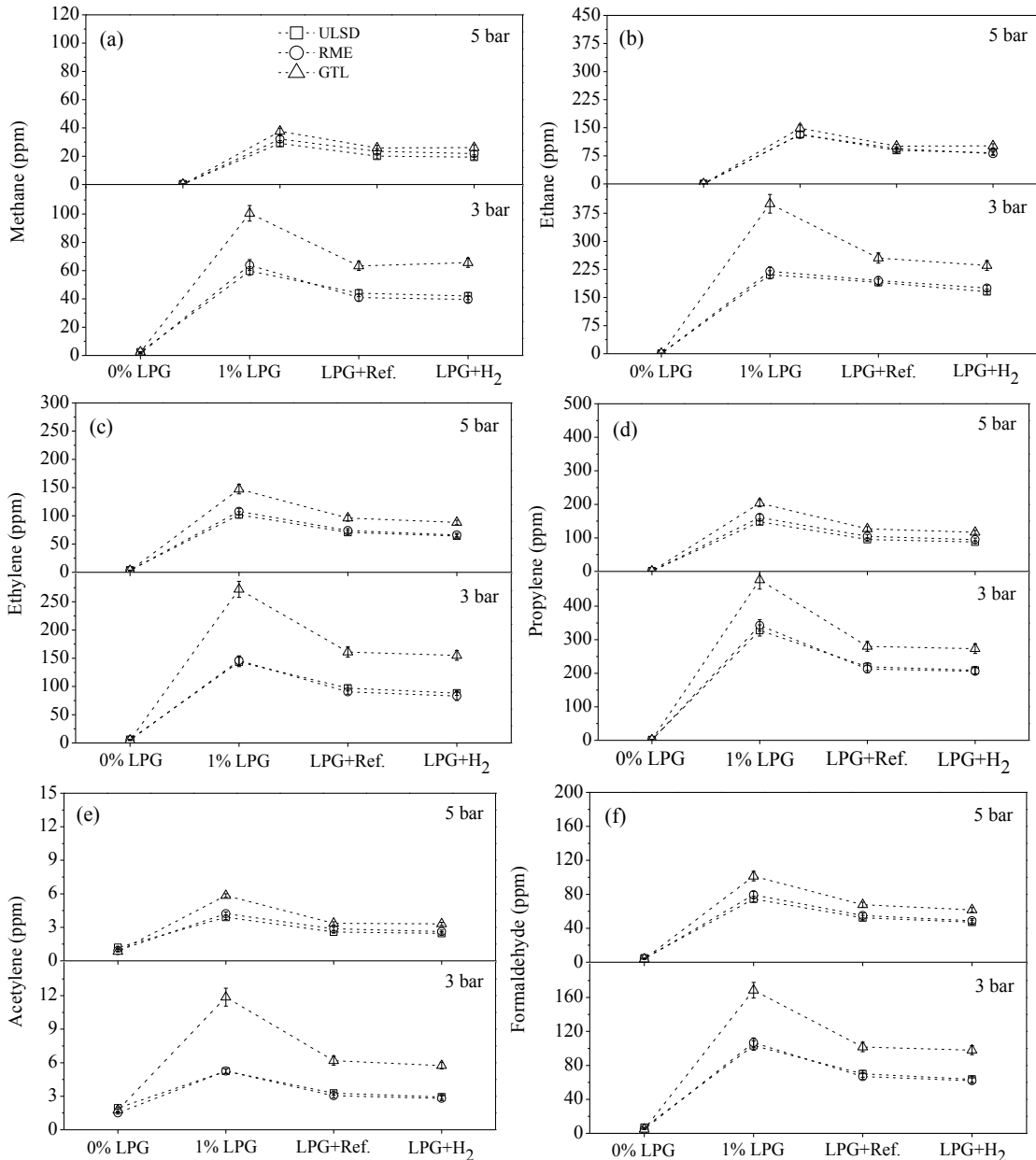
Figure 63. Hydrocarbon species and formaldehyde emissions for 1% LPG addition with hydrogen and reformate addition.

Smoke and particulate emissions.

The amount of smoke was lower in the case of the oxygenated (i.e. RME) and non-aromatic fuel (GTL) compared to the conventional fuel (ULSD) without LPG addition (Figure 61c and 61d). It was obtained that smoke emission of RME and GTL respectively was 112%

and 36.3% lower than that of ULSD at low load while it was 69.8% and 22.7% lower than that of ULSD at high load.

On the dual fuel operation where the air supply was limited, the RME ability to reduce soot was maintained or even more effective compared with only liquid fuel combustion. As a fuel-born oxygen, the oxygen in RME has better accessibility to the flame (Lapuerta et al., 2008a) improving mixture oxidation even in the locally fuel-rich regions resulting in a reduction in the smoke concentration. Apart from the oxygen content in RME, it is also suggested that the higher in-cylinder temperature in RME combustion could enhance OH formation than in the case of ULSD and GTL assisting further the soot oxidation process. In addition, the high oxygen availability in the combustion chamber with RME could react with hydrogen either from fuel or the syngas to produce more OH promoting soot precursors and soot oxidation. In addition, advanced SOI due to high bulk modulus of compressibility of RME led to better air-fuel mixture before SOC and advanced the start of combustion, hence provided longer residence time at high temperature for soot oxidation taking place. As GTL is a non-aromatic fuel, the propensity to produce soot precursors through pyrolysis might be inhibited. It occurred through the oxidation by the OH radical in the presence of high temperature due to the syngas combustion and limited soot precursors produced (specifically PAH) due to virtually no aromatic in GTL. Another reason for this soot reduction with RME and GTL is the C/H ratio which influences soot and particulate matter formation (Tree and Svensson, 2007). A large number of carbon atoms in the fuel (thus increasing C/H ratio) tend to form more particulates. Therefore, ULSD which has higher C/H ratio than that of RME and GTL produced more particulate matter whereas GTL which has higher H/C ratio decreases the tendency to produce soot and particulate matter. Additionally, retarded SOC in the GTL dual fuelling might increase soot but it can be balanced by the no aromatic content in GTL.
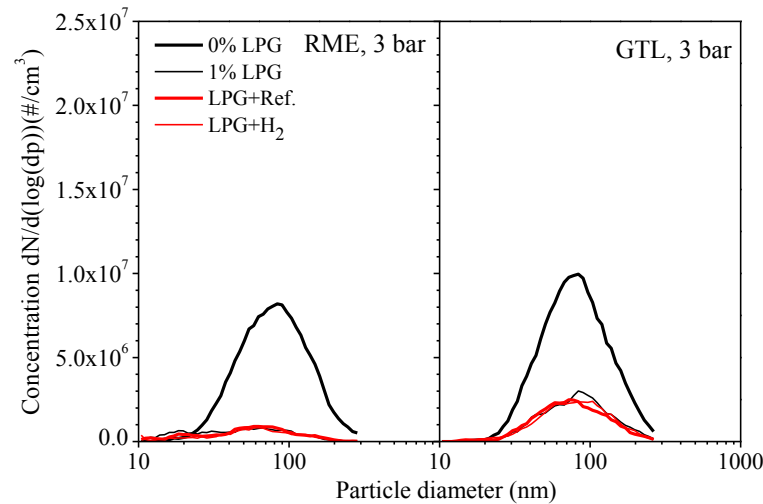
Figure 64. Particulate size distributions for RME and GTL-LPG combustion with hydrogen
and reformate addition.

It is clearly shown that the particulate number concentration (Figure 64) was reduced in every diameter size with the application of dual fuel mode, and the level concentration trend was kept similar to the baseline condition, and followed the general trend ULSD > GTL > RME. Apart from the reduced fuelling levels and the reasons explained in the smoke section, another argument for low PM can be the lower sulphate in RME and GTL compared with ULSD (Table 3) which results in low contribution to the sulphate fraction.

6.4 Summary

Reformate and H_2 combustion has shown to have the capability to increase the thermal efficiency and reduce gaseous (both regulated and unregulated) and particulate emission with respect to LPG-diesel dual fuel combustion. These benefits are heavily attributed to the chemical and physical H_2 characteristics contained in the LPG-reformed gas.

The formation and oxidation of soot through LPG-reformed gas was associated to thermal, dilution and chemistry effects. Smoke and PM emissions under H_2 addition was lower than those of reformate addition. It was also obtained that smoke and PM was improved

especially in the case of 0.2 and 0.5%, while there were not significant further reductions in 1% LPG addition. Therefore, the amount of the inducted H_2 can be optimised in order to get the best compromise between NO_X and soot.

RME as a pilot fuel in LPG-reformed diesel dual fuelling mode produced a synergistic effect with H_2 addition through better improvement in thermal efficiency and regulated emissions excluding NO_X than the rest of liquid fuels. These were achieved by high bulk modulus and oxygen content. However, in the case of GTL dual fuelling deterioration in both regulated (HC and CO) and unregulated emissions and also thermal efficiency were obtained as a result of its properties which affected the combustion characteristics and thus engine performance and emissions. The use of GTL in LPG-reformed dual fuel however, improved the soot-NO_X trade-off. It also showed a great potential where the increase of NO_X under reformate and H_2 addition could be minimised with the use of GTL.

CHAPTER 7

CONCLUSIONS

7.1 Concluding Remarks

An experimental study in dual fuel combustion mode has been carried out in order to explore the potential of alternative fuels, both gaseous and liquid fuels, in diesel engines with various engine operating conditions. The work is also extended to improve the engine performance and engine-out emissions by employing different approaches. This section summarises the findings of the works and recommends some future work to extend the knowledge in the dual fuelled engine operation.

7.1.1 Gaseous Fuel Effect

The introduction of gaseous fuels (biogas and LPG) in diesel engines (dual fuel combustion mode) was feasible as it offered simultaneous advantages in improving the soot – NO_X trade-off, fuel flexibility, and reduction in the conventional liquid fuel utilisation. All the benefits were achieved without employing significant additional devices or engine adaptation. However, there should be a maximum limit to the inducted gaseous fuels concentration to resist the deterioration in engine thermal efficiency and gaseous hydrocarbon emissions (HC, CO). This work showed that LPG was more promising for fuel saving as less LPG was required to replace a similar amount of liquid fuel compared to that of biogas. It indicated that upgrading the biogas quality by reducing CO_2 content might further improve its utilisation in dual fuelled engine. In addition, differences in the gaseous fuel properties affected the combustion characteristics differently (i.e. in-cylinder temperature) leading to a variation in

emitted emissions. In terms of NO_X emissions benefit, biogas had the potential to be applied at various concentrations and engine loads while LPG was shown to be effective in reducing the emissions only at low load conditions. Therefore, it is suggested that in LPG-diesel dual fuelling at high load the LPG concentration should be limited or the operation was coupled with EGR in order to reduce the NO_X deterioration. In addition, dual fuel combustion showed more beneficial effects at high load compared to that of low load as evidenced by higher thermal efficiency and lower emissions (CO and HC).

7.1.2 Liquid (pilot) Fuel Effect

The present work showed that there was a relationship between the pilot fuel quantity and the oxidation capability of the fuel – oxidant mixture. A higher quantity of pilot fuel contributed to the improved charge mixture oxidation and hence reduced HC and CO emission but NO_X emissions increased. This trade-off of the emissions was seen more obviously in biogas combustion compared to that of LPG. The type of liquid fuel used was one of the important factors that affected the dual fuelled combustion process. It revealed that the variations in pilot fuel properties (i.e. density, bulk modulus and CN) influenced the dynamics of pilot injection and the start of combustion (SOC) in dual fuel combustion. For example, the comparable SOC obtained between RME and GTL at the baseline conditions could not be maintained at dual fuel combustion where the SOC was further retarded in the case of GTL fuelling. It confirmed that the point of SOC at dual fuel combustion for a low density and bulk modulus fuel like GTL was very sensitive to the changes of pilot fuel quantity. The shift of the SOC and followed by alterations in the rest of the combustion characteristics (i.e. low in-cylinder temperature), where GTL showed the lowest in-cylinder temperature, was responsible for the variations in engine thermal efficiency and exhaust emissions. This GTL dual fuelling combustion characteristic led to deterioration in charge

mixture oxidation capability, increasing HC and CO. However, the GTL combustion can be advantageous for simultaneous soot – NO_X reduction. On the other hand, oxygen content in a fuel (like RME) correlated well with the reduction in HC, CO, and PM and it was continued at dual fuel combustion. In addition, there was a potential to implement a high quantity of EGR addition in LPG-RME dual fuel combustion in order to pursue simultaneous soot and NO_X benefits through oxygen availability and low combustion temperature.

7.1.3   Fuel Injection Timing Effect

One of the changes to have occurred in the combustion characteristics of a dual fuel engine was the retarded SOC. In a dual fuelled engine with a mechanical injection pump, the changes in the SOC were not only attributed to the combustion air availability but also the pilot fuel properties. Therefore, advanced injection timing was considered appropriate to be applied in GTL fuelling which showed the most retarded SOC in dual fuel combustion. On the other hand, RME, which has high density and bulk modulus, did not demonstrate a significant delay in SOC compared to that of its baseline condition specifically at high load, therefore, the method was not advisable to be applied. Advanced injection timing application demonstrated a greater effect on SOC at baseline conditions compared to that of dual fuel combustion. This revealed that the in-cylinder conditions (i.e. temperature and quantity and quality of pilot fuel) played a more important role in the pre-ignition activity and thus the SOC. Under the advanced injection timing mode, the alterations in combustion characteristics with respect to the standard injection timing such as longer ignition delay, high premixed combustion peak, and in-cylinder temperature contributed to the enhanced charge mixture oxidation. This can be characterised by emissions reduction (i.e. HC, CO, PM except NO_X) and improvement in engine thermal efficiency. Therefore, engine modification through readjusting the point of injection timing properly in dual fuel combustion using alternative

fuels such as GTL and LPG was a suitable option in improving engine performance and engine-out emissions.

7.1.4   Hydrogen and Reformate Effect

Hydrogen and reformate (hydrogen plus carbon monoxide) in this research work were produced from stoichiometric fuel reforming of biogas and LPG. It has been shown that the hydrogen-enriched gas addition into the biogas and LPG dual fuel combustion was very promising. With hydrogen, the mixture was provided with additional energy (i.e. increase in energy density) as well as an improved combustion process of dual fuelled engine mode. A simultaneous improvement in engine thermal efficiency, reduction in HC and its species, CO, and soot emissions with respect to non-hydrogen dual fuel combustion were obtained through a better mixture oxidation rate. Therefore, upgrading part of gaseous fuels to high-quality gaseous fuel (hydrogen) through a reforming process for dual fuel combustion mode could extend the range of engine operating conditions allowing more volume of the inducted gaseous fuel. However, in the case of reformate addition where the hydrogen concentration was decreased, the improvement in thermal efficiency and emitted emissions were reduced. Biogas and LPG showed different responses to the reformate addition in terms of CO emission where a greater increase was shown with biogas compared with LPG. The reduction in soot emission with the syngas addition involved some mechanisms such as dilution, chemical and thermal effects. However, the supremacy of hydrogen in reducing soot was slowed down at high LPG concentration. Therefore, an optimum amount of both LPG and hydrogen should be formulated in order to obtain the best simultaneous soot – NO_X reduction. The combination of hydrogen and RME showed great potential in improving thermal efficiency, gaseous and particulate emissions (except NO_X) through the hydrogen and oxygen – enriched in-cylinder mixture. On the other hand, the combination of hydrogen and GTL

showed good results in breaking the soot $-$ NO_X trade-off at low and high loads. This suggested that a modification in pilot fuel properties might further improve dual fuel combustion involving hydrogen.

7.2 Future Work

The results of the experimental work have suggested that there is scope for future work:

- The utilisation of biogas and LPG has been used intensively worldwide, driven by the high price of crude oil and their benefits in emissions. However, the concentration of CO_2 and butane in biogas and LPG respectively is different and depends on the production process. Therefore, research to explore the combustion and emissions characteristics using various concentrations of CO_2 in biogas and butane in LPG is suggested. In addition, research work on the use of other alternative fuels such as biomass to liquid (BTL), coal to liquid (CTL), natural gas is also required.

- It has been shown that the properties of the pilot fuel are very significant and played an important role in the performance and emissions in the dual fuel combustion mode. Research work in modifying the pilot fuel properties such as O_2, CN, density, bulk modulus, and H/C ratio by using different fuel additives will be useful. It is necessary to know and to specify the appropriate or the best pilot fuel characteristics for a specific gaseous fuel.

- Apart from fuel properties modifications, engine hardware modifications are worth investigating because of the direct effect on the combustion characteristics and emissions as well. Various fuel injection timings, multiple injections, application of EGR, and turbocharger are possible in the dual fuelled engine mode to further explore the fuel combustion characteristics.

- It has been proven that hydrogen-enriched gaseous fuel addition from fuel reforming of biogas and propane to the biogas and propane dual fuel combustion can improve engine performance and engine-out emissions. Therefore, an actual on-board fuel reforming coupled with engine testing will be beneficial.

- Investigation of HC species and other unregulated emissions derived from a dual fuelling system is necessary as the total HC produced is very high. The usage of GC-FID equipment is possible to achieve this purpose.

- The implementation of aftertreatment system by using HC-SCR and DOC systems can be one of the means to reduce HC and CO emissions. In addition, further understanding is expected to be reached in order to know more about the difference of HC emitted by biogas and propane. With the aftertreatment system, the achievement of better engine thermal efficiency can be maintained while gaining further benefits in gaseous emissions reduction.

APPENDICES

Appendix A: Measuring Equipment Technical Data

Table A.1. Technical data and performance of Horiba Mexa 7100-DEGR

Gas component	Method	repeatability	Linearity	Noise*
O_2	Magneto-pneumatic (MPA)	Within ± 0.5% of the full scale for zero point or within ± 0.5% of the readings for span point	Within ± 1% of the full scale or Within ± 2% of the readings	< 1% of full scale when O_2 is 5 vol% or more < 2% of full scale when O_2 is 5 vol% or less
CO, CO_2	Non-dispersive infrared absorption (NDIR)			< 1% of the full scale
NO_X	Chemiluminescence (CLD)			< 2% of full scale
HC	Flame ionisation (FID)			< 1% of the full scale

*peak-to-peak of total 5 minutes of duration

Table A.2. Technical data and performance of Horiba Mexa-1230PM

Component	Method	Measuring ranges	Repeatability
Soot	Diffusion charging (DC)	0 mg/m^3 – 15/75/150 mg/m^3 (with dilution ratio of 1 to 8/40/80)	Within ± 1% of full scale
SOF	Dual flame ionization detection (dual-FID)	0 mg/m^3 to 150 mg/m^3	

Appendix B: Gaseous fuels flow rate data

Table B.1. Gaseous fuels flow rate at 1200 rpm, 2 and 4 bar IMEP under biogas-Diesel dual fuelling

Engine operating conditions	Gaseous fuels flow rate (litre/minute)		
	biogas	hydrogen	carbon monoxide
ULSD	0	0	0
ULSD+2% biogas	8	0	0
ULSD+biogas+H$_2$	4	6.58	0
ULSD+biogas+reformate	4.83	3.29	3.29
ULSD+4% biogas	20	0	0

Table B.2. Gaseous fuels flow rate at 1500 rpm, 2 and 4 bar IMEP under biogas-Diesel dual fuelling

Engine operating conditions	Gaseous fuels flow rate (litre/minute)		
	biogas	hydrogen	carbon monoxide
ULSD	0	0	0
ULSD+2% biogas	10	0	0
ULSD+biogas+H$_2$	5	8.24	0
ULSD+biogas+reformate	6.04	4.12	4.12
ULSD+4% biogas	20	0	0

Table B.3. Gaseous fuels flow rate at 1500 rpm, 3 and 5 bar IMEP under LPG-Diesel dual fuelling

Engine operating conditions	Gaseous fuels flow rate (litre/minute)		
	LPG	hydrogen	carbon monoxide
ULSD	0	0	0
ULSD+0.2% LPG	1	0	0
ULSD+LPG+H$_2$	0.5	0.469	0
ULSD+LPG+reformate	0.5	0.305	0.164
ULSD+0.5% LPG	2.4	0	0
ULSD+LPG+H$_2$	1.2	1.126	0
ULSD+LPG+reformate	1.2	0.732	0.394
ULSD+1% LPG	4.8	0	0
ULSD+LPG+H$_2$	2.4	2.252	0
ULSD+LPG+reformate	2.4	1.464	0.788

Appendix C: In-cylinder pressure and ROHR of ULSD-LPG dual fuelled combustion
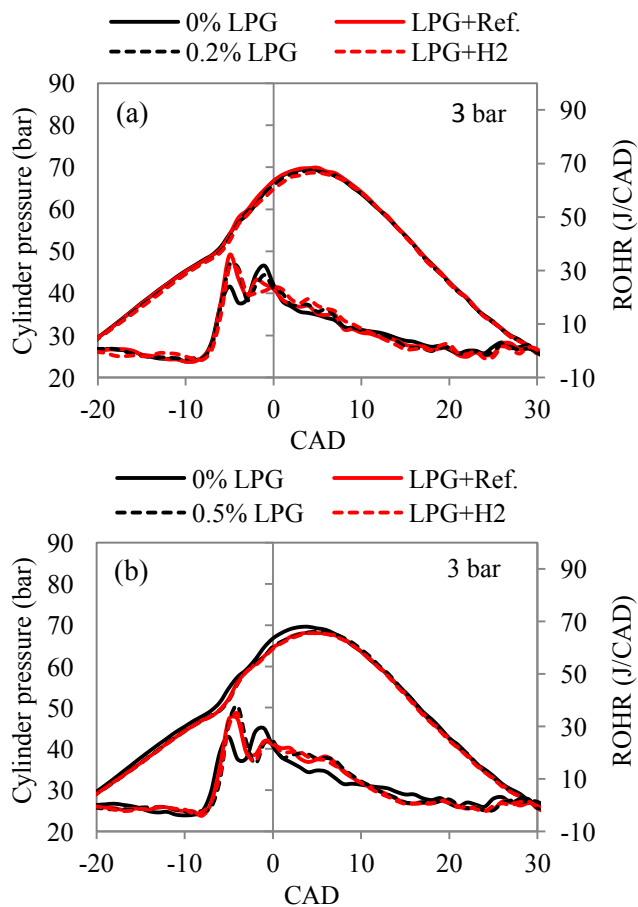
Figure C.1.   In-cylinder pressure and ROHR for ULSD-LPG combustion with hydrogen and reformate at 3 bar IMEP. (a) 0.2% LPG, (b) 0.5% LPG.
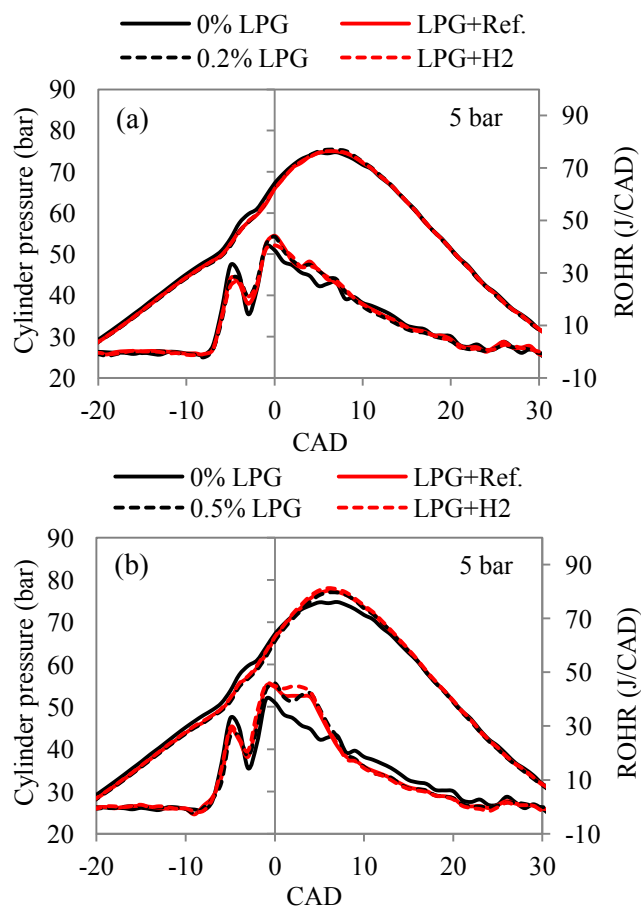
Figure C.2.   In-cylinder pressure and ROHR for ULSD-LPG combustion with hydrogen and reformate at 5 bar IMEP. (a) 0.2% LPG, (b) 0.5% LPG.

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