ENGINE PERFORMANCE AND PARTICULATE MATTER

SPECIATION FOR COMPRESSION IGNITION ENGINES POWERED

BY A RANGE OF FOSSIL AND BIOFUELS

By

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ABSTRACT

Fuels: Non-renewable fossil fuels are the largest man-made contributor to global warming. Biofuel market share will increase, promoted by renewability, inherent lower net CO_2 emissions, and legislation.

The environmental and human health impact of diesel exhaust emission particulate matter (PM) is a major concern. Fossil diesel PM aftertreatment systems exist. Near future fuel PM research and the evaluation of current aftertreatment technology, highlight a route for future development.

Using a holistic approach this body of work studies the interdependence between the fuel, the CI engine and associated aftertreatment system. The overall objective of this thesis is the evaluation of current diesel aftertreatment using renewable near future fuels.

Diesel blends with 1st and 2nd generation biodiesel fuels are viable. Carefully selected blends like B20G10 can make all round regulated emission improvements. Green additive dimethyl carbonate (DMC) enhances diesel combustion by oxygenation. Regulated emissions of THC, CO (>30% reduced) and PM (50% reduced) for 2% DMC in diesel.

1st generation biodiesel (RME) is widely available. Combustion produces significantly less solid PM than diesel (<50%) and slightly more liquid PM. RME produces less particulate at nearly all particle sizes, but more of the small nano sized liquid SOF. The potentially negative health effect of nano-sized SOF material raises questions. There is a case for more research into the health effects of nano-sized SOF material. Oxygenated fuel combustion PM contains more voids (facilitates DPF oxidation), plus unregulated carcinogenic compounds are reduced.

Aftertreatment: The efficiency of the oxidation catalyst for the near future fuels was comparable to diesel and PM matter at all particulate sizes is reduced for all near future fuels tested. Aftertreatment total PM filtration levels are >90% by mass >98% by number, for all fuels. For synthetically produced 2nd generation gas to liquid (GTL) fuels there are potentially DPF regeneration implications. Current aftertreatment solutions are as effective for bio alternatives as they are for fossil diesel. Biodiesels, green additives and aftertreatment are effective clean emissions improvements, until the promise of true zero emission vehicles is realised.

PREFACE AND THESIS OBJECTIVES

The works of this thesis were originally conceived to be an evaluation of 2 current aftertreatment solutions provided by the sponsor Johnson Matthey.

The aftertreatment devices are:

1. Diesel oxidation catalyst (DOC) (Primary objective)

2. Diesel Particulate filter (DPF) (Primary objective)

The evaluation concerned the effect that the introduction of new bio-alternatives to fossil diesel would have upon the performance of current and prototype aftertreatment products. The origins lie in legislative direction in the form of biofuel replacement targets in Europe that require the use of these fuels in blends with fossil diesel.

It soon became apparent during the course of the project that the primary objectives could only be achieved by interfacing a range of technical fields; fuel technology, engine performance, catalysis and physical filtration.

A range of secondary objectives would be required to construct an approach that would properly achieve the primary goals:

3. Evaluation of the performance of 1st Generation Biodiesel (fuel technology and engine performance)

4. Evaluation of the performance of 2nd Generation Biodiesel (fuel technology and engine performance)

5. Evaluate the contribution of fuel-borne oxygen (a key factor in biofuels) on combustion (fuel technology and engine performance)

ACKNOWLEDGMENTS

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Symbol	Units	
C_p	kJ/kg K	Specific heat capacity at constant pressure.
C_v	KJ/kg K	Specific heat capacity at constant volume.
LCV	MJ/kg	Lower calorific value,
λ		Air-fuel ratio.
Φ		Equivalence ratio =1/ λ.
ηth	%	Thermal efficiency.
C_r		Compression ratio.
R_c		Cutoff ratio.
γ		Ratio of specific heats at constant pressure and constant volume (Cp/Cv).
T_C		Ambient absolute temperature.
T_H		Absolute temperature at which the fuel burns.
N		Particle number (particulate number).
$\emptyset$		Outside diameter.

LIST OF ABBREVIATIONS

ASTM	American Society for Testing of Materials	HPLC	High performance liquid chromatograph
BDC	Bottom dead centre	HTFT	High temperature Fischer Tropsch
BTL	Biomass to liquid	HTU	Hydro thermal upgrading
BSM	Bosch smoke meter	IBP	Initial boiling point
BSN	Bosch smoke number	ICE	Internal combustion engine
CAD	Crank angle degree	IMEP	Indicated mean effective pressure
CCRT	Catalysed continuously regenerating technology	JM	Johnson Matthey
CI	Compression ignition	LNT	Lean NOx trap
CO	Carbon monoxide	LPM	Liquid particulate matter
CO_2	Carbon dioxide	NAC	NOx adsorber catalyst
COV	Coefficient of variation	NH_3	Ammonia
cpsi	Cells per square inch	NO	Nitrogen monoxide
C_2H_2	Acetylene	NO_2	Nitrogen dioxide
DC	Direct current	NOx	Nitrogen oxides
DC_h	Diffusion charging	N_2O	Nitrous oxide
DI	Direct injection	NSC	NOx storage catalyst
DMC	Dimethyl carbonate	NSR	NOx storage/reduction catalyst
DMF	Dimethylfuran	OC	Oxidation catalyst
DMS	Differential mobility spectrometer	PAH	Polycyclic aromatic hydrocarbons
DNT	DeNOx trap	PM	Particulate matter
DOC	Diesel oxidation catalyst	ppm	Parts per million
DPF	Diesel particulate filter	RME	Rapeseed methyl ester
EC	European Community	ROHR	Rate of heat release
ECU	Engine control unit	SCR	Selective catalytic reduction
EGR	Exhaust gas re-circulation	SI	Spark ignition
EHN	2-Ethylhexyl nitrate	SME	Soybean methyl ester
ESC	European stationary cycle	SMPS	Scanning mobility particle sizer
EVO	Exhaust valve opening	SOC	Start of combustion
FA	Fatty acid	SOF	Soluble organic fraction
FAME	Fatty acid methyl ester	SO_2	Sulphur dioxide
FBP	Final boiling point	SPM	Solid particulate matter
FID	Flame ionisation detection	TDC	Top dead centre
FT	Fischer Tropsch	TGA	Thermogravimetric analysis
GC	Gas chromatograph	THCs	Total hydrocarbons
GHG	Green house gas	ULS	Ultra low sulphur
GM	Genetic modification	ULSD	Ultra low sulphur diesel
GTL	Gas to liquid	UPM	United Paper Mills
HCCI	Homogenous charge compression ignition	US EPA	U.S. Environmental Protection Agency
HC	Hydrocarbon	VOC	Volatile organic compound
HD	Heavy Duty	VOM	Volatile organic matter
		VW TDI	Volkswagen turbo diesel injection

CHAPTER 1

INTRODUCTION

Since the inception of the wheel, transportation has evolved over millennia. The recent development of the reciprocating engine has made rapid transportation of goods and people possible across all continents. Developed nations enjoy large road networks that allow fast travel for everyone, over great distances. Road transportation of goods and transportation of people are both currently virtually wholly dependent upon a fossil liquid fuel infrastructure. The high energy density of fossil fuels and until recently relatively low cost, has meant that fossil fuel burning reciprocating engines prevail. Global warming concerns and the need to move away from non- renewable fossil fuels, has seen a move towards greener alternatives to fossil fuels. Ideally the aim is to develop an economic, zero emission transport system that will satisfy current and future transport requirements. Using available technology it is possible to meet these targets individually, but not in combination. Scientists and engineers are carrying out research using varying methods and technologies, in an effort to produce a cost effective zero emission vehicle.

Potential vehicles might be fuel cell powered electric vehicles or indeed electrically powered vehicles when the electricity is generated via a renewable, zero emission source. Other possibilities include; compressed air, flywheel, solar or near zero emission vehicles based upon hydrogen as the source fuel (Haisheng et al., 2011; Tripathy, 1992; Kongtragool & Wongwises, 2008; Fujinaka, 1992; Gomes Antunes et al., 2009; Panik, 1998). Each power source has potential, but indeed also limitations, whether it be the cost, the weight or scarcity of materials etc. It is perhaps some years before vehicles can achieve all of our ideal requirements, (though many new technologies are now becoming available).

Recently there have been many advances in combustion, for both spark ignition (SI) and compression ignition (CI) engines. Over the last 30 years fuel economy has been almost doubled (EPA, 1980; Volkswagen, 2010) and emissions have seen significant attention (Figure 1.2.). These reductions have been achieved by careful design and optimisation of the engine, combined with combustion strategies such as, EGR and exhaust aftertreatment systems. Currently CI (diesel) engines have become increasingly popular, most especially in Europe (Roberts, 2010). The trend is expected to continue, due to the high thermal efficiency, improved torque characteristics, reliability and longevity in comparison with SI engines. Modern diesel engines are already the premier road transport choice in Europe and are on the increase in North America and Asia. For the foreseeable future, it is widely believed that CI combustion systems will be prevalent in the road transport sector. CI engines are able to use a variety of fuels other than fossil diesel. Indeed military vehicles often utilise CI engines, due in part to the benefit of fuel source flexibility in scarce or uncertain environments.

Biofuels are derived from biomass, they are advantageous because they are renewable and can provide energy security. Biofuels can be viewed as near CO_2 neutral (when the full CO_2 life cycle is considered) so their use is seen as beneficial. In Europe legislative pressure such as Biofuels Directive 2009/28/EC (EC, 2009) has seen the introduction of fossil road transport fuel replacement targets. Environmental concerns, the move towards reduced pollutant emissions, combined with energy security provide the driving force for research in this field. This PhD thesis explores potential, near future, green fuels for the unmodified CI (diesel) engine and its aftertreatment system.

1.1   BACKGROUND

The following section presents an introduction to the main topics in this thesis, including a brief overview of CI combustion, detailing why CI engines are relevant for the foreseeable future. Developments in emissions legislation, how emissions are formed, abatement control mechanisms, and biofuels for CI are then discussed in some detail.

1.1.1   Compression Ignition CI Combustion

Compression ignition is when an internal combustion engine uses the heat generated in compression to initiate ignition of the fuel. High thermal efficiencies are realised due to the high compression ratios of CI engines (typically 15:1 – 25:1). CI engines can be 2 or 4-stroke. Here only the 4-stroke CI engine is discussed. 2-strokes, although of simpler construction and with higher specific power, are generally less efficient due to scavenge losses. As a result the 4-stroke is more common in automotive applications.

1.1.2   *4-stroke CI Operation*

A fresh intake charge of air is drawn into the cylinder by the piston descending from   top dead centre (TDC) to bottom dead centre (BDC) (Figure 1.1.) with the inlet valve/s open (intake stroke 1). The inlet valve/s now close/s and the piston returns towards the cylinder top (compression stroke 2). Work done
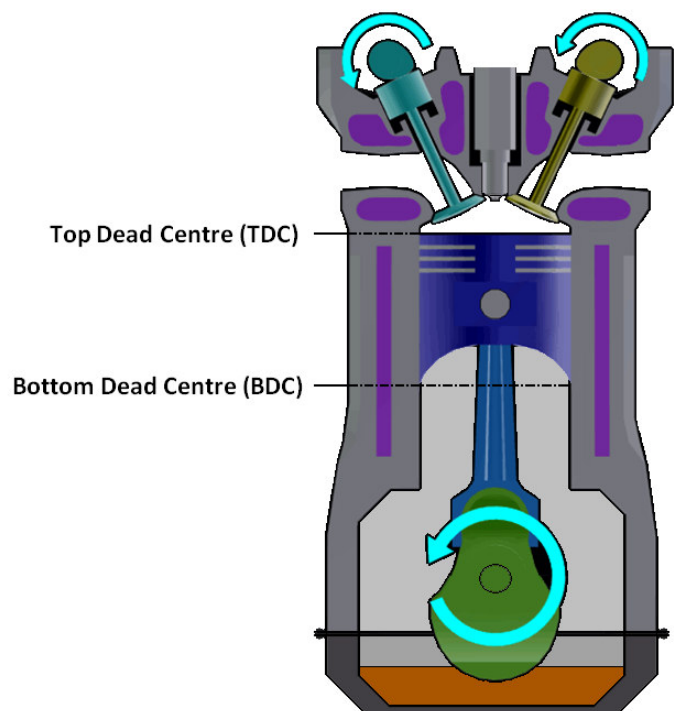
Figure 1.1.   4-stroke DI CI Engine Schematic.

during the compression stroke heats the air to (> 177 °C U.S. No.1 diesel) (Rosner, 1996). At close to the top of the compression stroke, fuel is injected into a pre-chamber or directly into a void in the top of the piston (engine design dependant). The fuel injector design enables the fuel to be broken down into small droplets, and distributed evenly. The heat of the compressed air vaporises fuel from the droplets. The start of vaporisation causes a delay period (ignition delay), the vapour reaches ignition temperature and causes an abrupt increase in pressure above the piston, and this gives the diesel engine its characteristic knock sound. The vapour is then ignited by the heat from the compressed air in the combustion chamber. The rapid expansion of the combustion gases drives the piston downwards, turning the crankshaft (power stroke 3). The exhaust valve/s now open and hot combustion gases are then pushed out (exhausted) by the piston returning to the top of the cylinder (exhaust stroke 4). It is now possible to repeat this whole process using the remaining momentum in the system.

1.2   REASONS FOR THE SUCCESS OF THE CI ENGINE

Briefly taking a look at fundamental thermodynamics (equation 1) it is possible to see the key advantage of CI engines over SI engines. This helps to explain the ongoing move in the automotive industry towards CI/dieselisation.

Thermal Efficiency for 4-stroke engines

SI engine (Otto Cycle)   *CI Engine (Diesel Cycle)*

$\eta th = (1 - Cr^{(1-\gamma)}) \times 100$ $\eta th = 1 - \left(\dfrac{Cr^{(1-\gamma)}(Rc^{\gamma-1})}{\gamma(Rc-1)} \right) \times 100$

Where: ηth - thermal efficiency, %   Cr - compression ratio

Rc - cutoff ratio, rc, (ratio of cylinder volume for the beginning and end of the combustion process)

γ - ratio of specific heats at constant pressure and constant volume (Cp/Cv)

Equation 1 Holman (1980).

Compression ratio is a governing factor in in-cylinder temperatures, so increased compression ratio means higher in-cylinder temperatures when the fuel burns and higher thermal efficiency. For SI engines the compression ratio has to be limited to prevent pre-ignition (knocking) i.e. the fuel air mixture ignites by compression before the spark plug fires. This is because typical SI engines undergo a premixed combustion i.e. the fuel is mixed with the air prior to entry to the combustion chamber, relying on a 'homogenous' type mixture. CI engines are not limited in this way, the fuel is instead introduced into the cylinder at almost the exact point at which it is required to ignite, allowing the engine to utilise an increased compression ratio. If the Carnot cycle efficiency (max possible thermal efficiency i.e. ideal no energy loss reversible heat engine) is now considered:

$$\eta\text{th} \le 1 - \frac{T_C}{T_H}$$ where: T_C – Ambient absolute temperature

T_H – Absolute temperature at which the fuel burns

Equation 2 Carnot Cycle Efficiency (Carnot, 1824; Carnot *et al.*, 2005).

CI engines running at high compression ratios are able to significantly increase T_H, meaning that the Carnot cycle efficiency can be increased. So for the same engine architecture (i.e. same energy losses) for CI compared to SI thermal efficiency is higher. Indeed CI engines are more thermally efficient than all other heat engines, for simplicity here, they are compared to SI engines because they are the most common form in automotive applications.

1.2.1 Friction Reduction

In part due to the increased compression ratio, the heat released in a CI engine occurs at lower engine speeds than in SI engines. This creates increased torque at low engine speeds. Since the power output of an engine is proportional to the product of its torque and speed, at reduced engine speed since friction losses are lower, there is an improvement in the brake power of diesel engines and this translates into a gain in overall thermal efficiency.

1.2.2 Reduced Pumping Losses

In a CI engine the power output is controlled by varying the rate of fuel (unlike SI where the inlet air is throttled). The air induction is limited only by the restriction of filters and the design of the induction system. This minimises the work done by the engine during air induction.

1.2.3 *Incidental additional advantages of the CI engine*

For CI combustion the heat is often released earlier in the combustion cycle, at a sudden rate, as a result robust engine construction is required. Engine designers in the past have created tough engine designs, able to cope with these requirements. Diesel engines have a reputation for outlasting the vehicle and reliability in terms of breakdowns. This will be due to a number of reasons, such as, rugged heavy weight engine construction, the lack of spark plugs, distributors and ignition systems and the reduced engine speeds at which they operate. The safety of the CI fuel could also be a factor as fuels that are suitable for CI combustion tend to be less flammable.

1.2.4 *Fuel Flexibility*

This is a key advantage/feature of the CI engine (also a focus for this thesis) and will be explored in some detail.

1.2.5 *Emissions Advantages of the CI Engine*

Tailpipe emissions are of principle concern for environmental and legislative reasons (see section 1.1.4) CI engines have base emission levels in specific terms i.e. g/kW-hr of CO and hydrocarbons (HCs) that are a small fraction of those of SI engines. Engine-out NO_x emissions, are also reduced on a specific basis compared to SI, though NOx and particulate are problematic (see section 1.6).

1.2.6 *Limitations of the CI engine*

There are several reasons for this:

- *Specific power output* levels for SI engines are higher than CI.

- *Noise,* is often cited as the principal reason why CI engines are undesirable for lightweight applications. Noise is both a regulated and an aesthetic vehicle property. The noise level is due to the rapid rate of pressure rise, due to the sudden early heat release, as fuel is injected in-cylinder. Recent developments such as monoblock construction, acoustic mounting and enclosure (Stone, 1999) and perhaps new stop start hybridisation, go some way to improve this trait (though idle noise remains noticeable for even the latest passenger vehicles).

- Engine *weight*. The engine must be of robust construction to deal with the increased compression ratio and the rapid way that heat is released in cylinder. Material selection, such as the direction taken by Mitsubishi with the 4N1 all alloy engine help to reduce engine weight. Other potential weight reduction strategies include engine downsizing via forced induction. Though these strategies are not unique to CI engine technology.

- Emissions of particulate matter (*PM)* are high and aftertreatment is necessitated for current and future legislation (see section 1.5.4 & 1.6.8)

- *NOx* emissions can also be a problem even though engine out specific NOx emissions are lower. New legislation (Figure 1.2.) standards require large NOx reductions for CI engines. The lean exhaust environment and reduced gas temperatures in CI engines make this more complicated when compared to SI engines.

- **_Drivetrains_** can be more expensive and weigh more. This is because high torque is developed at low engine speed. This is desirable for reduced friction loss, but it necessitates the use of a more robust drivetrain.

- **_Engine cost,_** the robust design and construction involves an engine manufacturing cost penalty. The precise fuel injection system is expensive. The robust nature of the engine also follows through to much of the auxiliary equipment which also costs more.

1.3   EMISSIONS

In general the term 'engine emissions' refers primarily to pollutants in the exhaust (Stone, 1999). CI engines convert chemical energy contained within the fuel into mechanical power. The fuel is made up of various hydrocarbons that in a theoretical complete combustion will produce carbon dioxide (CO_2) and water (H_2O) vapour. These gases are not harmful to health, but CO_2 is considered to be a negative as it is a greenhouse gas (Karl & Trenberth, 2003). These ideal combustion gases and any unused air make up the bulk of the exhaust from a real CI combustion engine. There are other emissions, some of which are toxic to human health or harmful to the environment. These emissions are the result of non-ideal processes that occur during real combustion. These emissions arise through; incomplete combustion of the fuel, combustion of lubricating oil, combustion of additives and non-hydrocarbon compounds such as sulphur (from fuel or lube oil), or indeed separate reactions or decompositions of the mixture components at high pressure/temperature.

1.3.1 Emissions Legislation

There is early evidence of the problem of combustion emissions. Edward I (1272-1307) established an early air pollution control policy on the burning of coal. This policy saw enforcement during the reign of Edward II (1307-1327). A blacksmith who violated the ban on burning coal while the king was in town was tragically beheaded, Sawyer (1981). Much later, when the internal combustion engine (ICE) had become successful, Frenkel (1909) attributed the production of 'evil smelling gases' to the incomplete combustion of the fuel. Very sadly, a real danger of CO in ICE exhaust was highlighted by the Nazis. They used it to carry out mass murder at the Belzic concentration camp during 1930s and 40s (U.S. Holocaust Memorial Museum, 1942). Later in the U.S. during the late 1950s and 60s, emissions gained worldwide attention. In Los Angeles, the large numbers of vehicles combined with local atmospheric conditions and certain geographical features led to the appearance of photochemical smog, due to the emissions of NOx and HCs from mainly SI (gasoline) engines. This led to the first widespread emissions legislation in 1967, it set limits for HC, CO and NOx (Blackmoore & Thomas, 1976).

1.3.2 Regulated Emissions

Today in Europe, the U.S. and Japan (the 3 major regions) there are currently regulated limits for:

- ***Nitrogen Oxides (NOx)***, This can refer to any binary compound of nitrogen and oxygen however, for automotive emissions this means nitric oxide (NO) and nitrogen dioxide (NO_2). NO represents approximately 90% and NO_2 10% of NOx created by an ICE.

- ***Particulate Matter (PM)*** can be referred to as DPM (diesel particulate matter) or TPM (total particulate matter). Diesel PM is a mixture of carbonaceous soot, as well as other solid and liquid material.

- ***Hydrocarbons (HC)*** either total hydrocarbons (THC) or the non-methane hydrocarbons (NMHC).

- ***Carbon Monoxide (CO)***.

Figure 1.2. details the trend which European emissions regulations have followed during the last 18 years and how they are projected to be for Euro 6 in 2014. It should also be considered that since Euro 5 there is an additional PM requirement, for a PM total number limit at $6 * 10^{11}$ km^{-1} (EC, 2007).
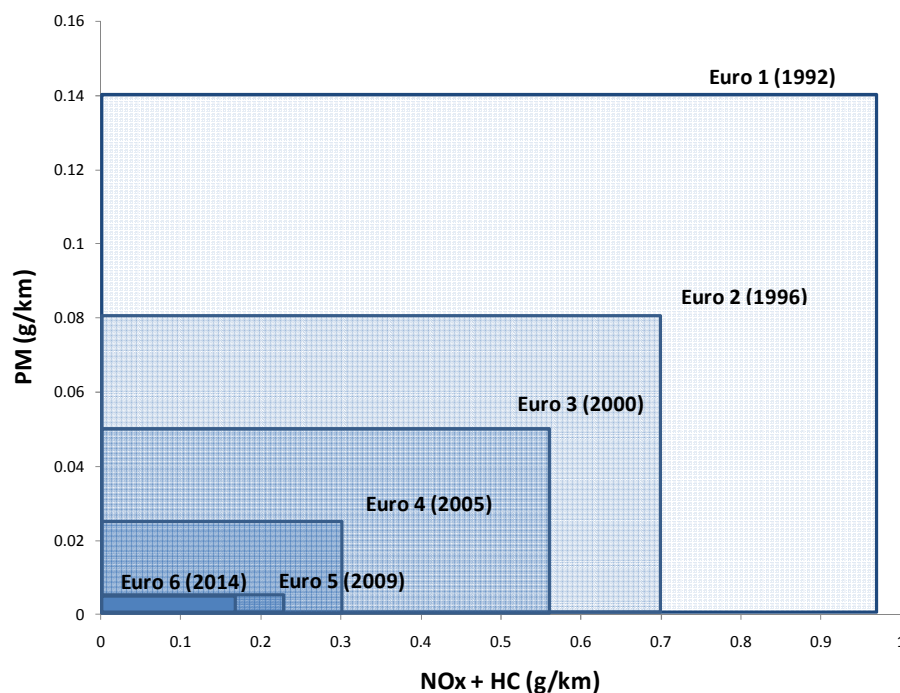
Figure 1.2. European emission standards for passenger cars (EEC, 1993; EC, 1994; EC, 1996; EC, 1998a; EC, 1998b; EC, 2002; EC, 2007).

1.3.3 Unregulated Emissions (pollutant emissions where there is an argument for future regulation)

There are several additional unregulated pollutants that have been found in CI engine exhaust, many are at much lower concentration levels than the regulated emissions. Indeed, some represent a part of the complex PM emission whereas others are gas phase species. The following are potential future regulated compounds:

- *Polycyclic aromatic hydrocarbons* (PAHs) are atmospheric pollutants that consist of fused aromatic rings. Some PAH compounds have been identified as carcinogenic (US EPA, 2002).

- *Nitrous oxide*, N_2O (not included in NOx measurements) is a possible future concern as it is promoted in some aftertreatment systems for use as an oxidant. As a pollutant it is a powerful greenhouse gas at 298 times the effect of CO_2, though how long it would remain as N_2O is debatable as it reacts with oxygen to form NO (Forster et al., 2007).

- *Aldehydes* are a part of the gaseous emission from CI engines, acetaldehyde and formaldehyde are probable carcinogens that may also produce other health effects (US DHHS, 2005). Aldehydes can be identified by their O=CH at the end of a group R of in determined length, formaldehyde is the simplest (CH_2O).

- *Sulphur dioxide*, SO_2, from sulphur present in the fuel and the lube oil. Previously fuel sulphur levels were/are at high levels (>400 ppm). These levels may still exist in some developing markets. Sulphur dioxide is a precursor of acid rain and atmospheric particulate (Holleman & Wiberg, 2001). The problem of sulphur poisoning has seen

much recent attention and not just because of the direct pollution. Automotive catalysts can be rendered ineffective (poisoned) by sulphur, as it deactivates the catalytic sites of the catalyst (Bartholomew, 2001). This has led to the reduction/elimination of fuel and lube oil sulphur levels by the oil companies and legislative authorities.

- **Metal oxides and metallic PM** several fuel and engine oil additives include metallic compounds. This results in some metal oxide and elemental emissions, including metals such as; iron, copper, zinc, cerium, calcium (added to the fuel for PM reduction) and phosphorus, (Keskin *et al.,* 2010) . Metal oxide emissions and small nano metallic particulate can be toxic and carcinogenic (most especially nano particulate), (Matti Maricq, 2007; Chen et al., 2006; Zhu et al., 2008).

- **Nitrogen dioxide**, (NO_2), constitutes a part of the NOx emission (it is more toxic than NO, the other component of NOx) it could be anticipated that in the future NO_2 may be regulated individually.

- **Dioxins** (polychlorinated dibenzodioxins) — Dioxins have lipophilic (dissolve in fats) properties, and are known teratogens (cause birth defects), mutagens, and suspected human carcinogens. This is a large area for research in environmental health (US EPA, 2003) thankfully dioxin emissions are a problem only when chlorine is present during combustion. Consequently chlorine levels in diesel are now strictly controlled. Potentially biodiesels can contain small levels of chlorine, if certain herbicides are used in production and this must be avoided.

1.3.4 Tailpipe Emissions from CI Engines

The formation of regulated emissions receives the most attention, as these are deemed to have the highest level of importance, so these will be discussed in more detail.

CI combustion is principally heterogeneous, i.e. the fuel and air are distinct phases. Emissions from a CI engine are formed as a result of burning a heterogeneous fuel air mixture. The exact composition of the emission is complex and depends on many conditions, primarily during combustion, but also during the expansion stroke and just prior to exhaust valve opening (EVO). There are many factors that affect the emission and these include the preparation of the mixture during ignition delay, the quality of the fuel ignition, the residence time at different combustion temperatures and the duration of the expansion stroke. Many inherent design features of the engine can also play a role in emissions formation. If the engine and exhaust system is considered as a whole, any reduction in emissions by the aftertreatment system is also included, (Heywood, 1988; Stone, 1999; Eastwood, 2000).

Perhaps the best way to describe emissions formation in combustion is to consider an example. To achieve this, an explanation of the phases of combustion will be required as a start point, leading to a later explanation of the emission formation for individual species. For brevity, only the direct injection (DI) CI engine, considered as they have many advantages and are now the most common.

1.4   PHASES OF COMBUSTION AND HEAT RELEASE RATE ANALYSIS

Rate of heat release (ROHR) analysis can be a useful tool when used to describe and understand CI combustion. It is calculated/derived from in-cylinder pressure data (Lyn, 1963) i.e. the pressure signal from an in cylinder pressure sensor. It represents the rate at which the system converts chemical energy from the fuel, so in chemical terms it might be considered as the rate of reaction. In a 4-stroke CI engine, the important time period when the reaction takes place is a brief period at and around top dead centre (TDC) between the compression and expansion stroke (Figure 1.1.) when the fuel is injected into the cylinder. Figure 1.3. shows the rate of heat release for a typical DI CI engine operation using diesel fuel.
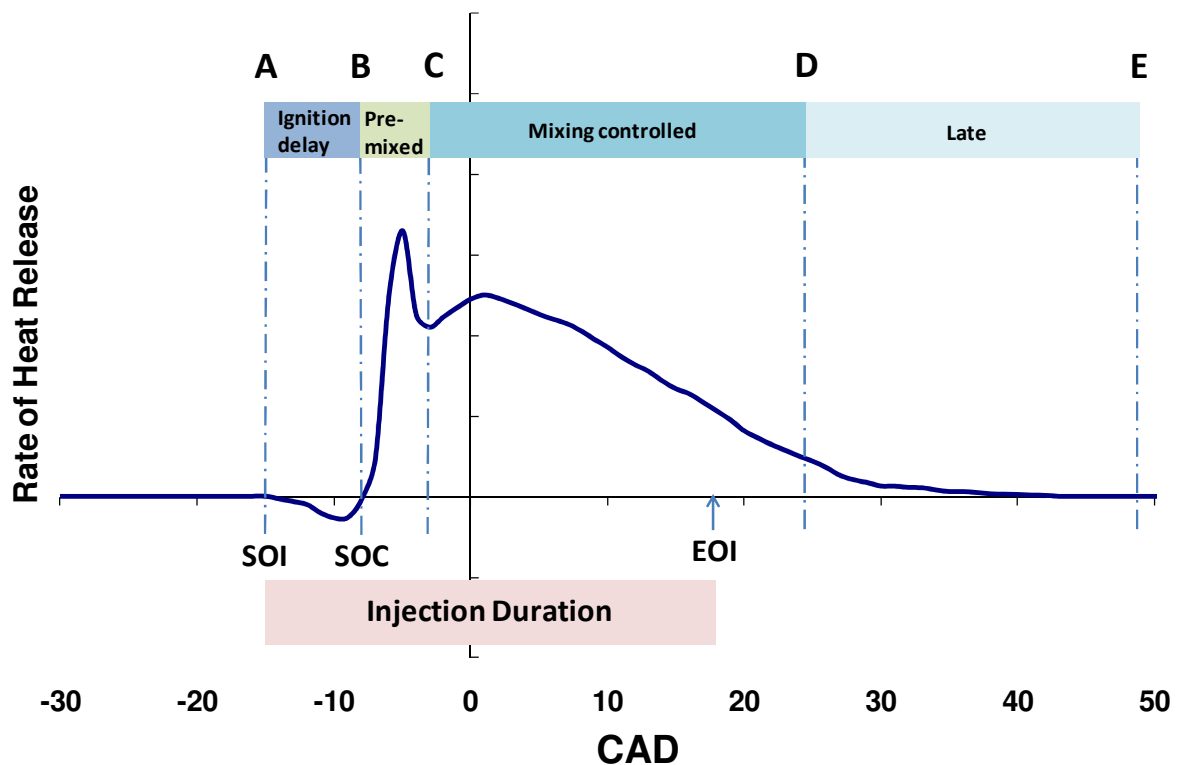
Figure 1.3. The phases of combustion for a DI CI engine, adapted from Lyn (1963) and Heywood (1988).

1.4.1 A-B *Ignition delay*- this is the period of time between the start of fuel injection and the start of combustion (SOC). This is a period of fuel vaporisation (notice the initial slight negative ROHR Figure 1.3.). The SOC (or reaction/burn start) is defined at the first positive ROHR.

1.4.2 B-C *Premixed combustion phase*- in this period fuel that has been mixing with air during the ignition delay (i.e. pre-mixed fuel-air) period burns rapidly. This is because the fuel and air have had time to mix, and the mixture achieves its flammability limit and burns within a few crank angle degree (CAD). At the same time fuel is being injected into this hot burning mixture and in combination the heat is released. This gives the premixed phase its sharp characteristic peak.

1.4.3 *Mixing controlled/diffusion combustion phase*- the mixing controlled combustion phase represents the bulk of the CI combustion. In a short time, all the pre-mixed mixture due to the ignition delay is burnt. At this point the heat release rate can only be controlled by the rate at which the mixture becomes available to burn. There are many processes involved in this 'rate at which the mixture becomes available' and these are explained in more detail in Figure 1.4. (Dec's model). Primarily this rate is controlled by the fuel vapour-air mixing process (which is of course affected by many parameters (Heywood, 1988).

1.4.4 D-E *Late combustion phase*- this combustion phase extends into the expansion stroke. Heat released during this period, may be because a small proportion of fuel has remained unburned, or perhaps, some of the previous combustion was previously incomplete (i.e. CO) and the mixture is able to now further release heat from these

incompletely combusted by-products. This may be in part because the expanding cylinder promotes mixing within the cylinder. Bear in mind that heat release will be at lower levels during this period as the cylinder temperatures are reducing due to the expansion of the stroke.

Though perhaps NOx emissions formation might take precedence due to their toxic effects and difficulty in abatement, the following model is succinct, considering the soot and NO formation ensemble. The works considered are the fruit of many optical studies and are currently widely believed to represent the best/most likely representation of soot and NO formation in DI CI (using diesel) combustion.

1.5   DEC'S MODEL FOR NO AND SOOT FORMATION

Figure 1.4. shows the principal features of a 'free' reacting diesel fuel jet during the 'quasi-steady period' of combustion (occurring between the end of the premixed burn and the end of fuel injection). This period during the mixing controlled combustion phase is when the bulk of the fuel is burnt. Figure 1.4. is an idealised cross-sectional slice through the mid-plane of a fuel jet. It shows how the combustion occurs in the absence of external interactions such as with the cylinder walls and swirl. The model also gives insight into the form of the CI in-cylinder fuel spray (the exact spray will of course depend upon the injector type and most employ multiple nozzles, designed to optimise the dispersion within the cylinder).

The period of the injection detailed in Figure 1.4. is just after the premixed combustion (most of C-D, Figure 1.3.) and it is where the majority of the fuel is injected. This phenomenon has been extensively observed in optical studies. In a free reacting diesel fuel jet, gases are entrained along the length of the combusting jet as it expands downstream.
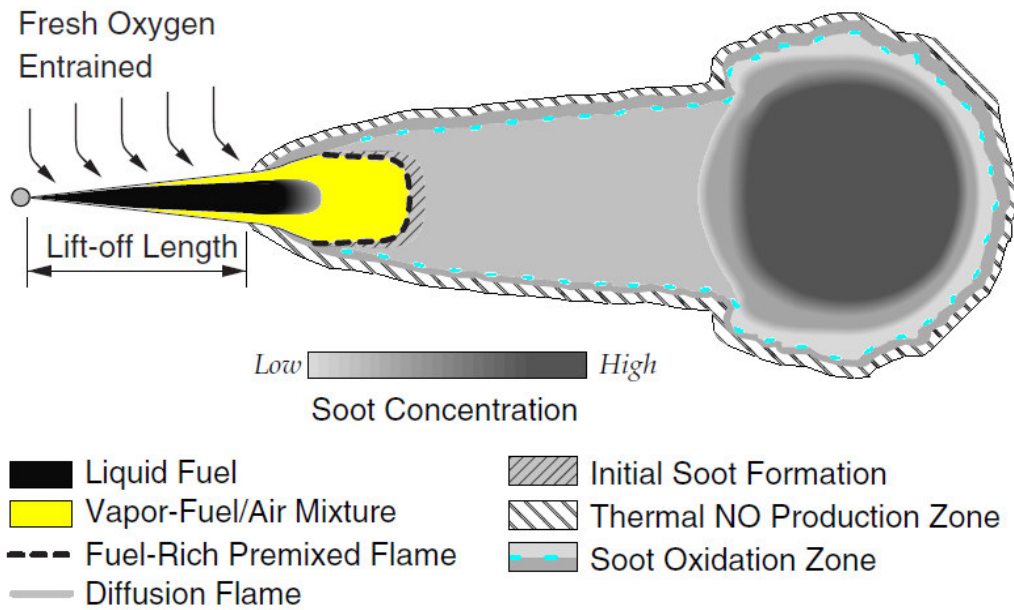
Figure 1.4. Free reacting diesel fuel jet (Dec's model). Adapted from refs; Dec (1997), Flynn et al. (1999), Musculus et al. (2002), Mueller et al. (2003).

Downstream of the lift-off length (Figure 1.4.), oxygen in the entrained gas is consumed by the fast high temperature reactions in the diffusion flame region. In the central region of this jet, oxygen can only be transported via combustion products of the diffusion flame. In the upstream lift-off length region of the jet, oxygen can be entrained into the jet (the arrows) and this mixes with the fuel forming a vaporised fuel (yellow) which is forced downstream. The vapour is hot and has been shown in planar laser imaging experiments to be (700-900K for diesel) (Mueller *et al.* 2003). An exothermic reaction occurs around the rim of the premixed combustion zone (around the yellow area within the jet). This raises the local temperatures to (1300-1600K for diesel) (Mueller *et al.,* 2003) as the available oxygen is consumed. At these temperatures soot formation and soot growth become more likely, especially further downstream in the centre of the jet (notice the dark circular region centre right hand side of Figure 1.4, indicating a high soot concentration) (Musculus *et al.*, 2002).

On the periphery of the diesel jet the combustion temperatures are high and since there is a readily available source of oxygen (the surrounding air) the combustion will be close to stoichiometric conditions. These conditions present near perfect conditions for the formation of thermal NO (the dominant NO production mechanism) on the lean side of the jet periphery (Dec, 1997). In Figure 1.4. this area is labelled the 'Thermal NO Production Zone'. Dec however, wisely points out that this would probably not be where the bulk of the thermal NO is produced as thermal NO production is a relatively slow process. So the bulk of the thermal NO production will be produced after injection has finished in the hot gas regions (remember, Figure 1.4. only provides a snapshot of the period when the bulk of the fuel is injected).

1.5.1   NOx Formation in DI CI Combustion

NOx emissions are not the focus of this thesis, though they are perhaps the most important engine out emission, due to their toxic effects and difficulty in abatement. It is widely understood that the thermal mechanism is responsible for the majority of NOx formation in CI engines, as peak combustion temperatures can be in excess of 2000 K. The thermal mechanism shown in Equation 3 was devised by Yakov Borisovich Zel'dovich, a physicist perhaps most famous for his work on the development of Soviet nuclear weapons (Zel'dovich, 1946). The three chemical reactions that are important in this mechanism are:

$$1) \quad O + N_2 \leftrightarrow NO + N$$

$$2) \quad N + O_2 \leftrightarrow NO + O$$

$$3) \quad N + OH \leftrightarrow NO + H$$
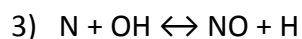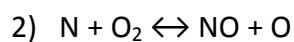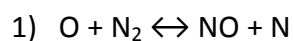
Equation 3 Extended Zel'dovich Mechanism, step 3 added by Lavoie & Blumberg (1973).

The overall reaction rate for this mechanism is quite slow and is very temperature sensitive. Thermal NO can only appear in significant amounts well after the start of heat release (See Figure 1.3.). The mechanisms strong temperature dependence is due to the forward rate of reaction 1. This mechanism is of particular importance at high temperatures and at air/fuel mixtures that are close to stoichiometric, as in the flame zone in a CI fuel spray (see Figure 1.4.). However, the extended Zel'dovich mechanism is not the only source of NO formation.

1.5.2 N_2O Pathway NO Formation Mechanism

At high pressures, oxygen atoms reacting with N_2 can result in the formation of nitrous oxide through a three body reaction:

$$4) \qquad O + N_2 + M \leftrightarrow N_2O + M$$
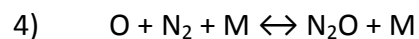
M is the third body and is a molecule of another compound, it is used to remove energy in order to complete the reaction. With no third body, the energy released in a collision between the two reactants (O and N_2) would be sufficient to cause them to decompose back into the original reactants (O and N_2). When the additional molecule is present the energy released is absorbed by molecule M and this prevents the N_2O from decomposing. Three body reactions like this are pressure sensitive and therefore, the importance of this reaction will increase at high pressures (Mellor *et al.*, 1998).

Usually N_2O reverts back to N_2 through:

$$5) \qquad H + N_2O \leftrightarrow N_2 + OH$$

$$6) \qquad O + N_2O \leftrightarrow N_2 + O_2$$
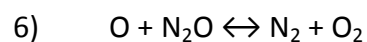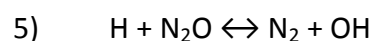
However, under conditions when the air-fuel ratio is lean, NO can form through the reaction:

7) $N_2O + O \leftrightarrow NO + NO$
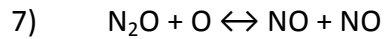
The O in 7) comes from:

8) $O_2 + M \leftrightarrow 2O + M$

I.e. O comes from the third body molecules interaction in an oxygen rich zone. This N_2O third body reaction can be used to explain NO formation when temperatures are lower, but pressures are high. At these conditions the three body reaction 4) becomes competitive with reaction 1) of the thermal mechanism.

NO represents around 90% of the NOx emission, the remaining 10% is the more toxic NO_2.

1.5.3   NO$_2$ Formation

NO_2 is formed from NO by the reaction:

9) $NO + HO_2 \leftrightarrow NO_2 + OH$
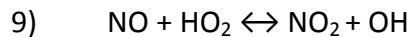
At temperatures below 1200K NO_2 will now be exhausted from the engine (Klimistra & Westing, 1995). At higher temperatures such as those typical of the flame zone, it reverts back to NO by the reaction:

10) $NO_2 + O \leftrightarrow NO + O_2$
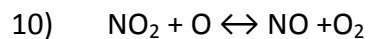
At low temperatures, unburnt fuel molecules can form the hydroperoxyl radicals (HO_2) needed to form NO_2 by reaction 11:

11) $RH + O_2 \leftrightarrow R + HO_2$
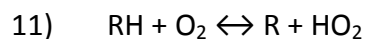
So, the formation of toxic NO_2 in this case is a by-product of thermal NO and incomplete fuel combustion.

1.5.4 Particulate Matter (PM) Formation in DI CI Combustion

The EC (European Community), the EPA (U.S. Environmental Protection Agency) and the Japanese Ministry of the Environment (the 3 most established emissions legislation regions) are yet to definitively define PM.

Generally PM is defined (for sampling purposes) as any matter in the exhaust that can be trapped on a sampling filter medium at below 52°C (EPA) or 47°C (EC). There are currently many problems with PM sampling methods. This is because the filter medium, the exact temperature, ratio and gas of dilution, have yet to be definitively defined. The dilution gas must therefore simply be sufficient to bring down the hot exhaust gas temperature to below circa 50°C. The makeup of the dilution gas is also debatable as there is an argument for an inert dilution gas as well as for air, which more accurately simulates a real life emissions dilution. It can be difficult to make accurate PM emission measurement comparisons where collection methods are dissimilar.

Though PM sampling is not yet well defined for combustion and emissions, it is known that PM itself is a complex emission, that includes many components. For clarity here the types of PM are separated into 3 categories:

1)   Solid Fraction (Solid Particulate Matter (SPM)),

<div style="text-align:center">

a)   carbonaceous soot

b)   ash (including metallic)

</div>

2)   Soluble Organic Fraction (Liquid Particulate Matter (LPM))

a) organic material derived from the fuel (range of boiling point (BP) hydrocarbons)

b) organic material derived from the engine lubricating oil (higher BP hydrocarbons)

3)   Water Particulate (LPM)

a)   water

b)   sulphuric acid SO_4 (when fuel sulphur is present)

1.5.6   Carbonaceous Soot formation in DI CI Combustion

Figure 1.5.shows the mechanisms that led to carbonaceous particulate formation and potential subsequent oxidation. The variables detailed by Broome and Khan (1971) remain true today. Though, Figure 1.5. has been modernised by the author to include forced induction (boost pressure) and EGR, which have become common in the intervening years. Underlined variables are variables that can either be controlled directly or perhaps optimised to reduce/increase the linked affects. At the top of the chart it is shown that as the amount of incompletely mixed fuel and its equivalence ratio Φ ($\Phi = \frac{1}{\lambda}$) increases, carbonaceous particulate release increases. The chart indicates logically, that carbonaceous particulate results from diffusion burning rather than combustion of a well-mixed fuel and air mixture whose equivalence ratio is close or equal to stoichiometric (this has been somewhat elucidated by Dec's model Figure 1.4.). For example it is known, that diffusion burning will be enhanced when fuel is injected after the start of ignition, during the mixing controlled combustion phase. The factors that affect diffusion burning are many. The main ones are; the ignition delay, the physical-chemistry, the injection rate and duration (potential sources can be traced using Figure 1.6.). A high initial injection rate or early start of a multiple injection can increase the premixed portion of the fuel and reduce

Net Carbon Release   **Oxidation of Net Carbon Release**

Amount of Diffusion Burning

Fuel Introduction After Ignition ── Ignition Delay ── Cetane No. of Fuel

Unmixed Fraction of Fuel Accumulated During Delay ── Rate & Duration of Injection

Compression Ratio

Injection Timing

Rate of Diffusion smoke Burning ── Overall Air/Fuel Ratio ── Fuel Injection Pressure

Rate of Injection ── Injection Nozzle

Inj. Nozzle Holes No. – Diameter Length

Flame smoke Temperature ── Fuel Distribution ── Configuration of

Fuel Sprays

Boost Pressure

Premixing During Delay ── Fuel Atomisation & Evaporation ── Fuel Injection Pressure

Compression Ratio ── Fuel Penetration & Impingement ── EGR Ratio

Heat Loss to Walls ── Air Velocity & Turbulence ── Combustion Chamber Design

Engine Speed

Inlet Port Design

Soot Burnup ── Air Velocity & Turbulence

Fuel Type

Gas Temperature ── Rate & Timing of Heat Release

Heat Loss to Walls   NOTE: Underlined variables can be controlled

Compression Ratio

Oxygen Available ── Overall Fuel/Air Ratio

Increase in variable increases exhaust

EGR Ratio

Time Available ── Boost Pressure

Increase in variable decreases exhaust

Mixing of Combustion Products

Engine Speed

Figure 1.5. A summary of diesel engine variables that affect soot particle formation and oxidation, adapted from Broome and Khan (1971).

carbonaceous particulate (Abdullah *et al.*, 2009).

From Figure 1.5. it is possible to see that the designer of a diesel combustion engine has many design opportunities. One is to increase compression ratio. This provides excess heat (and increased premixed B-C Figure 1.3.) avoiding excessive diffusion combustion and therefore carbon release. Other design development options are non engine based parameters such as, increasing the fuel cetane number which improves the evaporation and mixing processes, reducing diffusion burning and particulate formation. PM formation is just one aspect of the engine out emission. After formation of soot a proportion of the soot will oxidise in the vigorous high temperature environment in which the soot has formed. On the right hand side of Figure 1.5. the factors controlling the oxidation rate of the newly formed carbon is detailed. By increasing the time available for combustion, it can be possible to allow the incomplete combustion products (i.e. soot but perhaps others too) to mix with lean pockets in-cylinder. With a slow combustion the high temperature in-cylinder, when combined with time for mixing improves the amount of oxidation, thereby reducing soot (and indeed other incomplete combustion products like CO and unburnt HCs). The simplest most effective way to do this is of course is by reducing the speed of the engine.

For engine designers, a magic solution to soot formation and oxidation is improbable. There are many reasons for this. Perhaps the easiest way to explain why, is by explaining a 'trade-off' example, in this case, between NOx and soot. This however, is not the only 'trade-off' the engine designer has to consider, there are many and they are application dependant.

1.5.7 NOx Soot 'Trade-Off'

The engine designer would like to produce an engine that gave both low NOx and low PM emissions. *This is difficult.*
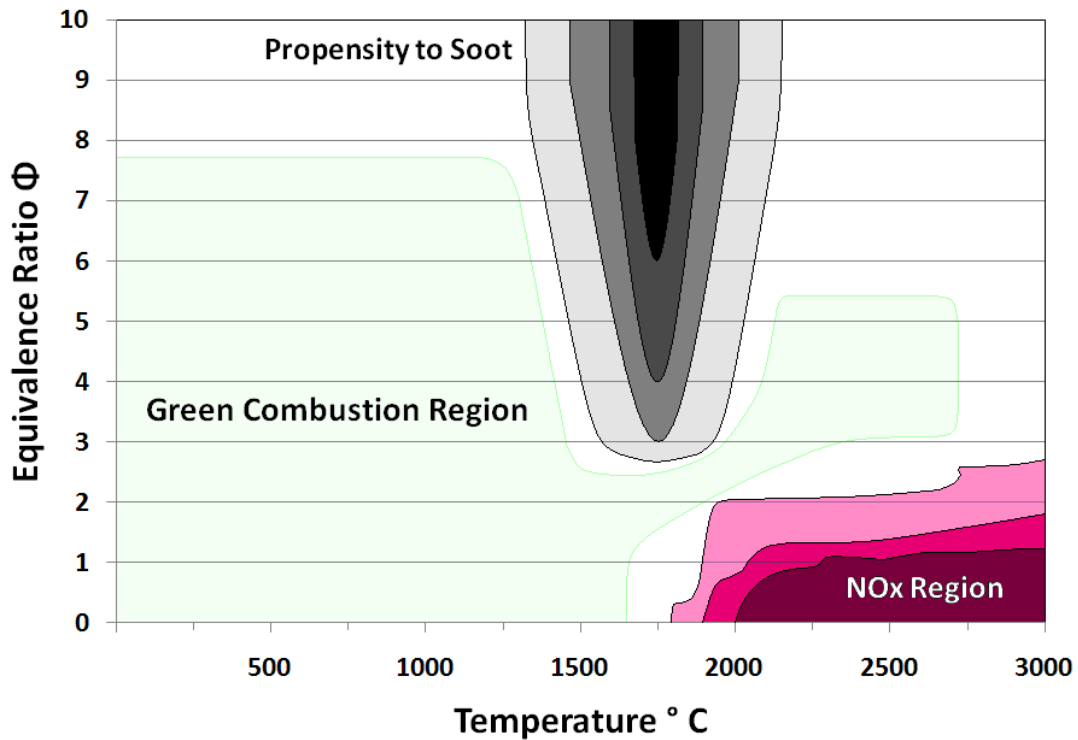
Figure 1.6.   NOx soot Emission Map, adapted from Kamimoto & Bae (1988).

It is difficult because smoke (PM) emissions reduce as time passes at high temperature (when O_2 is present). For NOx the opposite is true, as time passes at extreme temperature with O_2 available NOx increases. So it could be said, that what is good for one, is not good for the other. The engine designer has to make a compromise. Figure 1.6.details the NOx-Smoke emissions map against equivalence ratio Φ ($\Phi = \frac{1}{\lambda}$). This emissions map is adapted from Kamimoto & Bae (1988). Emissions maps such as this can be used as an effective illustrative argument for low temperature lean combustion strategies, for example homogenous charge compression ignition (HCCI). This strategy has merit, however there are many control issues. A contour map of soot- NOx emissions is especially interesting, as it

intuitively shows, that soot is most likely when the fuel level is high and the level of air is low at high temperature. It also shows that NOx is most likely at high temperature when air is readily available. This map also begs the question as to why for CI (lean combustion) soot is produced in relatively large amounts. Remembering that globally the equivalence ratio is around 0.5 (i.e. λ = 2). The answer therefore, would indicate that in some regions of the cylinder, the local equivalence ratio must be much higher.

This seems to make sense if combined with the optical work by Dec and others, Figure 1.4., as it is seen that most soot is produced within the injected fuel jet and away from the fresh air. It also holds true with NOx forming at the periphery (Figure 1.4.) of the fuel jet where the mixture will be leaner.

Until this point the initial formation of soot, talking generally about the position at which the soot forms and why as well as the environment under which the soot has formed has been considered. The potential subsequent oxidation of the soot has been touched briefly on, though not on the nature of the soot and how it forms.

1.5.8 Soot Particle Formation (including hydrocarbon formation)

Interestingly, soot often, though not always (extreme temperature), forms via precursor particulate condensate. These precursors are believed to be hydrocarbon molecules that have undergone some oxidation and/or pyrolysis. Alkynes from acetylene (C_2H_2) upwards as well as PAH are believed to be precursors of soot (Heywood, 1988). These small condensate precursors provide a site for the first appearance of soot and are considered as the nuclei of the soot particle. For this reason, the smallest (nano) particulate that contain just, or mainly, the nucleus of the particulate, are referred to as nuclei mode particulate 0-50nm (Kittelson, 1998).

1.5.9 Soot & Hydrocarbon Particulate Growth and Formation

There are 5 modes by which soot particulate can grow or be reduced; surface growth, coagulation, aggregation, oxidation and adsorption.

• *Surface Growth*   Gas phase species attach to the surface of small nuclei mode particulate (i.e. hydrocarbon condensate). If the hydrogen makeup of the hydrocarbon is low, surface growth of hydrogen occurs. Alternatively, when the hydrogen makeup of the hydrocarbon is high, a process of dehydrogenation may occur, adding the remaining carbon to the surface. The reality is a complex combination that is perhaps still not fully understood. Heywood (1988) makes a more detailed account of this. Surface growth leads to an increase in the size of the particulate, but not the number (N) of particulate. The majority of the soot in CI combustion with diesel fuel is generated this way.

• *Coagulation*   As the name suggests, coagulation is when two soot particles collide with one another and coalesce to form one particulate. This mode decreases the overall number (N) by forming a new single soot particulate of increased size (usually accumulation mode sized).

• *Aggregation/ agglomeration*   This is when a particle that has finished its surface growth stage, comes into contact with other particulate, but does not coalesce. Instead the particulate remains as separate particulate, definable by N. This particulate has weak cohesive bonding with the other particulate. The particles now aggregate into chains and clusters making larger course mode particulate Figure 1.7.c.

a) 2 Primary particles b) Agglomeration into a chain c) Particle cluster forms from chains
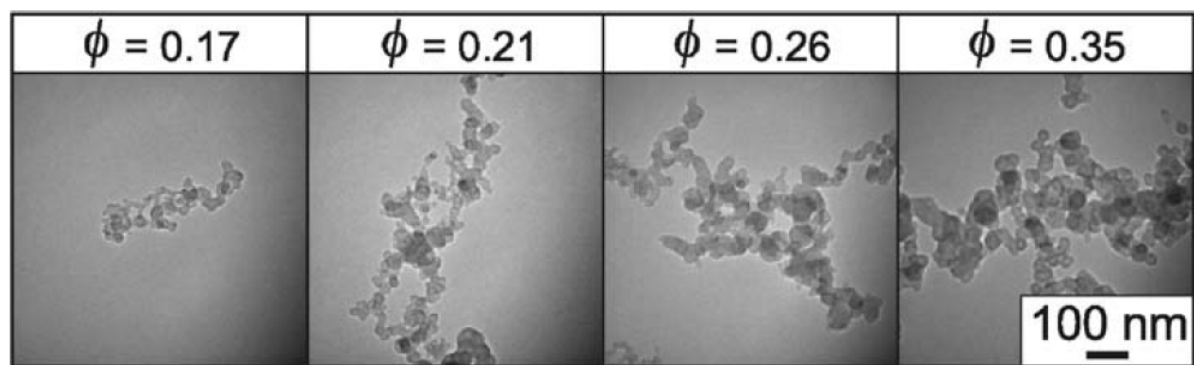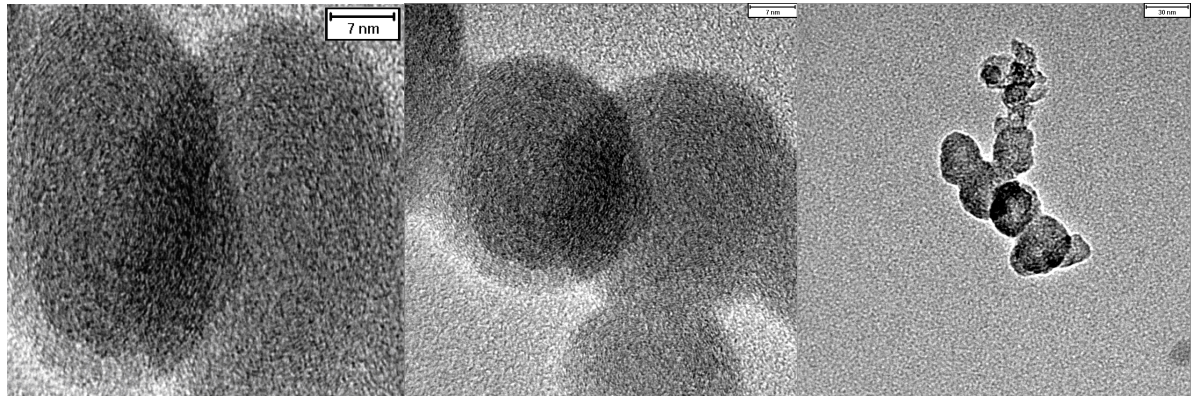
Figure 1.7. TEM images of exhaust gas particles. *Upper images* (a, b and c) have been reproduced by permission from Lapuerta *et al.* (2007). The *Lower images* were sampled at four different values of the fuel/air equivalence ratio Φ from a DI CI, taken from Kock *et al.* (2006).

- *Oxidation* At all stages of the soot formation process, it is also possible for oxidation of the newly formed soot, or the precursor to occur, forming gaseous CO and CO_2. This can happen when turbulence in the hot environment moves the soot into a lean pocket in cylinder. The final emission of soot is therefore dependent upon the ratio of formation – ratio of oxidation (often called burnout ratio).

- *Adsorption* & condensation of unburnt hydrocarbons, happens when hot engine gases containing soot are exhausted from the engine and mixed/diluted with the surrounding air. This creates a thin layer of adsorbate hydrocarbon molecules, on the surface of previously formed particulate. This unburnt hydrocarbon particulate adheres to the

surface by a combination of chemical and/or physical forces, as well as, condensation of individual hydrocarbons. This is due to the dilution effect, which reduces the global temperature. This real life dilution is simulated for the purposes of emissions sampling (see beginning of section 1.5.4). It is understandable that this process is sensitive, as more adsorption and condensation will occur as temperature is reduced (higher dilution), so vapour pressure decreases, as dilution ratio increases. This is because the hydrocarbon concentration is reduced. Condensation is of course most likely when concentrations of hydrocarbons are higher, so the ratio of adsorption – condensation will also be dilution ratio dependant.

- **_Water Particulate Matter Formation_** Water PM is a product of complete combustion, it is also naturally present in air. Water PM can (in the same way as unburnt hydrocarbons) adsorb and condense during the dilution process. Not all definitions of PM include water e.g. Stone (1998) as it is benign and therefore not a pollutant. However, water, by strict physical definition is particulate matter at 52 °C or less (EPA) and it can be a pollutant in combination, most especially when sulphur is present.

1.5.10 Hydrocarbon Formation

A good deal of hydrocarbon formation has been covered in section 1.5.8, as much of the hydrocarbon emission is formed alongside soot formation as previously detailed. For clarity, hydrocarbons are now considered as an individual emission (as some of the emitted HC will not be soot associated) though it should be noted how these emissions can be related. HCs in the exhaust of a CI engine consist of unburnt fuel, partially decomposed fuel molecules and recombined intermediate compounds. Potentially the HCs in CI exhaust can also

originate from the lubricating oil. The source of HCs in DI CI engines predominantly originate through insufficient mixing of fuel and air, poor mixture formation and the appearance of cold quench layers on combustion chamber surfaces. For an optimised modern DI CI engine, it is thought that there are several main sources of HCs:

1. Fuel can dribble out of the injector sac volume (The "sac" is a small volume within the fuel flow path of a fuel injector (Dreeben *et al.*, 1992)) and lean mixtures that are formed during the ignition delay period.

2. Liquid films form on combustion chamber surfaces.

3. Quenching in the squish volume outside the piston bowl.

4. For light duty diesel engines, a high power density is required. To achieve this higher RPM is utilised (higher RPM reduces the time for mixing so it is more difficult to achieve complete mixing during combustion).

Some interesting work by Paul Miles at Sandia National Laboratories (U.S.) highlights the conditions and sources of unburnt hydrocarbon (UHC) (Figure 1.8.). During the ignition delay (premixed) period, the fuel injected, mixes with air and can produce a wide range of equivalence ratios, (Figure 1.8.). This is because some regions in the combustion chamber are too lean to support combustion, whilst others fall within the flammability limits and finally some regions are too rich and evaporate too slowly to combust. Overall (globally) however, the mixture is lean.

Figure 1.8. apparently highlights the potential danger of fuel combustion chamber wall interactions, as well as, the co-dependence of hydrocarbon and soot formation (the green circled region.
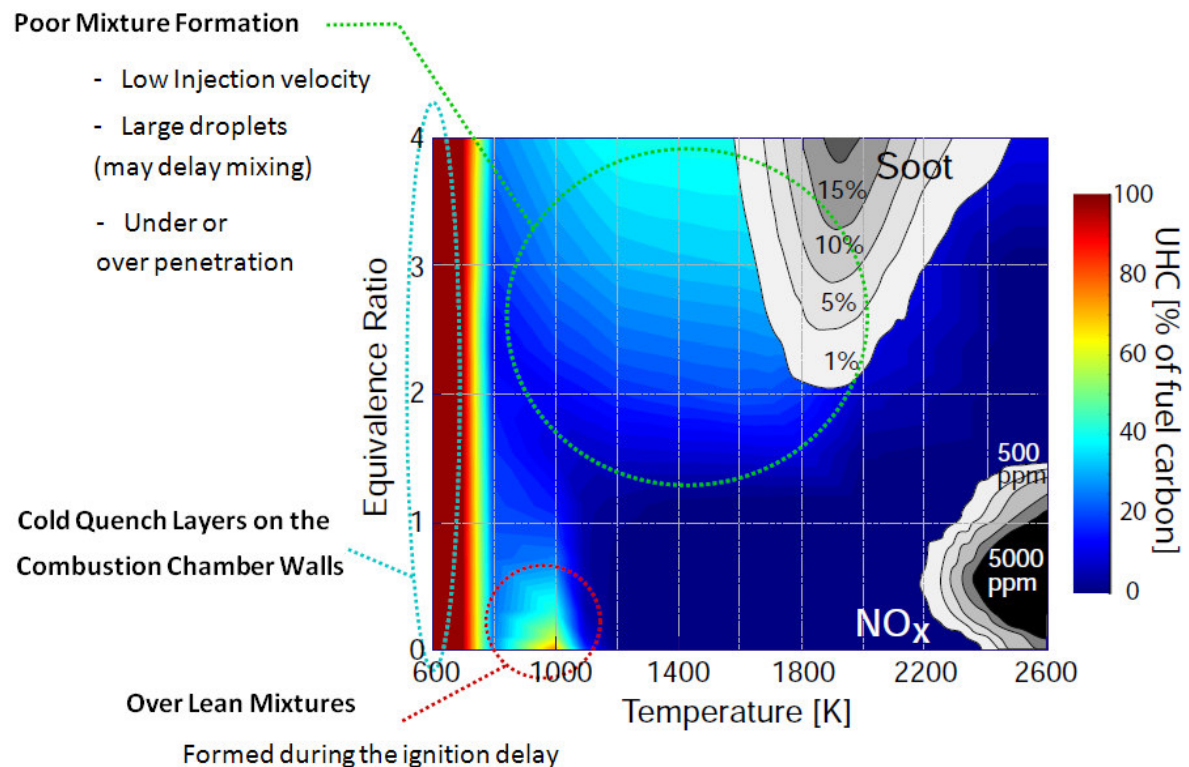
Figure 1.8. Conditions of UHC formation highlighting sources, adapted from Miles (2007) which uses a NOx – Soot map created by Kitamura *et al.* (2002).

Specifically considering fuel injected after the start of combustion, (in the mixing controlled combustion region C-D, (in Figure 1.4.) fuel pyrolysis may occur, (due to the vigorous environment into which the fuel is being injected) or, where oxygen is available, there will be a rapid oxidation. Any conditions that slow down the rate of pyrolysis and/or oxidation, may lead to a localised rich mixture and therefore, a delay/ lack of combustion. When this happens the exhaust is likely to contain more UHC.

1.5.11 CO Formation

Carbon monoxide is generated by oxygen deficient combustion of material containing carbon (this is almost universally true, apart from dissociation of CO_2). It could be said that the air fuel ratio (λ or $\frac{1}{\phi}$) drives its formation. I.e. when there is not enough available oxygen

to burn all the fuel, a partial reaction product (CO) is created (Eastwood, 2000). The created CO is usually accompanied by corresponding HCs.

Diesel CO emissions are low because the mixture is globally lean. But since this mixture is highly heterogeneous a certain amount of CO is generated locally in the combustion chamber. Attention is drawn again to a well presented depiction of CO formation conditions by Miles (2007) (Figure 1.9.).
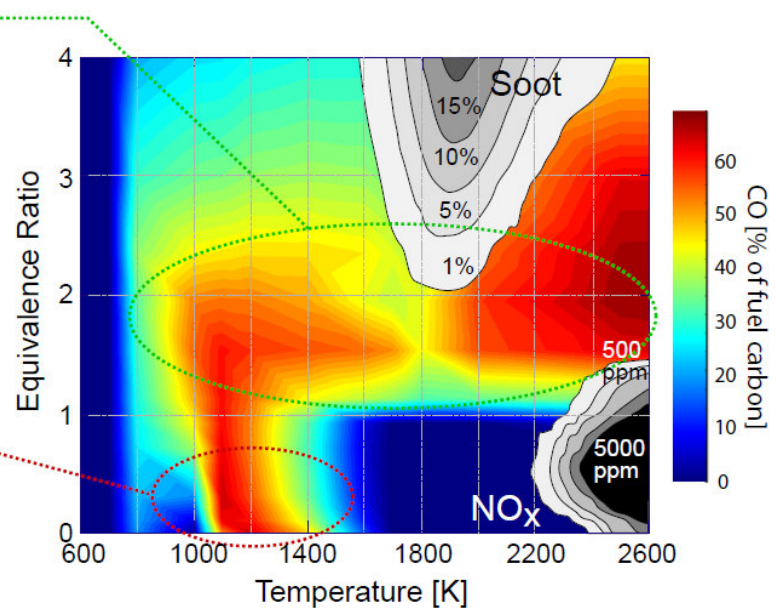
Figure 1.9. Conditions of CO Formation Highlighting Load Sources, adapted from Miles (2007) which uses a NOx – Soot map created by Kitamura *et al.* (2002).

Importantly in Figure 1.9. it is shown that (for a heavy duty modern CI engine using diesel), CO emissions can form in (globally) both fuel-rich and fuel-lean regions.

1.6 STRATEGIES AND AFTERTREATMENT TO CLEAN-UP EMISSIONS

This section details how current emissions strategies and aftertreatment are used to clean-up CI engine emissions. Currently exhaust clean-up is focused upon the prevailing CI fuel, diesel. So, the strategies and technologies have been developed with diesel combustion in mind.

The most important (regulated) emissions remain the focus of this section and aftertreatment will be the core issue.

1.6.1 Exhaust Gas Re-circulation EGR

EGR is utilised primarily as a nitrogen oxide (NOx) emissions reduction technique. The EGR technique was originally developed from flue gas re-circulation for stationary engines. It was first applied to SI engines in the 1970s to reduce NOx emissions. Since then it has been applied with success to CI engines. EGR is achieved by allowing a proportion of the exhaust to be looped back to the inlet manifold and mixed with the fresh charge of air. The re-circulated gas displaces a portion of the fresh air charge. The most efficient EGR systems are water jacket cooled, to minimise thermal throttling. Figure 1.10. is an engine schematic outlining a cooled EGR system.

The key to EGR, is the effect that it has in reducing cylinder temperatures. This makes the reactions of the extended Zel'dovich mechanism (Equation 3) less likely and this can really be appreciated by observing the NOx formation map (Figure 1.6.). Many interesting works by Ladommatos and Zhao at Brunel University research the reasons for the temperature reduction. Ladommatos *et al.* (2000) is of specific interest, as this paper makes real efforts to eliminate variables and rank the causes of reduced cylinder temperatures.
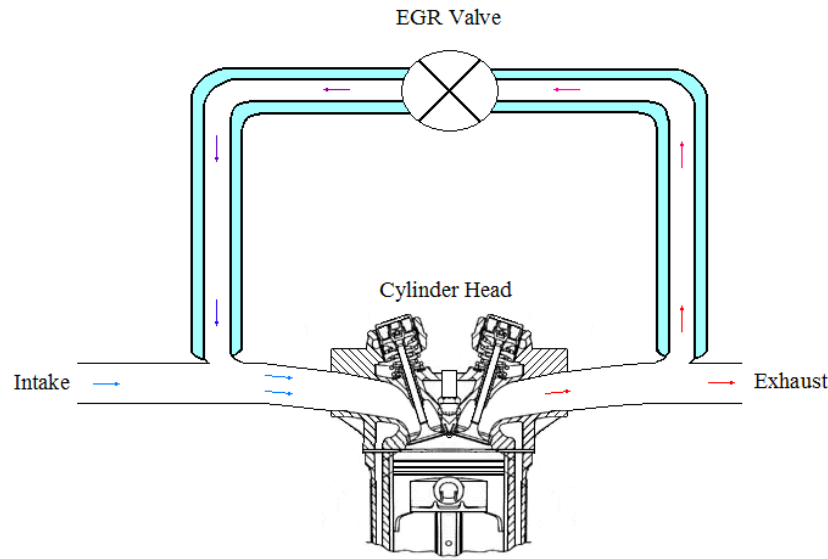
Figure 1.10. Cooled EGR adapted from Rounce *et al.* (2010).

Temperatures are reduced primarily due to the reduction of oxygen availability during combustion (dilution effect). The dilution effect is when the reduction in available oxygen means that locally, flames must broaden themselves and this dilutes the local flame temperature. Dilution accounts for around 90% of the in-cylinder temperature reduction (and therefore, NOx reduction), the remaining 10% is attributed to the chemical effect. The chemical effect is due to CO_2 and H_2O dissociation at high temperature, as well as potential active participation of EGR reactants. The result of these chemical processes affects the equilibrium of the combustion reaction. Very little in-cylinder temperature reduction is due to the thermal effect i.e. specific heat capacity increase of reactants during EGR (this had previously been thought to be a major factor).

High EGR rates can reduce the burn rate and increase cycle-cycle variation, this can give an unstable combustion. To overcome this, the proportion of EGR circulated has to be limited. Under certain conditions, for example light loads, it is actually possible to utilise EGR

to not only reduce NOx but also PM, (Herzog *et al.*, 1992). This can be appreciated by referring to Figure 1.6. detailing the NOx soot map.

Use of EGR has several negative effects, such as increased amounts of incomplete combustion products like HCs, CO and soot. Figure 1.11. shows how EGR rate effects the major emissions for a light duty common modern diesel engine.
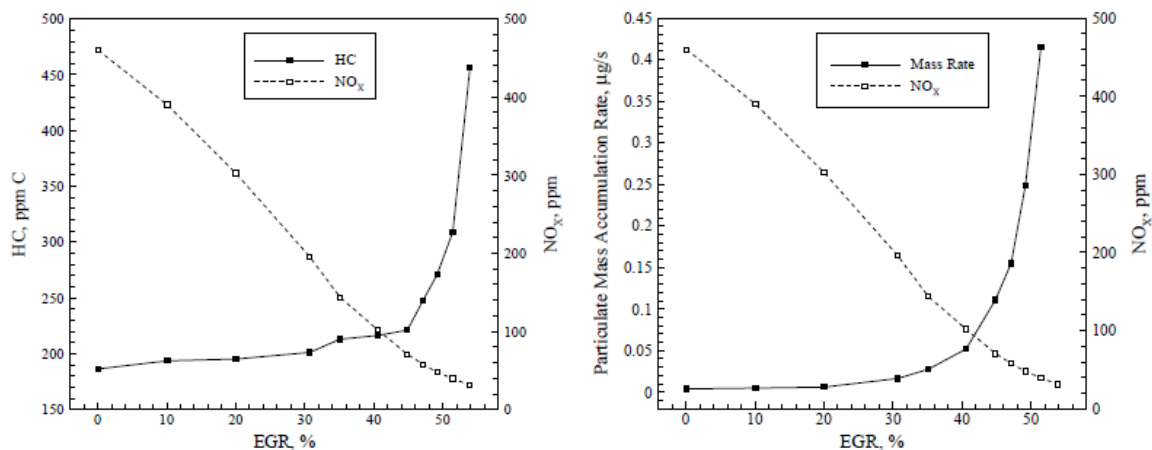
Figure 1.11. Effect of EGR ratio on the NOx/HC & NOx/PM emission trade-off for a 1.9L VW TDI engine, 1200 rpm at 30% load. Taken from Wagner *et al.* (2000).

Understandably, with EGR and most especially for re-circulation of PM, there will be an effect on the service interval of internal engine components and the life of the lubricating oil. EGR has become essential for the modern CI engine to meet NOx emissions legislation such as, Euro V (Figure 1.2.). As a consequence, the resulting incomplete combustion products have to be dealt with by the aftertreatment system.

1.6.2   Aftertreatment Catalysts

A catalyst is a substance which can change the rate at which a chemical reaction can take place, without the catalyst being consumed in the reaction, though in practice, slow deactivation is almost always seen. Catalysts have been observed, for many years (though

perhaps not truly understood), indeed Sir Humphry Davy (1817) provides an early account of

'... a new and curious series of phenomena' using platinum and palladium coils in coal gas.

With the benefit of hindsight these 'phenomena' were examples of catalysis.

Catalysts work by providing an alternate reaction mechanism that has lower activation

energy, they do this by providing a different transition state. As a consequence, more of the

molecular collisions of a fluid have sufficient energy to reach the transition state. Put simply,

reactions can happen at lower temperatures than might otherwise be possible without the

catalyst. (Bowker, 1998; Eastwood, 2000)

For automotive applications heterogeneous catalysts (where the catalyst is in a different

phase to the reactants) are the principal concern. This means that the catalyst in auto

applications is usually a solid which interacts with the exhaust gas. To ensure that as much

gas as possible interacts with the catalyst, the catalyst is manufactured to have a very large

surface area. The catalyst is usually distributed evenly over a substrate of another
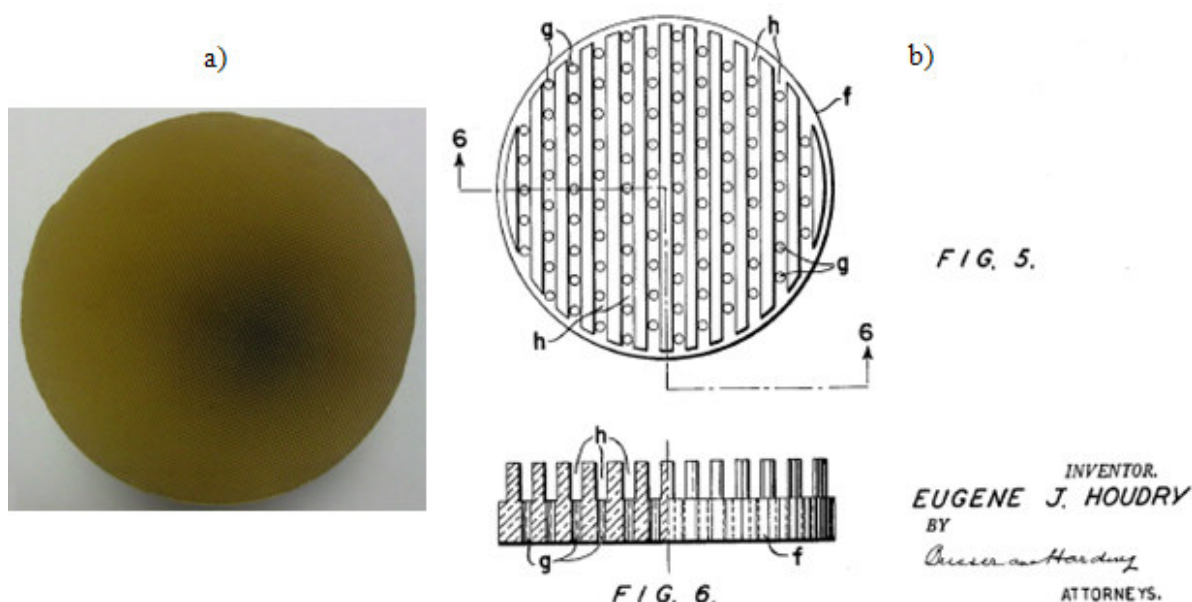
Figure 1.12. a) A typical automotive catalyst with high cell density b) Monolith metal oxide washcoat containing catalyst supported on a ceramic monolith, taken from Houdry's Catalytic Structure and Composition patent (Houdry, 1956).

Material, to provide support, create effective surface dispersion, minimise pressure drop and to reduce cost (see Figure 1.12.a). Catalysts are defined by two fundamental properties:

- Activity - measure of the catalyst's ability to enhance the rate of a reaction.

- Selectivity - the catalyst's ability to accelerate certain reactions in preference to others.

The concept of catalytic pollution removal for combustion engines is not new. The first automobile to use a four stroke internal combustion engine was patented by Karl Benz (1886) and Rudolph Diesel made the first diesel (CI) engine in (1897) (Benz, 1886; Moon, 1974). It was not long, until '....the production of evil smelling gases by motor-vehicles...' was noted and a potential extra catalytic combustion using a platinum catalyst in an exhaust box was devised (Frenkel, 1909). Frenkel's paper is also relevant because it highlights how SI exhaust has sufficient temperature for catalytic oxidation, as well as how diameter and length of the exhaust box could be adjusted to account for changes in engine size.

It could be said that the modern heterogeneous catalytic converter was invented by Eugen Houdry in the 1950s see Figure 1.12.b. This design bears some resemblance to a modern day monolith automotive catalyst, though sadly Houdry was unable to bring his invention to a production vehicle, as legislation at the time did not necessitate their use.

1.6.3 Catalytic Reduction of NOx

Lean CI combustion yields exhaust with abundant oxygen (lean exhaust), the temperature is also low compared to SI, typically 180 - 450 °C. These conditions are suitable for catalytic removal of HCs, CO and PM via oxidising reactions, but they are more difficult for NOx removal. Ideally a catalyst would be developed that could break down NO or NO_2 directly into N_2 and O_2. Initially this was considered a possibility as NO and NO_2 are

thermodynamically less stable than N_2 and O_2. Many catalysts have been investigated and some have been found to be active in the reduced state, but any oxygen in the feed gas (especially for lean CI) or released by the decomposition of NO cause problems. The oxygen competes with the NOx for reductant, and as competes with NO for the adsorption sites and thus, poisons the catalysts activity (Harrison *et al.*, 1982; Iwamoto & Hamada, 1991). The only known ways to counteract this using today's catalysts, are by removing the surface oxygen and thereby regenerating the catalytic activity. This could be achieved by using extreme reaction temperatures or via a gaseous reductant. Equation 4 a) shows the catalytic route for NO and NO_2 removal that was adopted for stoichiometric SI combustion developed during the 1980s (used in the ubiquitous 3-way catalytic converter).

Reduction of NO/NO$_2$ into N$_2$

$$NO \text{ (or } NO_2) + CO \rightarrow \tfrac{1}{2}N_2 + CO_2 \tag{1}$$

$$NO \text{ (or } NO_2) + H_2 \rightarrow \tfrac{1}{2}N_2 + H_2O \tag{2}$$

$$(2 + \tfrac{n}{2})NO \text{ (or } NO_2) + C_yH_n \rightarrow (1 + \tfrac{n}{4})N_2 + yCO_2 + \tfrac{n}{2}H_2O \tag{3}$$
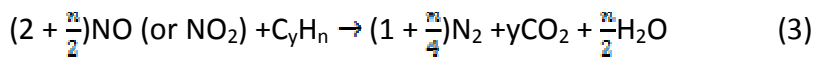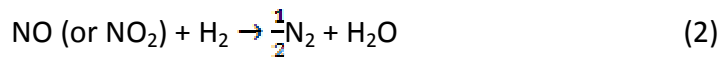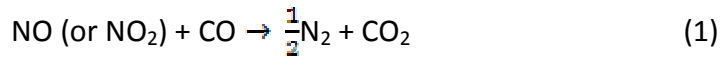
Equation 4 a) NOx reduction in a 3-way catalytic converter

For lean CI exhaust, CO and HC oxidation are promoted by the lean conditions over the catalyst, so, reactions 1 & 2 in Equation 4 a) become less likely over the catalyst. Eastwood (2000) humorously equates NOx removal in lean exhaust to "drying washing in the rain". To date, the problem of NOx reduction in lean exhaust has no simple solution. Several methods have been proposed, though only 2 have realised significant success in production vehicles, consequently these will be discussed in detail:

1) Direct NO Decomposition

2) Urea selective catalytic reduction   * (Commercial success)

3) Plasma O_3 and OH radical formation & direct thermal decomposition of NOx [1,2]

4) NOx storage catalytic converters   * (Commercial success)

5) Reforming of Hydrogen for selective catalytic reduction (SCR) [3,4]

References   1   Hammer (1999)   2   Chung *et al.* (2000)

3   Tsolakis *et al.* (2004)   4   Sitshebo *et al.* (2009)

1.6.4   Ammonia Selective Catalytic Reduction for Stationary Powerplants

Using nitrogen compounds, such as, ammonia or urea in a SCR process was originally developed for stationary power plant applications. There are two main types of ammonia that can be used in stationary SCR systems. Pure anhydrous ammonia, and aqueous ammonia. Anhydrous ammonia is toxic, and requires pressurised storage tanks and piping due to its high vapour pressure. Aqueous ammonia, $NH_3 \cdot H_2O$, is less hazardous and easier to handle. The process works by injecting ammonia/aqueous ammonia into the exhaust flue gas stream of the power plant before the catalyst.

Many chemical reactions occur in an ammonia SCR system, Reactions (4-8) (Cho, 1994). All of these desirable reactions reduce NOx to N_2. (5) in Equation 4 b) is the dominant reaction mechanism:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad\qquad (4)$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad\qquad (5)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad\qquad (6)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad\qquad (7)$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \qquad\qquad (8)$$
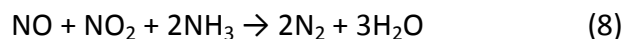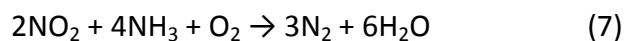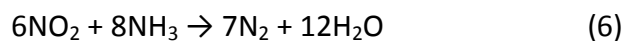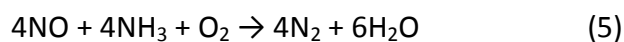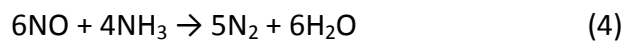
Equation 4 b) Ammonia NOx reduction reactions

At elevated temperatures, undesired reactions can consume NH_3. An example is the formation of nitrous oxide (N_2O):

$$4\ NO_2 + 4\ NH_3 + O_2 \rightarrow 4\ N_2O + 6\ H_2O \qquad (9)$$
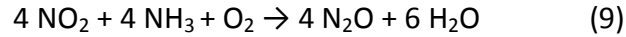
Care must also be taken to avoid the oxidation of NH_3 as oxidation will consume the ammonia and in the worst case (10) (direct oxidation of NH_3) results in NO production:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (10)$$
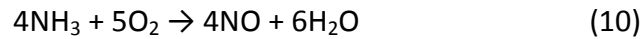
SCR requires precise control of the injection rate of ammonia. If the injection is too small the NOx conversion is low. An injection rate which is too high can result in release of ammonia to the atmosphere, this is known as ammonia slip (Koebel *et al.*, 2000). This 'slip' of ammonia increases as the proportion NH3:NOx increases. This can be rectified with a downstream oxidation catalyst (OC).

1.6.5   Urea for Mobile SCR

Ammonia is toxic and has potential handling problems. A source of NH_3 that is non toxic, with no handling problems, that could decompose readily and completely in a reactor to form ammonia, whilst creating no harmful by-products was sought. Combining these factors with cost and availability, led to a water solution containing urea $CO(NH_2)_2$ becoming the preferred choice. Urea is produced commercially by the dehydration of ammonium carbamate. It is estimated that the total world production would only have to increase by only a few percent to supply all the urea required for automobile combustion applications (Tiax, 2003).

On injection into the hot exhaust gas, the water in the urea solution evaporates. Thermal decomposition of the urea then occurs by reaction (11) forming ammonia and isocyanic acid in gaseous form:

41

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO \qquad\qquad (11)$$

Hydrolysis over the catalyst of the isocyanic acid then occurs reaction (12):

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad\qquad (12)$$
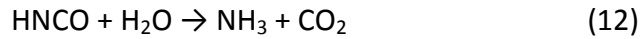
Now that ammonia has been formed from urea (11 & 12), the ammonia is able to perform reactions (4-8) over the catalyst. The end result is a significant removal of NOx from the exhaust stream, usually more than 80%, (Shimizu *et al.*, 2007).

Urea injection systems are not fail-safe. They rely on a local urea infrastructure and the ethics of the end user who has to replenish the urea reservoir (as there is no immediately apparent benefit to the user, just a cost).

To date urea SCR systems have been the most successful, particularly for heavy duty applications where packaging issues are reduced.

1.6.7   NOx Storage Catalysts

NOx adsorber-catalysts were developed to control NOx emissions from lean burn SI engines and from CI engines. The adsorbers, are incorporated into the catalyst washcoat, they chemically bind nitrogen oxides during lean operation. When the adsorber capacity becomes saturated, the system is regenerated by a period of rich engine operation, and the released NOx is catalytically reduced to nitrogen.

This technique has many different names, for clarity here are some of the well known ones:

• Lean NOx trap (LNT),

• NOx adsorber catalyst (NAC),

• DeNOx trap (DNT)

•NOx storage/reduction (NSR) catalyst

•NOx storage catalyst (NSC)

NOx adsorbers are more effective at trapping NO_2 than NO (NO is prevalent >90%), (Epling, *et al.*, 2004). Consequently NO is first oxidised over a (usually platinum) catalyst via:

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \qquad\qquad (13)$$

NOx accumulates over and on the catalyst surface, due to NOx adsorption, forming nitrates or nitrites with ionic bonds. Reactio (14) shows adsorption of NO_2 by barium nitrate.

$$BaCO_3 + NO_2 + \frac{1}{2}O_2 \rightarrow Ba(NO_3)_2 + CO_2 \qquad\qquad (14)$$
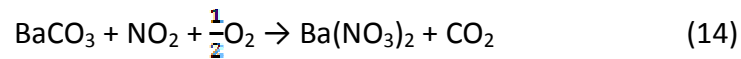
Barium oxides are a typical material used for nitrate and nitrite storage (Chaize *et al.* 1998). Reactions 13 and 14 are depicted in the left hand side (LHS) of (Figure 1.13.).
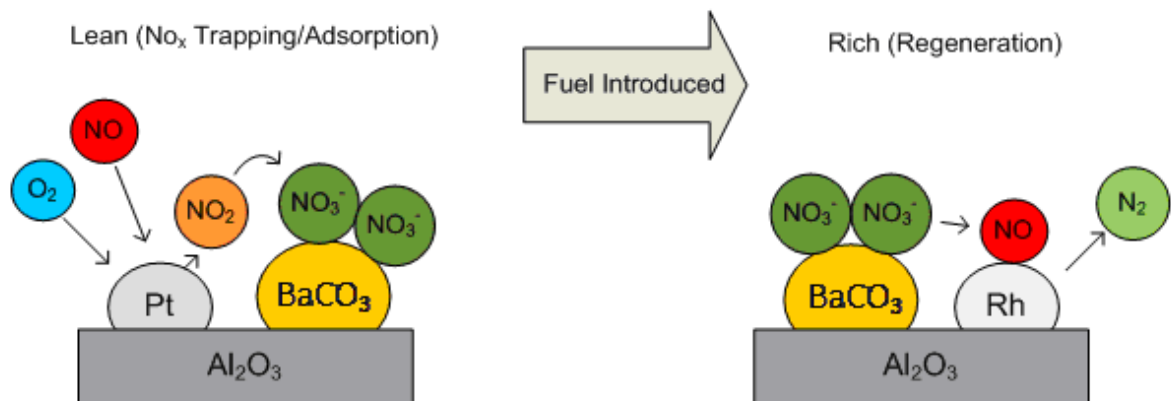
Figure 1.13. NOx Removal by Adsorption and Periodic Regeneration, adapted from Miyoshi *et al.* (1995) and Krämer *et al.* (1999).

After a typical period of about 60 seconds the trapping component (barium oxide) will become saturated with NO_3 (Klingstedt *et al.*, 2006). The exhaust condition is now switched to a fuel rich condition i.e. more fuel is injected, this can be achieved via an additional injection in-cylinder during the exhaust stroke, or via another fuel injector in the exhaust system. When the additional fuel is introduced, oxygen is replaced (and often consumed via

an upstream oxidation catalyst) by the hydrocarbons, carbon monoxide, and hydrogen and the local temperature may be increased. The rich condition lasts for about 8 seconds.

If the engine runs rich or at extreme temperatures the nitrate species become thermodynamically unstable and they will decompose to produce NO or NO_2 (15 & 16):

$$Ba(NO_3)_2 \rightarrow BaO + 2NO + 1\tfrac{1}{2}O_2 \qquad (15)$$

$$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + \tfrac{1}{2}O_2 \qquad (16)$$
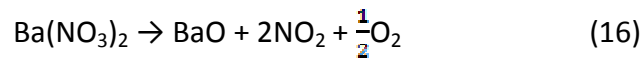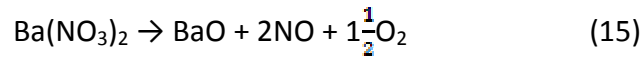
Under rich conditions, the nitrogen oxides are reduced in an analogous fashion to NOx removal for SI engines, i.e. reactions (1-3) by CO, H_2 and HCs over the reduction catalyst, in the conventional three-way catalytic process. After a short period, the rich condition is stopped and reactions 13 & 14 take over, re-starting the whole process.

The adsorber catalyst is particularly susceptible to sulphur poisoning, so ultra low or zero sulphur fuel is preferred. In 2001, the US EPA commissioned a 'proof of concept' to show that future emissions standards (beyond 2004) were both feasible and achievable. The impressive aftertreatment system demonstrated, (using an adsorber catalyst) comfortably meets the much later US2007 heavy duty (HD) diesel emission standards (Schenk *et al.*, 2001). In this system a minimum NOx reduction of 86% was achieved for the worst tested condition. NOx adsorber systems are perhaps not so efficient at low exhaust gas temperatures, but with no need for additional reservoirs, infrastructure or driver input, these systems are becoming more popular.

1.6.8 Aftertreatment of Particulate Matter

PM emissions from internal combustion (IC) engines are of paramount importance, as certain PM emissions are dangerous to human health and the environment (Gordon *et al.*, 1998; Pope *et al.*, 2002; US EPA, 2004a; US EPA, 2004b; Krzyzanowski, 2005;). As a result these emissions are stringently limited. In Europe, PM emissions are becoming more tightly controlled (Figure 1.14.), with for example, the Euro V PM regulations since September 2009, now including a PM total number limit at $6 * 10^{11}$ km^{-1} (EC, 2007). It is widely believed that in order to meet these emission regulations, improvements in engine design, fuels and the incorporation of aftertreatment are required. Health studies have shown that solid PM can be hazardous to human health, (Pope, 2000; Samet *et al.*, 2000; Peters *et al.*, 2001;) small nano particulate can have a magnified affect (Hartogg *et al.*, 2003; Helfenstein *et al.*, 2008).
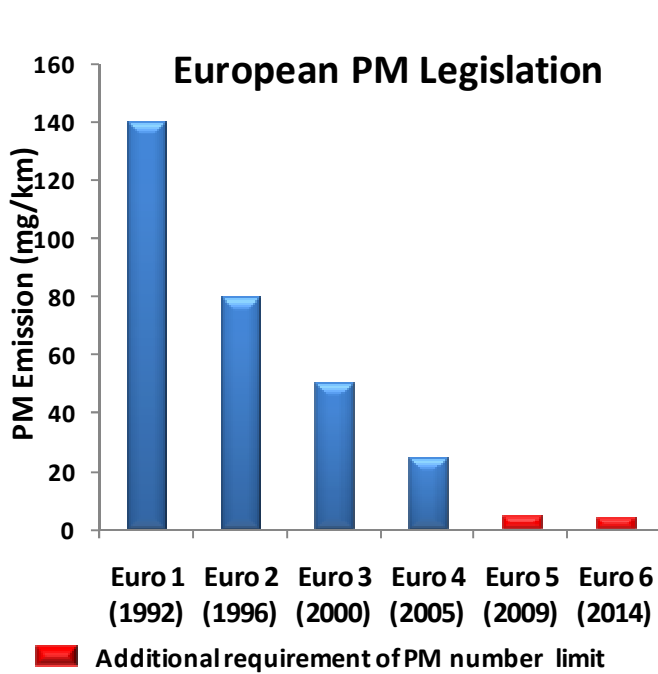
Table 1.1. Particulate Makeup

Solid Fraction Solid PM	
Origin	
Carbon	Fuel & Lube Oil
	Additives & Engine
Ash	Wear

Soluble Organic Fraction (SOF) Liquid PM (< 47 ° C)	
Origin	
Hydrocarbons	Fuel & Lube Oil
Water	Fuel & Background
Sulphates	Fuel & Lube Oil
(SO$_X$)	Sulphur

Figure 1.14. PM emission limits since 1992.

The composition of particulate matter sampled from cooled and diluted exhaust is defined in Table 1.

Health studies to date have focused upon the damage caused by solid particulate (Pope, 2000; Samet *et al.*, 2000; Peters *et al.*, 2001; Hartogg *et al.*, 2003; Helfenstein *et al.*, 2008). Thus with a widening of the range of fuels in use in the future, it will be important to study the health effects of a wide range of PM types, and this may also become an important distinction for future PM legislation.

Since PM consists of a variety of both solid (e.g. carbon) and liquid (e.g. water) constituents. Liquid PM can often be gaseous at early stages of the exhaust and aftertreatment process and this is highly dependent on the local exhaust gas temperature. Clearly to treat these two phases of PM emissions, both gaseous fluid interaction and physical filtration are required.

1.6.9 Liquid Particulate Matter Cleanup, Oxidation Catalysts

Oxidation catalysts (OC) (AKA diesel oxidation catalysts (DOCs)) are utilised in CI engines to promote chemical oxidation of HCs and CO as well as the soluble organic fraction (SOF) portion of CI engine particulate (i.e. LPM when diluted). The OC utilises the abundant oxygen which is present in (lean) CI engine exhaust, to oxidise the unburnt HCs, CO and SOF fraction of particulate. The OC additionally is of some benefit in the control of several (identified as dangerous) unregulated HC related species, namely PAHs (US EPA, 2002). The basic oxidation of HCs and CO is detailed in equations 17 & 18:

$$C_nH_{2m} + (n + \frac{m}{2})O_2 \rightarrow nCO_2 + mH_2O \qquad (17)$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad (18)$$
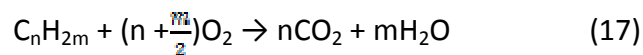
The reaction mechanism in OCs can be explained by the presence of the active catalytic sites on the surface of the catalyst carrier. These sites have the ability to adsorb the oxygen from the carrier gas. There are three stages in catalytic oxidation:

1. Oxygen becomes bonded to a catalytic site

2. HCs and CO, diffuse to the surface and then react with the oxygen

3. CO_2 and H_2O, desorb from the catalytic site into the exhaust.

It is possible for a highly loaded platinum or palladium OC of high cell density and sufficient length, to eliminate CO and almost eliminate HCs from diesel exhaust (with just a small reduction in volumetric efficiency).

1.6.10 Solid Particulate Matter Cleanup

Diesel particulate filters (DPFs) are physical filtration devices that can remove soot (solid PM) from a diesel engines emission. There are many ways that this can be achieved, the most popular method is the wall flow monolith DPF. Exhaust gas containing particulate (red arrows) enters the filter from the left (Figure 1.15.). The cells of the filter are plugged at the downstream end of the filter so the exhaust cannot exit the cell directly. The exhaust gas must instead pass through the porous walls of the filter channels. The solid particulate now becomes trapped within the porous walls, and the inlet channel surface (Figure 1.15.) on the upstream side of the filter and clean exhaust gas exits the filter (blue arrows). Catalysed DPFs such as the CCRT® (catalysed continuously regenerating technology) by Johnson Matthey have been shown to remove 99% of PM by mass and 85-99% by particulate number for diesel fuel (Lakkireddy et al., 2006).
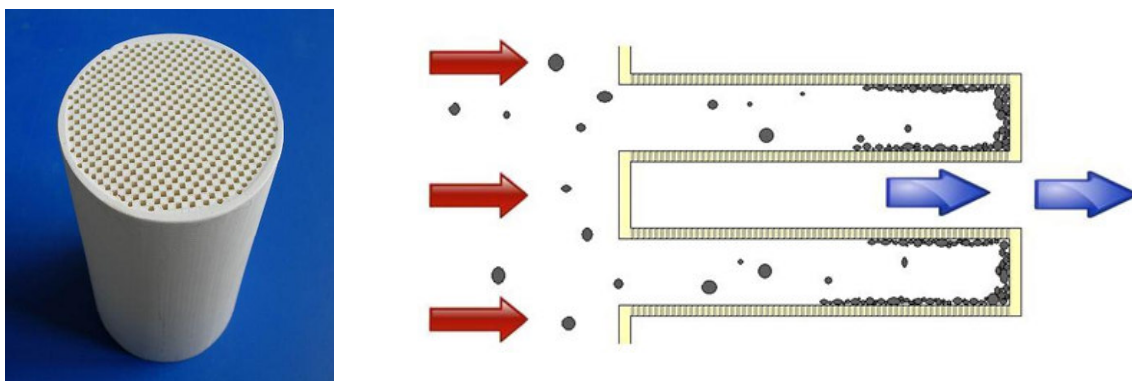
Figure 1.15. Cordierite diesel particulate filter (wall-flow monolith).

PM will gradually fill the DPF so it has to be removed from the filter or it will cause blockage. This can be achieved by oxidation of the soot in a regeneration process. There are several available routes to achieve this, either actively (by raising local temperatures) and passively (at the exhaust temperature). Active regeneration requires a periodic input of energy, resulting in reduced fuel economy. While passive regeneration does not. For example, the CCRT$^{®}$ is a passive system which utilises a more powerful oxidant than O_2. NO_2 can oxidise diesel particulate at higher rates and lower temperatures than O_2 even as low as 250° C (Allansson *et al.,* 2002). A proportion of NO_2 exists naturally in diesel exhaust. A diesel oxidation catalyst is installed upstream of the DPF, an increased proportion of NO_2 becomes available due to the oxidation ~ $NO + 1/2O_2 \leftrightarrow NO_2$ which is promoted in the diesel oxidation catalyst (DOC).

Chapters 6, 7 & 8 in this thesis will assess filtration technologies (Prototype bi-functional DOC/NOx storage catalyst, DOC and DPF) for ULS diesel and several future green fuels, in an attempt to highlight similarities and differences between PM produced from diesel combustion and the fuels of the near future.

CHAPTER 2

RENEWABLE ALTERNATIVES TO FOSSIL DIESEL

The search for alternatives to fossil diesel fuel has currently become a pivotal issue for the automotive industry. The main reasons for this are detailed in Table 2.1.:

Fossil Fuel Problems and Factors that Promote Change	Biofuel Advantages
1. Greenhouse gas emissions from burning fossil fuels exceed the rate at which the planet can naturally deal with them.	Biofuels generally have lower net greenhouse gas emissions.[1,2]
2. Global energy demand is growing exponentially.	Biofuels provide an additional energy source.
3. Photochemical smog.	Hydrocarbon emissions are reduced for most biofuel combustion.
4. Acid rain.	There is little or no sulphur in biofuels.
5. Carcinogenic, mutanogenic and teratogenic effects caused by emissions.	Hydrocarbon emissions are reduced for most biofuel combustion.
6. Fossil fuels are not renewable in a realistic time frame.	Biofuels are renewable.
7. The costs of fossil fuels are rising above local rates of inflation.	Biofuels provide an additional option for consumers.
8. Fossil fuel production is controlled by a small number of states and companies (cartels).	Biofuels can be derived from many sources, they can also provide income to poorer countries that have less natural resources.
9. Environmental lobbying.	Biofuels are seen to have less environmental impact.
10. Legislation and taxation of fossil fuels.	Biofuels may meet legislative substitution targets,[3] or local tax breaks.
11. Some of the public have lost faith (rightly or wrongly) in nuclear power generation.	Biofuels in some cases may be seen as an environmental alternative to nuclear power (arguable).

Table 2.1. Fossil Fuel Problems and Biofuel Advantage.
References   1 Adler *et al.* (2007) 2 Reijnders *et al.* (2008)   3 EU Directive 2009/28/EC

Alongside the scientific argument, public and governmental pressure for renewable alternatives to fossil diesel is ever increasing.

Today the automotive industry relies heavily upon the diesel engine, especially in Europe. An instant move away from this power source to the cleanest road transport solutions, for

example, fuel cells and electric vehicles is not currently feasible. In section 1.2 the reasons for the success of the DI CI engine were detailed. There are several criteria which a renewable alternative to fossil diesel will have to satisfy. Most of the criteria are understandably primarily for practical reasons, that relate to the fuel properties. Basically, the alternative fuels considered in this thesis are chosen because they are liquid fuels that can be utilised in an unmodified, basic DI CI engine. The concept behind this, is that if a renewable fuel can perform in an unmodified basic DI CI engine, it should be able to perform in all existing diesel engines in common use, as well as the near future CI engines.

What is a renewable Fuel? A renewable fuel is either a biofuel, or a fuel synthesized from a sustainable source. Biofuels are fuels derived from a biomass source. Most of the major biofuels that can be utilised in unmodified SI and CI engines are listed in Table 2.2. There are two main categories of biofuels, 1st and 2nd generation. Only liquid biofuels are considered.

2.1 1st GENERATION BIOFUELS

There are 2 main groups of 1st generation biofuels; bioalcohols and biodiesels. 1st generation bioalcohols are biologically produced alcohols that are produced by enzymes and micro-organisms via the fermentation of sugars or starches (the simplest way), or from cellulose (more difficult). It is possible to produce bioalcohols from countless sugar containing crops (any crop from which alcohol has been traditionally distilled). Ethanol has been produced and used as a gasoline substitute in Brazil for many years, (Weiss, 1990). There are also many interesting possible routes towards non food bioalcohols, for example, all plants contain lignin and cellulose. Lignin and cellulose are more complex carbohydrates (sugar based molecules). Ligno and cellulosic ethanol can be made by using enzymes, steam

heating, or via other pre-treatments to release sugar molecules from cellulose and lignin. It is then possible to use the sugars to produce alcohols, (this is sometimes labelled as a 2nd generation biofuel). Ligno-cellulosic processes have the ability to diversify the potential feedstocks for bioalcohols enormously.

Biodiesel (usually mono-alkyl ester) is a non-petroleum-based diesel fuel consisting of long chain alkyl (methyl, propyl or ethyl) esters, made by transesterification of vegetable oils or animal fats (tallow), (Van Gerpen *et al.*, 2004). There are many (perhaps hundreds) of viable oil producing feedstocks for 1st generation biodiesels. Some are listed in table 3. In Europe the established (common) biodiesel is rapeseed methyl ester (RME). In the U.S. soybean methyl ester (SME) predominates. First generation biofuels are useful, but may be limited. In some instances it may not be possible to produce enough biofuel without competing with food supplies and biodiversity (such as rainforest destruction), (Fitzherbert *et al.*, 2008). This argument is controversial and complicated. Indeed, there are good counter arguments to this 'food vs. fuel' debate. Simões (2007) argues that less developed nations can use large areas of unutilised arable land to grow fuel, earning money locally. New revenue streams could actually prevent poverty, providing income to fight hunger. Perhaps, it can be simply argued, that the 'food vs. fuel' debate, is really a debate about the cost of energy itself. It is also conceivable that this debate may have been promoted by some of the fossil fuel cartels to discourage competition.

	Biofuel	Feedstock	Pros	Cons	Compared to Fossil			
					NOx	PM	HCs	CO
1st Generation Bioalcohols	Ethanol	Fermentation of sugars (e.g.wheat, corn, sugar beets, sugar cane, molasses).	Low cost.	Food vs. Fuel.	=	-	-	-
	Propanol			Food vs. Fuel.	=	-	-	-
	Butanol	↓		Food vs. Fuel.	=	-	-	-
	Methanol	↓		Fuel system mods. High fuel consumption.	=	-	-	-
1st Generation Biodiesels	Rapeseed Methyl Ester	Rapeseed (Canola) oil.	Proven track record.	Food vs. Fuel.	+	-	-	-
	Soy Methyl Ester	Soybean oil.	Proven track record.	Food vs. Fuel.	+	-	-	-
	Palm Methyl Ester	Pulp of the fruit of a palm tree.	Cost, potential to satisfy both food and fuel.	Threat to biodiversity.[1] Lower yields in esterification.	+	-	-	-
	Jatropha Methyl Ester	Jatropha curcas seeds.	Use of poor soil in arid conditions, non edible.		+	-	-	-
	Olive Methyl Ester	Olive oil.[2]		Food vs. Fuel. Low cetane no.	+	-	-	-
	Mahua Methyl Ester	Madhuca Indica seed oil.[3]	Several uses (medical, edible flowers).	Food vs. Fuel.	+	-	-	-
	Sunflower Methyl Ester	Sunflower seed oil.[4]		Food vs. Fuel.	+	-	-	-
	Flax Methyl Ester	Linseed oil.[5]	Several uses (linen, soap, wood treatment).	Food vs. Fuel.	+	-	-	-
	Hemp Methyl Ester	Hemp oil.	High growth rate easy to cultivate. The waste stalks can also be fermented to make ethanol.	Illegal in some regions, (related to the cannabis drug).	+	-	-	-
	Field Pennycress Methyl Ester	Pennycress oil.	Grown in winter between soybean crops.		+	-	-	-
	Peanut Methyl Ester	Peanut oil [6]		Food vs. Fuel.	+	-	-	-
	Pongamia Pinnata Methyl Ester	Honge oil. (Pea family).[7]	Use of poor soil in arid conditions, Non Edible.		+	-	-	-
	Algae Methyl Ester	Algae oil. (Oilgae)	Highest yield/m^2, doesn't use farmland the oil is produced by most of the algae.[8]	New & yields unproven.	+	-	-	-
	Tallow Methyl Ester	Animal carcasses and food waste.	Waste material, Low cost.	Hot ambient required. Lower yields in esterification.	+	-	-	-
2nd Generation Biodiesel	BTL Diesel	Biomass gas to liquid (any biomass) Uses the Fischer Tropsch process.	Low exhaust emissions, many bio-feedstocks.	Cost.	-	-	-	-
	HTU Diesel	Biomass to liquid (any biomass). Hydrothermal upgrading.	Low exhaust emissions, many bio-feedstocks.	Cost, Unproven.	-	-	-	-
Biogasoline	BTL Gasoline	Biomass gas to liquid (any bio feedstock) Uses the Mobil process.	Low exhaust emissions, many bio-feedstocks.	Cost.	=	-	=	=
	Dimethylfuran (DMF)	Biomass gas to liquid.	High energy density (like gasoline).	Cost.	=	-	-	-
Bioalcohols	Ethanol	Produced from biogas.	Many bio-feedstocks.	Cost.	=	-	-	-
	Propanol	↓	Many bio-feedstocks.	Cost.	=	-	-	-
	Butanol	↓	Many bio-feedstocks.	Cost.	=	-	-	-
	Methanol	↓	Many bio-feedstocks, efficient.	Cost.	=	-	-	-
	Methanol	Pyrolysis (usually from wood)	Many potential bio-feedstocks, non edible.	Cost.	=	-	-	-
Bio Oil	Fuel-Bio Oil	Pyrolysis from a biomass tar.	Can be produced from waste.	Quality.	+	+	+	+

References 1 Fitzherbert *et al.* (2008)   2 Dorado *et al.* (2003)   3 Puhan *et al.* (2005)   4 Kaufman & Ziejewski (1984)
5 Demirbas (2009)   6 Kaya *et al.* (2009)   7 Karmee & Chadha (2005)   8 Demirbas & Demirbas (2011)

Table 2.2. Major biofuels that can be used in unmodified SI and CI engines.

2.2   2nd GENERATION BIOFUELS

The idea behind second generation biofuel is to increase the amount of biofuel that can be produced. This can be achieved by utilising biomass sources that may not be suitable for sugar or oil crops. It is for this reason that some would classify lignocellulosic produced bioalcohols as 2nd generation, though the second part of the process is 1st generation. 2nd generation fuels are often biomass to liquid fuels. There are a few potential routes to achieve this, perhaps the most famous is gas to liquid (GTL) via the Fischer Tropsch process (see section 2.4). In this process a biomass such as, wood can be gasified and turned into high quality liquid petroleum fuels. Gasified biomass can also be used to produce a range of bioalcohols including biomethanol.

In the 1970's Mobil developed a process to convert natural gas into gasoline. With biomethanol as a feedstock it is possible to use this process to produce a high quality synthetic gasoline (Table2), (Yurchaka, 1988). Dimethylfuran (DMF) is a high energy density bioalternative to gasoline. It can be made from fructose and glucose using a catalytic biomass-to-liquid process, (Roman-Leshkov, 2007).

Another extremely interesting technology is Shell's hydro thermal upgrading (HTU) diesel fuel. To make this fuel a biomass such as wood, is finely chopped up and combined with water to make a slurry. This slurry undergoes high pressure and heat to produce a biocrude oil (with long hydrocarbon chains). The created biocrude oil can then be cracked in the same way as conventional crude oil to create a high quality diesel, (Naber *et al.,* 1997). This is a technology that would appear to emulate the action of nature in a fraction of the time. However HTU research is in the early stages. If HTU derived diesel had been available (as is the case with algaeoil) it would certainly have been tested in this thesis.

Pyrolysis oils are another interesting 2nd generation fuel. Pyrolysis is a thermochemical decomposition of biomass at temperatures above 430 °C in the absence of oxygen. From this process it is possible to create an acidic biocrude oil of low cetane number, though to run this oil neat in a diesel (CI) engine would require engine modification, (Chiaramonti *et al.*, 2003). It is also unproven that this biocrude can be cracked to make a diesel. It seems that the quality is low and feedstock dependant. However this field of research should not be overlooked, as there is still potential to gasify the oil, create a syngas and use the Fischer Tropsch process to make a high quality bio GTL.

1st and 2nd generation biofuels are not the only biofuel categories on record. Recently some biofuels have been perhaps arguably mis-labelled as 3rd (algae oil) and even 4th generation (pyrolysis, gasification, solar to fuel and genetically engineered organisms that might secrete hydrocarbons). It is thought that 3rd and 4th generation fuels are sometimes artistically labelled, in an attempt to promote them and distance them from the 'food vs. fuel' debate which some 1st generation fuels endure. E.g. the labelling of algae oil as 3rd generation, (because algae do not use traditional farmed land and algae is not a food crop). By this definition it could be argued that Jatropha, Milletia Pinnata (Pongamia) and perhaps even Field Pennycress should also be labelled as 3rd generation. A more realistic position for all these biodiesels, seems to be 1st generation as they are (usually) crop oils that have been esterified in the same manner as the other 1st gen biodiesels. It is also thought that 4th generation fuels should realistically be labelled as 2nd generation (otherwise, soon '5th, 6th & 7th generation' descriptions will be coined).

There are many routes towards bio liquid fuels. The most environmentally friendly appear to require the most effort to develop and produce which requires higher investment.

For the purpose of this thesis, resource and time constraints meant that it was not possible to look at all the major bio-alternatives. It was decided that a sensible approach would be to concentrate on a selected 1st and a 2nd generation biodiesel to be compared during standard CI combustion. The 1st generation biodiesel chosen was RME, and the 2nd generation fuel chosen was biomass gas to liquid.

2.3   BIODIESEL 1st GENERATION RAPESEED METHYL ESTER (RME)

Rapeseed is a bright yellow flower of the Cruciferae family (more commonly known as either the mustard, or cabbage family), (Jussieu, 1789) (Figure 2.1.). Rapeseed is sometimes (in the U.S.) called Canola. Canola is actually a trademark for a hybrid variety of rape, it is an acronym for Canadian oil, low acid, (Bell, 1984). Rapeseed is the most efficient crop oil, i.e. the yield of oil/m^2 is high. Rapeseed oil is made by crushing the rapeseed (Figure 2.1. b). More than 40% of a seed is oil. The remainder of the crop can be used as rapeseed meal for animals.
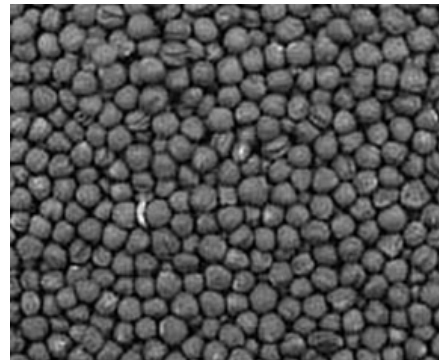
Figure 2.1. a) Rapeseed Crop   b) Rapeseeds

Rapeseed has been developed as a crop in much the same way as wheat, via the use of selective breeding and more recently genetic modification (GM), (Canola Council of Canada, 2005). Rapeseed can have a low impact on the local soils. Where GM strains are used, the yields are higher, less fertilizers are required, (a green house gas (GHG) source) alongside

reduced tilling of the fields. Rapeseed oil is a popular edible vegetable oil with low levels of unhealthy trans fats. The farming of rapeseed is efficient and well established, in China, Europe and North America (all net food producers). These strong arguments for rapeseed as a food crop, can also be applied to rapeseed as a biofuel, especially as these nations are net food producers. As net food producers it would seem sensible, for these nations to reduce their local dependence on overseas fossil fuels, by using this resource for fuel. Perhaps the 'food vs. fuel' debate should be focused in this way i.e. where locally there is low food production (no net exports) the crops should be used for food only and where there is locally a net surplus, it might be used as biofuel.

Rapeseed oil and indeed other fatty acid (FA) oils are not really considered to be suitable for automotive applications in neat form. Over a long period engine deposits appear that cause several problems. Fuel injectors may become blocked, the piston rings can stick and gelling with the lube oil can take place. To avoid these problems, improve the flow, pour and cloud point, rapeseed oil is transesterified to make a suitable rapeseed biodiesel (Babu & Devaradjane, 2003). It is believed that this process to transform vegetable oils for their use as fuels, was first patented in Belgium, (Chavanne, 1937).
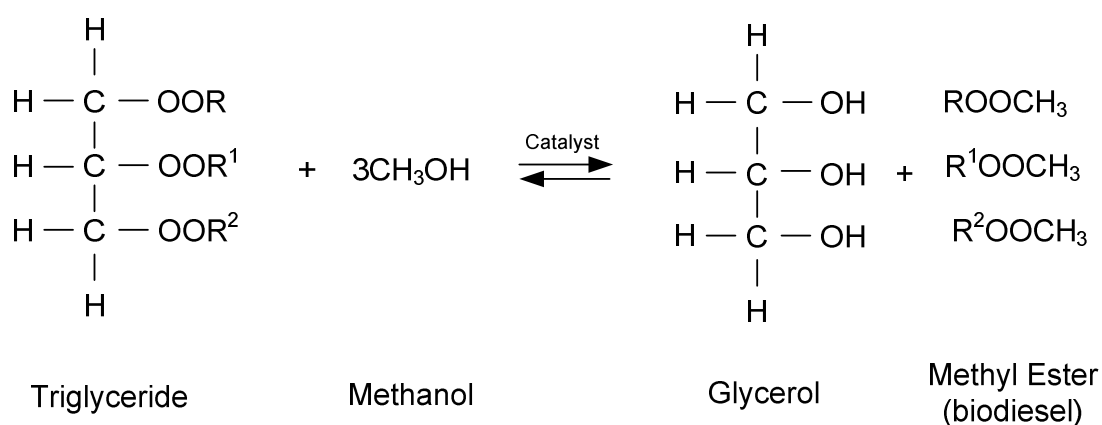
Figure 2.2. Transesterification of vegetable oils and animal fats (triglycerides), adapted from Kim *et al.* (2004).

Transesterification is the process by which the organic group R of an ester is exchanged, with the organic group R of an alcohol (usually methanol). Transesterification is outlined in Figure 2.2..

To form rapeseed methyl ester, the addition of methanol and the application of heat are required during transesterification. The source of this methanol and heat should be considered in net CO_2 calculations. Glycerol is a by-product of the reaction at approximately 1:10 fuel (mass basis). The value of glycerol has dropped significantly in recent years as biodiesel production has increased. The specific fatty acid profile of rapeseed methyl ester is depicted in Table 2.3. Reference 7 is from a recent work by co-workers and the author, in which the individual fatty acid components were assessed for their affect on combustion and emissions. The details of tests undertaken to determine the makeup of RME are detailed in Chapter 3.

Fatty Acid	Structure	RME						
		References						
		1	2	3	4	5	6	7
Myristic acid	C14:0	0.0	-	-	0.1	-	0.1	-
Palmitic acid	C16:0	5.0	4.3	3.3–6.0	4.4	2.7	4.6	4.5
Palmitoleic acid	C16:1	-	-	0–3.0	-	-	0.3	-
Stearic acid	C18:0	3.0	1.6	4–6	1.5	2.8	1.8	1.5
Oleic acid	C18:1	59.0	58.3	52–65	63.4	21.9	60.7	63.1
Linoleic acid	C18:2	21.0	20.9	18–25	19.9	13.1	19.1	19.9
Linolenic acid	C18:3	9.0	10.5	10–11	7.9	8.6	8.3	9.0
Arachidic acid	C20:0	0.5	-	-	1.3	-	0.6	-
Gadoleic acid	C20:1	1.0	-	-	-	-	1.4	0.6
Behenic acid	C22:0	0.5	-	-	-	-	0.3	-
Erucic acid	C22:1	1.0	-	-	-	50.9	0.3	1.5
Lignoceric acid	C24:0	-	-	-	-	-	0.1	-
Nervonic acid	C24:1	-	-	-	-	-	0.1	-
Other fatty acid		-	4.4	0–7.4	-	-	0.4	-

References 1 Glaude *et al.* (2010)   2 Johanson & Johanson (2008)   3 Chuck *et al.* (2010)

4 Karavalakis *et al.* (2009)   5 Sun *et al.* (2010)   6 Schönborn *et al.* (2009)

7 Pinzi *et al.* (2011) (*RME used throughout this thesis*)

Table 2.3. Fatty Acid Profile of Rapeseed Methyl Ester.

RME is predominantly the ester formed from oleic (olive) acid, ($C_{18}H_{34}O_2$). RME is essentially made up from as few as the esters of 7 FAs, (this is quite unlike diesel which is made up from thousands of hydrocarbon compounds over a large range of chain lengths). For this reason the initial boiling point (IBP) and final (FBP) for fatty acid methyl ester (FAME) fuels lie within a much more compact temperature range. The physical properties of RME are detailed in Table 3.6. There have been many combustion and emissions studies concerning RME combustion in DI CI engines e.g. Staat & Gateau (1995), Krahl *et al.* (1996), Graboski & McCormick (1998), Yamane *et al.* (2001), Labeckas & Slavinskas (2006), Tsolakis *et al.* (2007), Wu *et al.* (2009). The general consensus is that HCs, CO and particulates are reduced and that NOx is slightly increased. The reasons are discussed in more detail in Chapters 4 & 5. The emissions for 1st generation biodiesels present a somewhat different dilemma when compared to diesel emissions. Much of the research in this thesis is focused upon the potential impact that increased use of 1st generation biodiesel will have upon emissions strategies and how an aftertreatment solution will perform and be optimised for this fuel type.

2.4 BIODIESEL 2nd GENERATION BIOMASS TO LIQUID (Fischer Tropsch GTL)

1st generation biofuel production converts only a fraction of the biomass into fuel. For biodiesels this is often just a proportion of the seed (which itself represents a fraction of the overall crop). Potentially, biomass gasification can convert all the biomass into a syngas for fuel synthesis. Gasification of biomass is quite complicated, it involves the conversion of the carbonaceous material in the biomass into carbon monoxide and hydrogen. This is achieved by the reaction of the raw material at very high temperatures with a controlled amount of oxygen and (probably) steam. This produces a bio syngas that could then be used in a gas to

liquid process (a 2nd generation biomass to liquid fuel). True 2nd generation biomass to liquid fuels are not currently available on a large scale. Perhaps United Paper Mills (UPM) of Finland has come closest. UPM have been developing gasification of logging residues, wood chips, stumps and bark. A Fischer Tropsch GTL process is then applied at a bio-refinery adjacent to the paper mill, (UPM, 2010).

The Fischer Tropsch GTL process was developed in the 1920s in Germany, (Fischer & Tropsch, 1930). The Fischer Tropsch process first saw major use during World War 2. It was used by crude oil-poor (but coal-rich) Germany, to make several fuels from gasified coal. As much as one million tonnes was produced annually in the 1940s, (Leckel, 2009). Since the war it has been adopted on a large scale by Sasol in South Africa, in part due to large coal reserves, but also due to the trade embargo during the apartheid era, (Gross, 2006).

The following is a simple example of how a biomass gas to liquid fuel could be produced (from wood). This could be from sustainable forestry and therefore be removed from the 'food vs. fuel' argument, (Seiler *et al.*, 2010). In theory any biomass could be used as the feedstock, though gasification reactor type and optimisation will depend on the feedstock.

2.4.1   Biomass to Liquid Example

2.4.1.1 Gasification of Wood (2-Stage) Tijmensen et al. (2002), Cummer & Brown (2002).

Wood gasifiers use dried wood chips, sawdust and charcoal (all in a fine form) as the feedstock.

- *Stage 1 Pyrolysis* In the initial stage the feedstock undergoes pyrolysis (thermochemical decomposition, heat without oxygen) in a sealed reactor. Light volatiles such as hydrogen and methane are released, the remainder of the feedstock is significantly reduced in

weight and has become a carbon rich char. Yield can be increased by pressurising this stage.

- **Stage 2 Partial Combustion** The char (and some of the volatile material) is now partially combusted by supplying a measured quantity of oxygen to the reactor to make CO. This exothermic reaction helps to supply heat for the subsequent gasification reactions. Full combustion may also occur, however in time, providing the O_2 input is controlled carefully, the char can also react with any CO_2 produced to make more CO.

- **Steam Reforming** Simultaneously water can be introduced into the hot environment to promote char removal and the reforming of hydrogen according to: $C + H_2O \rightarrow H_2 + CO$ Additionally the introduction of steam has a highly exothermic effect, as the water-gas shift reaction occurs: $CO + H_2O \leftrightarrow CO_2 + H_2$ this reaction balances the quantities of CO, steam CO_2 and hydrogen. The created syngas is now siphoned off from the reactor. An ash/slag deposit will remain in the reactor and there are many ingenious ways to remove the deposit. Gasification can be completed in single or multiple stages in a batch or continuous process. Catalysts can also be employed to improve the rate of reforming.

2.4.1.2 Syngas Clean-up

The syngas that has been produced by gasification contains many contaminants, e.g. condensable tars, particulates, alkali compounds, NH_3, HCN, H_2S, HCl, (Faaij, 1997). All these contaminants can poison the sensitive catalysts used in the Fischer Tropsch process. Therefore removal is paramount. Figure 2.3. is a process diagram detailing the steps involved to remove contaminants and make the syngas suitable for the Fischer Tropsch process. Figure 2.3. also highlights some of the complexities of syngas cleanup. This explains why to

date there are no commercially available biomass gas to liquid fuels. Once the syngas has been cleaned, it can be upgraded to make it a suitable feedstock for the Fischer Tropsch process.

2.4.1.3 Syngas Upgrading

There are two main types of Fischer Tropsch (FT) reactors (low and high temperature). The syngas feedstock requirement is specific to the reactor type. Ideally the Fischer Tropsch reactor needs $CO + H_2$ in the following ratio:

$$CO + 2.15H_2 \rightarrow hydrocarbons + H_2O$$
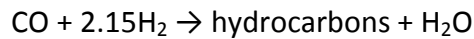
In reality there will also be CO_2 in the syngas. For a high temperature Fischer Tropsch (HTFT) reactor the ideal feedstock of these 3 gases would be $H_2/(2CO+3CO_2)$ at a ratio of 1.05 for a cobalt catalyst, (Dry, 2002). Realistically, syngas also contains some HC species, consequently the syngas will need to be catalytically reformed in an autothermal reactor (dry reforming) and by selective addition of water:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \text{Dry reforming}$$
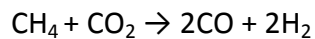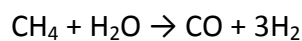
$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{Steam reforming (high temperature)}$$
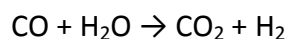
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{Water gas shift (low temperature)}$$

With the gas ratios adjusted in this manner, the syngas is suitable for FT synthesis.

Biomass Gasification

Tar Scrubber

Gas is slowly cooled using scrubbing oil. Heavy tar particles condense and are collected, after which they are separated from the scrubbing oil and recycled to the gasifier.

Cyclone Separator

Removes particulates from the syngas through vortex separation. Rotational effects and gravity are used to separate solid particulate from the syngas.

Baghouse Dust Removal

Fabric collectors use physical filtration to separate fine particulates (99%+ efficiency).

Sulphur Removal

H_2S removal and COS hydrolysis via the modified Claus process:

COS hydrolysis

$MOH + COS + H_2O \rightarrow MCO_2SH + H_2O \rightarrow H_2S + CO_2 + M$ (compound M) Bachelier et al. (1993)

Claus reaction

$10H_2S + 5O_2 \rightarrow 2H_2S + SO_2 + 7/2S_2 + 8 H_2O$ Gary and Handwerk (1984)

The removal of COS and H_2S is a two stage catalytic and absorbent process, which involves the hydrolysis of the COS and the subsequent absorption of the H_2S, (CS_2 is also removed).

Water Scrubbers

The syngas is forced through a pool (or the reagent is sprayed into the gas) of a reagent water solution containing NaOH (to remove HCL) and H_2SO_4 (to remove HCN & NH_3).

Guard Bed

The guard bed is a mineral oil/methanol catalyst containing slurry (Cu & ZnO catalysts) this final stage further reduces the contaminants to levels sufficient for the Fischer Tropsch process, 12 reactions are detailed in Quinn & Toseland (2008).

Fischer Tropsch Process

Figure 2.3. Biomass Syngas Cleanup (6-Step). Modified and enhanced from Tijmensen *et al.* (2002).

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2.4.2 FT Synthesis

The synthesis of long chain hydrocarbon (paraffins or alkanes) from CO and H_2 is complicated, requiring 3 steps:

1. The hydrogenation of CO

2. The hydrogenolysis of C-O bonds

3. The formation of C-C bonds

The main reaction is: $2H_2 + CO \rightarrow -(CH_2)- + H_2O$ *FT Synthesis*

Where -(CH2)- is a growing hydrocarbon chain, (Sie *et al.,* 1991).

This reaction happens over a catalyst (often cobalt) and benefits from pressurisation. It can take place in both low and high temperature reactors. There are some competing reactions that result in the formation of alkenes, alcohols and other oxygenated hydrocarbons, though the amounts are low. Overall, FT synthesis creates a mixture of liquid and wax hydrocarbons, at a ratio of around 1:1. It is possible to further convert the waxes to liquid hydrocarbons by cracking them with hydrogen. The final synthetic FT crude oil is distilled into two fractions: middle distillates and naphtha. The naphtha can be used for ethylene production and the distillates for diesel, kerosene, and aviation fuel.

FT fuels are composed almost entirely of paraffins and olefins, (with little or no aromatic compounds). The major fuel properties of a synthetic diesel fuel are listed (GTL) in Table 3.6. FT diesel is high quality (high cetane) it is free (or virtually) of aromatic hydrocarbons and sulphur, it is also less toxic than diesel. Physically it is translucent and more viscous than diesel, but of a lower density. There have been many studies that have looked at combustion and emissions from FT diesel, (Knottenbelt, 2002; Alleman & McCormick, 2003; Myburgh *et al.,* 2003 ; Kitano *et al.,* 2005 ; Schaberg *et al.,* 2005 ; Yongcheng *et al.,* 2006 ; Larsson &

Denbratt, 2007; Szybist *et al.,* 2007; Uchida *et al.*, 2008; Gill *et al.,* 2010). The general consensus is that if combustion strategy is specifically optimised for FT diesel, it is possible to see reductions in all the regulated emissions. When FT fuels are utilised with no optimisation it has been reported that particulates are increased (Abu-Jrai *et al.,* 2006).

In this thesis a FT diesel (Shell GTL) made from a feedstock of natural gas, is tested. This FT diesel is seen as a prototype for a future biomass FT diesel, as potentially biomass FT could be tailored to a similar composition as natural gas FT.

2.5   ADDITIVES FOR DIESEL COMBUSTION

Fuel refiners currently have to ensure that their products meet local specifications e.g. the American Society for Testing of Materials (ASTM) (U.S.) and in Europe (EN) standards. These standards have been devised to ensure that fuel quality is consistent and that it is suitable for the intended use. Fuel properties can be improved through the use of additives. Additives are currently employed regularly to meet fuel specifications, e.g. lubricity additives for low sulphur and FT fuels.

There are many additives such as; cetane improvers, combustion catalysts, detergents, antifoam, lubricity, pour point reducer/flow improver, oxidants, antioxidants and biocides, (Bacha *et al.*, 1998). Perhaps the most well known diesel additive is 2-Ethylhexyl nitrate (EHN), used to improve the quality (cetane No.) of diesels, to reduce the noise created during combustion and potentially reduce emissions, (Thompson *et al.*, 1997). This additive is especially effective in combination with low aromatic content fuels like FT, (Gill *et al.*, 2010). It would be valuable to determine if this additive is effective in combination with FAME fuels (also low aromatics). Inclusion of this type of additive increases the fuel-borne

nitrogen level, (providing another NOx production mechanism) and this should be factored into net emission calculations.

There are some arguably questionable suppliers of aftermarket additives such as organometallic/organic combustion catalysts who make ambitious claims of large fuel economy savings by improving combustion efficiency. Use of metallic additive doping of course requires a downstream DPF and these additives will slowly build up in this DPF, this may facilitate filter regeneration, (a clear benefit). However, fuel economy improvement is somewhat difficult to justify when modern CI engines have a combustion efficiency of more than 99%. Realistically, these additives are often cetane improvers, or cetane improvers in combination with a combustion catalyst (Suppes *et al.*, 1996). There are even works on this subject that omit key combustion analysis e.g. Valentine *et al.* (2000) as combustion analysis would clearly indicate the effect of any cetane improvement (changes in ignition delay) and would be simple to provide. Fuel economy savings of even 1-2% would be extremely attractive, therefore it would be highly probable that the large oil and automotive companies would have already covered this base through significant research investment.

2.5.1 Bio-additives

As the name suggests bio-additives are additives that are produced from a biological source. If it is possible to synthesize an additive from a biological source, it is a renewable 'green' additive, which is also likely to be less toxic. This means that it can also contribute to legislative substitution targets similar to Directive 2009/28/EC (EC, 2009). For this reason only potentially bio-oxygenated additives are considered Table 2.4.

Compound	Class	Chemical Formula	Oxygen % Weight	Cetane Number	Density Ratio-Diesel	LCV (MJ/kg)	Pros	Cons
Diesel	Diesel	$C_{12}H_{23}$ (average)	0	53.9	1	42.7	/	/
Rapeseed Methyl Ester	Ester	$C_{19}H_{34}O_2$ (average)	10.8	54.7	1.07	39 [7]	Efficiency in production Economics	
Dimethoxymethane	Ether	$C_3H_8O_2$	42.1	30	1.05 [9]	22.4 [6]	No carbon-carbon bonds (sootless combustion), non toxic [3]	High vapour pressure[4] boiling point 45.5°C [5]
Ethanol	Alcohol	C_2H_6O	34.8	8	0.95	27.7 [7]	Economics, (sootless combustion)	Miscibility with diesel
Ethylene Glycol	Glycol	$C_2H_6O_2$	51.6	18	1.04 [10]	26 [8]	Antifreeze additive produced commercially [2]	Toxic
1.1-diethoxyethane	Acetal	$C_6H_{14}O_2$	25	39	1 [1]	31*	Same density diesel[1]	Low flash point [1]
Dimethyl Carbonate	Carbonate	$C_3H_6O_3$	53.3	35.5	1.29 [11]	15.78 [8]	Non toxic, no carbon-carbon bonds (sootless combustion)	Melting point 2°C
2-methoxyethyl Acetate	Acetate	$C_5H_{10}O_3$	40.7	-	1.22 [12]	21.1 [12]	Miscibility with diesel [12] (sootless combustion)	

References

1. Frusteri *et al.* (2007)   2. Rebsdat & Mayer (2010)   3. Mench (2008)   4. U.S. Department of Energy (2000)

5. Kéranguéven *et al.* (2008)   6. Frusteri *et al.* (2007)   7. Ren *et al.* (2006)   8. Tsolakis & Megaritis (2008)

9. Yanxia & Yongqi (2007)   10. Zheng *et al.* (2008)   11. Yang *et al.* (2009)   12. Zhoua *et al.* (2010)

* calculated   N.B. Methyl Tertiary Butyl Ether (MTBE) though well known is not included due to its toxicity in spillage.

Table 2.4. 21 Potential bio-oxygenated additives suitable for substitution in petroleum diesel.

2.5.2   Bio 'Green' Oxygenative Additives

Combustion studies have shown that fuel-borne oxygen aids fuel oxygen entrainment, so that even in fuel rich localities there is oxygen available from the fuel, (Hribernik & Kegl, 2007; Lapuerta *et al.*, 2008; Yoshida *et al.*, 2008; Nanjundaswamy *et al.*, 2009). This improved fuel oxygen entrainment is thought to enhance the combustion in several ways: The improved mixture allows an increased possibility for complete diesel combustion. In the simplest terms, this is due to oxygen availability (reactants). When there is not enough oxygen, incomplete combustion can dominate. This is of course unfavourable, as less fuel burnt means less useful power, as well as potentially dangerous emissions of unburnt HCs and CO.

It has been observed that a reduction in both the formation and growth of soot nuclei occurs due to fuel-borne oxygen, (Eastwood, 2000; Kitamura *et al.*, 2003). Indeed studies have shown that when fuel-borne oxygen content is above 30%, combustion is smokeless, (Miyamoto *et al.*, 1998; Siebers & Higgins, 2001; Chen *et al.*, 2008). There are several compounds that can be used to add oxygen to a fuel. These include esters, ethers, alcohols glycols, acetates, and carbonates, (Teng & McCandless, 2006). Some researchers have found that there is a small difference in the effect upon emissions due to the structure and size of the molecule used to add oxygen to a fuel and that the controlling factor is the quantity of oxygen added, (Spreen *et al.*, 1995; Tsurutani *et al.*, 1995; Stoner & Litzingerm 1999; Ren *et al.*, 2008).

Table 2.4. details some potential bio oxygenated additives for diesel fuel, it details the composition and some important properties as well as relevant pros and cons. For a suitable green future bioxygenate additive for diesel, three of the compounds in Table 2.4. were seen

as promising:. Dimethoxymethane, dimethyl carbonate and 2-methoxyethyl acetate. For

each compound a case can be made, for example each has low toxicity or is non toxic (which

is important for road transport fuels and was the main reason that the previously popular

MTBE was not included). Dimethoxymethane was finally discarded because it has a fairly

high vapour pressure and low boiling point. 2-methoxyethyl acetate was discarded partly

due to a lack of literature and information relating to potential green production (though it is

envisioned that information will become available and this additive will undergo further

scrutiny).
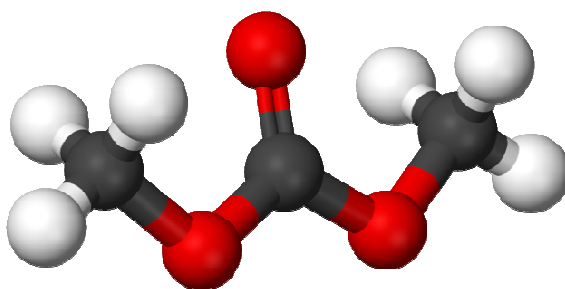
Figure 2.4. Dimethyl carbonate ($C_3H_6O_3$).

Dimethyl carbonate (DMC) is a nontoxic compound, $C_3H_6O_3$ (Figure 2.4.). The principal

interest in DMC is generated by its high oxygen weighting at around 53%. There have been

many previous studies that have attempted to examine the effect of fuel-borne oxygen,

(Akasaka & Sakurai, 1994; Spreen *et al.*, 1995 ; Tsurutani *et al. ,* 1995 ; Miyamoto *et al.*,

1998 ; Stoner & Litzinger, 1999 ; Siebers & Higgins, 2001 ; Kitamura *et al.*, 2003 ; Lu *et al.*,

2005 ; Teng & McCandless, 2006; Chen *et al.*, 2008 ; Ren *et al.*, 2008). Perhaps the most

difficult problem that these studies have encountered is the decoupling of the effect that the

fuel-borne oxygen additive has in changing various fuel properties simultaneously. DMC,

though still not ideal, has the lowest possible impact upon other various important characteristics of the fuel.

Previous studies have indicated the potential of DMC in emissions reduction of PM, HCs, CO, and in some cases NOx and increased thermal efficiency, (Huang *et al.*, 2005; Zhang *et al.*, 2005). In recent years it has become possible to produce DMC by catalytic oxidative carbonylation of methanol with oxygen, (Tundo & Selva, 2002; Zhu *et al.*, 2009). This step has seen the elimination of dangerous phosgene which was a component of DMC synthesis.

Using a feedstock of bioderived methanol and potentially waste supercritical CO_2 from CO_2 sequestration in the latest generation power stations, it is conceivable that it could be possible to generate DMC as a green biofuel in an economical way. DMC as an additive for ULS diesel is demonstrated and evaluated in Chapter 5.

CHAPTER 3
EXPERIMENTAL FACILITIES

This Chapter attempts to describe the means by which the research contained in this thesis was collected. The engines, their ancillaries, the various test criteria, emissions analysers, as well as the physical PM collection and the analytic sampling methods employed will be explained. All the hardware for catalyst appraisal and particulate sampling are new/novel and most parts where possible have been manufactured in house, either by the author or colleagues. Detailed parts drawings of all hardware remain with the Future Power Systems Group at the University of Birmingham.

3.1   PRIMARY TEST ENGINE

Table 3.1. Primary Engine Specification

Lister Petter-TR1	
Cylinders	1
Displacement Volume	773 cm^3
Bore	98.4mm
Stroke	101.6
Compression Ratio	15.5:1
Peak Power (kW)	8.6@2500 rpm
Peak Torque (Nm)	39.2@ 1800 rpm
Pump-line-nozzle	3 hole
Injection System	Ø 0.25 mm
Piston	Bowl-in-piston

Figure 3.1. Lister Petter TR1.

The British made Lister Petter TR1 (Figure 3.1.) is a single cylinder, DI CI engine that has been designed for petroleum diesel combustion. The fuel injector is located near the

combustion chamber centre and it has an opening pressure of 180 bar. The combustion chamber is a bowl-in-piston design. Table 3.1. shows a detailed engine specification.

This engine has been modified to accept an externally cooled EGR system. The EGR flow is controlled manually by a valve. The EGR level is determined volumetrically as the percentage reduction in volume flow rate of air at a fixed engine operating point. Intake airflow is measured using a Romet G65 rotary airflow meter. The accuracy of this EGR method has been tested using the EGR function of the Horiba tower at each of the tested conditions, the maximum difference recorded between the analyser and the volume reduction technique is <1% at 30% EGR. The reduction is adjusted on a test by test basis to compensate for any day to day variability.

Generally the injection timing is maintained at the manufacturers settings, however when indicated advanced injection timing is achieved by placing shims (provided by Lister Petter) under the fuel pump. The general torque/power as a function of engine speed for the Lister Petter TR1 engine running with ULS diesel is detailed in Figure 3.2.
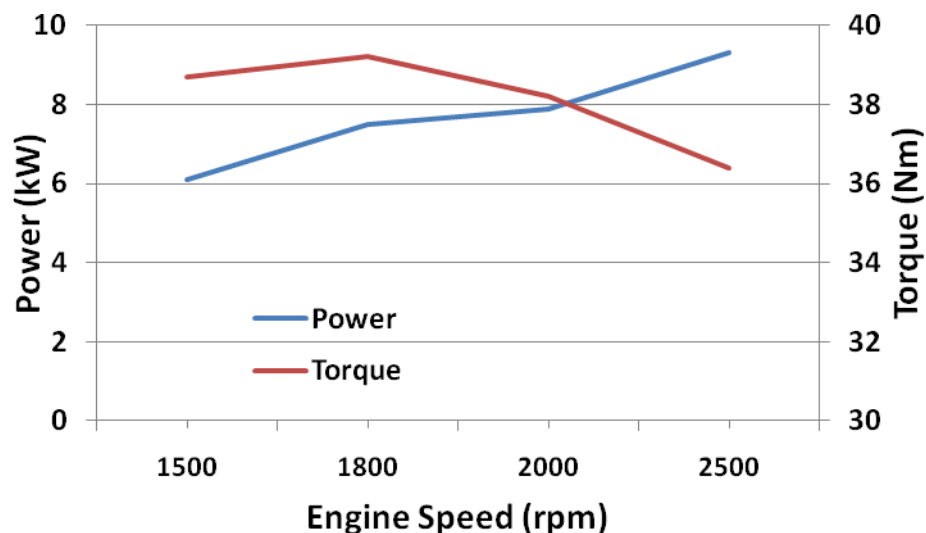
Figure 3.2. Lister Petter TR1 Power torque curve for a range of rpm.

All the tests in this thesis are steady state, and they were chosen as they represent mode points 3,4,5,6,7,9,11,12 & 13 of the 13-Mode European Stationary Cycle (ESC), i.e. 25% 50% and 75% load for (1200) (5,6,7) 1500 (3,4,9) and 2000 rpm (11,12,13). The 13 mode ESC or ELR (European Load Response) test, was designed for the emission certification of heavy-duty diesel engines in Europe starting in the year 2000 (EC, 1999).
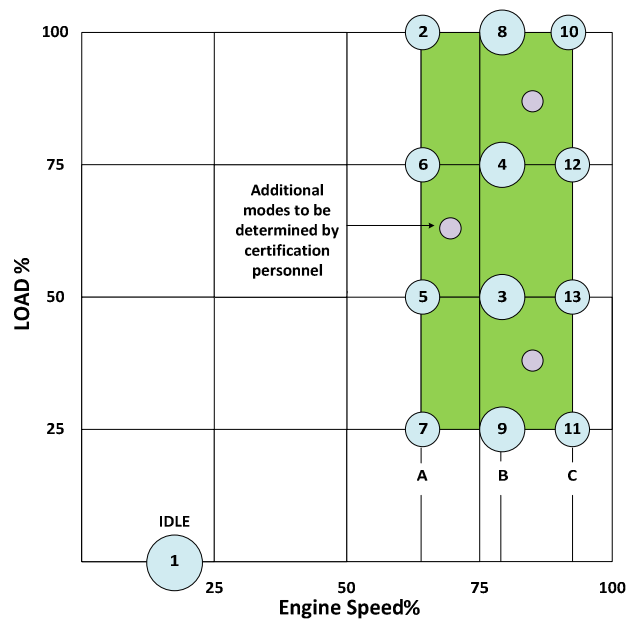
Table 3.2. ESC Test Modes

Mode	Engine Speed	% Load	Weight Factor %	Duration
1	Low idle	0	15	4 minutes
2	A	100	8	2 minutes
3	B	50	10	2 minutes
4	B	75	10	2 minutes
5	A	50	5	2 minutes
6	A	75	5	2 minutes
7	A	25	5	2 minutes
8	B	100	9	2 minutes
9	B	25	10	2 minutes
10	C	100	8	2 minutes
11	C	25	5	2 minutes
12	C	75	5	2 minutes
13	C	50	5	2 minutes

Figure 3.3. 13 Mode European Stationary Cycle.
(EC, 1999)

In Figure 3.3. the area shaded in green is thought to represent the region in which an automotive engine is most frequently operated within. Apart from idle the 3 most important modes are 9, 3 and 4. For the Lister Petter TR1 this has been determined to be 2, 4 and 5 BarIMEP at 1500 rpm.

3.1.1 Engine Instrumentation

The single cylinder diesel engine test rig (Figure 3.1.) consists of a thyristor-controlled DC motor-generator machine dynamometer coupled to a load cell and it is used to load and motor the engine. In-cylinder pressure traces were acquired by a Kistler 6125B quartz type

pressure transducer with a Kistler 5011 charge amplifier at crank shaft positions determined by a 360-ppr incremental shaft encoder (Baumer BDK 1605A360-5-4) with data recorded by a data acquisition board (National Instruments PCI-MIO-16E-4) installed in a PC (see Figure 3.4.). In-house developed LabVIEW space based software is used to obtain pressure data and analyse combustion parameters (e.g., coefficient of variation (COV) of indicated mean effective pressure (IMEP), peak pressure, indicated power, and heat release). Readings of atmospheric conditions, temperature, pressure, and humidity, are recorded and used for the combustion and emissions analysis. The experimental system also involves other standard engine test rig instrumentation, i.e. a fuel flow meter and several local thermocouples.
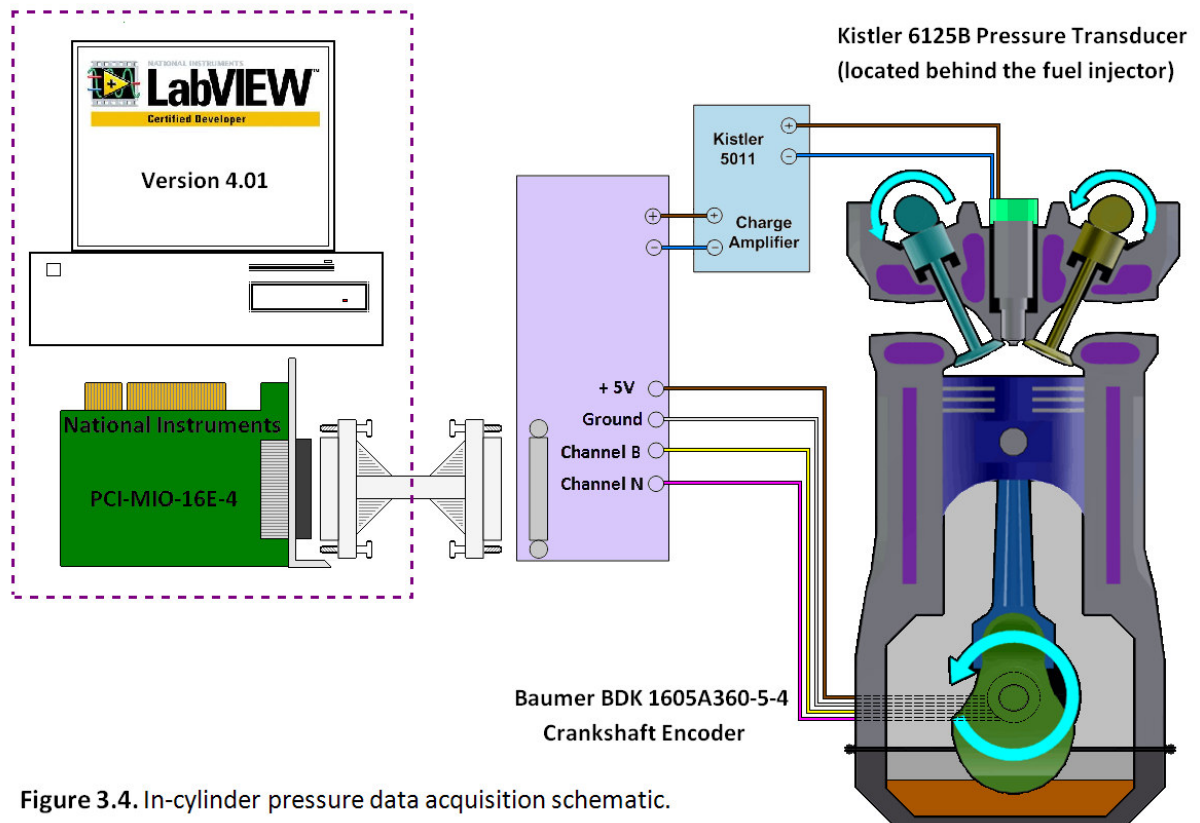
Figure 3.4. In-cylinder pressure data acquisition schematic.

3.1.2   Test Procedure

All tests were steady state and were set at engine speeds of 1200, 1500 and 2000 rpm. Tests were carried out at 2, 4 and 5 bar IMEP. To study the effects of EGR, the engine was kept running at constant load with EGR variation of 0%, 10%, 20% and 30% respectively. To perform the combustion analysis, the LabVIEW based software was used to acquire data in consecutive engine cycles. This makes it possible to study the statistics of peak cylinder pressure, COV of peak pressure, IMEP etc. For each test condition, the cylinder pressure data from 200 consecutive engine cycles has been acquired and an average value determined.

All tests were made a minimum of three times on at least two separate occasions and a mean reading from all these tests was taken. A minimum of 2 minutes was allowed for stabilisation before any readings are taken. The emissions software records for 100 seconds, taking a reading every 10 seconds. Then an average is taken. All tests were carried out between 19° C ambient and 27° C after the engine oil reached sufficient temperature. Readings of atmospheric conditions: temperature, pressure, and humidity were recorded and used for the combustion and emissions analysis.

3.1.3   Combustion Analysis

Cylinder pressure traces and heat release patterns are the heat release calculated from the in-cylinder pressure data versus crank angle positions (Figure 3.4.). It has been shown to be a suitable method of analysis to yield the release rate of a fuel's chemical energy (Heywood, 1988). For a direct injection engine analogous to the one used in these tests, the first law of thermodynamics for a single open system was used for the calculation of the rate of heat release.

3.2 EMISSIONS ANALYSIS

3.2.1 Regulated Emissions

A Horiba Mexa 7100DEGR analyser was employed to measure the concentrations of NOx, CO, CO_2, O_2 and THCs. The Horiba measures NOx (NO + NO_2) by chemiluminescence, CO and CO_2 are measured using non-dispersive infrared (NDIR), O_2 by an electrochemical method and total hydrocarbons (THCs) by FID.

A Horiba Mexa 1230PM analyser was used to continuously measure soot and SOF. The instrument utilises a diffusion charging (DC_h) detector with a diluter for soot measurement and 2 FIDs for SOF measurement (Fukushima *et al.*, 2011). The dilution ratio was 1 part exhaust to 40 air (Mexa 1230PM).

Engine smoke was also measured using a Bosch smoke meter (BSM). This filter darkening method is limited as it only measures the concentration of black smoke. The BSM determines soot density by measuring the amount of light reflected from a filter (through which a known volume of exhaust is drawn). A BSN from 0-10 results, (0=low 10=high smoke). Tables can be used to convert BSN to specific PM emission.

3.2.2 Partially Regulated and Unregulated Emissions

The following analysers are focused specifically towards PM measurement, these state of the art analysers give information beyond the current regulations. There are 2 analysers that have the ability to determine PM concentration for a cold dilution though dilution ratios are not the same (DMS 10:1 SMPS 100:1). The Scanning Mobility Particle Sizer (SMPS) was also able to perform a hot dilution i.e. no SOF (liquid PM).

3.2.2.1 Differential Mobility Spectrometer (DMS)

Particulate number concentration and size distribution measurements were carried out using a Cambustion Differential Mobility Spectrometer model DMS500 (Reavell, 2002a; Reavell *et al.*, 2002b). A dilution ratio of 10:1 was used at ambient temperature. The particle size sampling was carried out from the same point located downstream of the catalyst housing with and without the catalyst at all conditions. No thermodenuder was used to remove the volatile organic compounds, water and the sulfates from the exhaust. The DMS uses electrical mobility to classify the size of PM it can sample particulate continuously, though the resolution is not high.

3.2.2.2 Scanning Mobility Particle Sizer (SMPS)

A TSI SMPS 3080 particle number and size classifier with thermodiluter was employed to measure the total number and size distribution of PM emitted from the engine. The SMPS uses electrical mobility but is separated into 2 parts, a particle classifier and a counter. A volume of exhaust is drawn in, the classifier ramps through voltages over time and PM is released to the counter when the voltage corresponds to a particular size of PM. This method has higher resolution than the DMS, but it is not a continuous technique, so it is only suitable for steady state testing. The dilution ratio was 1 part exhaust to 100 air. Tests were accomplished for a cold dilution (Thermo diluter not employed) to yield PM total (liquid and solid). The thermodiluter was then set at 300° C for a series of tests (to drive off water and volatile organic compounds prior to the SMPS) to yield the total number and particle size distribution for specifically carbon (soot) and ash (solid PM).

3.2.2.3 Thermogravimetric Analysis (TGA)

PM was collected using an in-house developed Venturi nozzle diluter (8:1) located at the same position in the exhaust as all the analysers utilised. The PM was collected on 47 mm diameter glass fibre filters (Whatman) by drawing the cooled diluted gas through the filter at 10 l/min for 30 minutes. Filters were then kept sealed and refrigerated. Thermogravimetric analysis was then used to analyse the PM composition on the glass fibre filters. To achieve this, a Perkin Elmer diamond TG/DTA with autosampler was utilised to determine PM composition. The heating programme is detailed in Table 3.3.

A slow $5°$ min^{-1} ramp was employed as this would allow sufficient time for volatilisation of organic compounds. Nitrogen only until $400°$ C was chosen to volatilise the vast majority of the organic

Table 3.3. TGA heating programme.

1	Initial atmosphere: nitrogen
2	Isothermal for 15 min at $30°$ C
3	Ramp $5°$ C min^{-1} to $400°$ C
4	Switch gas to air at $400°$ C
5	Ramp $5°$ C min^{-1} to $630°$ C
6	Isothermal for 10 min at $630°$ C

compounds. Research has shown that for diesel combustion it is possible to determine the origin of the unburnt hydrocarbons using TGA (Andrews *et al.*, 1998; Statakis *et al.*, 2003; Ayrault *et al.*, 2010). In earlier studies it has been noticed that the weight loss in a TGA analysis below the IBP of the fuel can be fully attributed to the fuels contribution and that a proportion of the weight loss up to the FBP of the fuel can also be attributed to the fuel. The weight loss above the fuels FBP (whilst inert) can be attributed to the longer chain hydrocarbons from the lube oil. However, it is not believed, that this methodology should be applied for RME and other fatty acid methyl esters (FAMEs) as they have a significantly greater IBP (Table 3.4.) and some of the lube oil contribution to unburnt HCs would not be considered.

Table 3.4.   Potential TGA SOF determination.

Fuel	Water PM	Fuel SOF	Fuel & Lube Oil SOF	Lube Oil SOF
ULSD	20 - 105	105 – 164.6	164.6 - 352	352 - Start of Carbon Oxidation
RME	20 - 105	105 - 315	315 - 348	348 - Start of Carbon Oxidation

Figure 3.5. shows a typical ULSD filter TGA ramp, it also attempts to highlight the process by

which the PM can be determined.
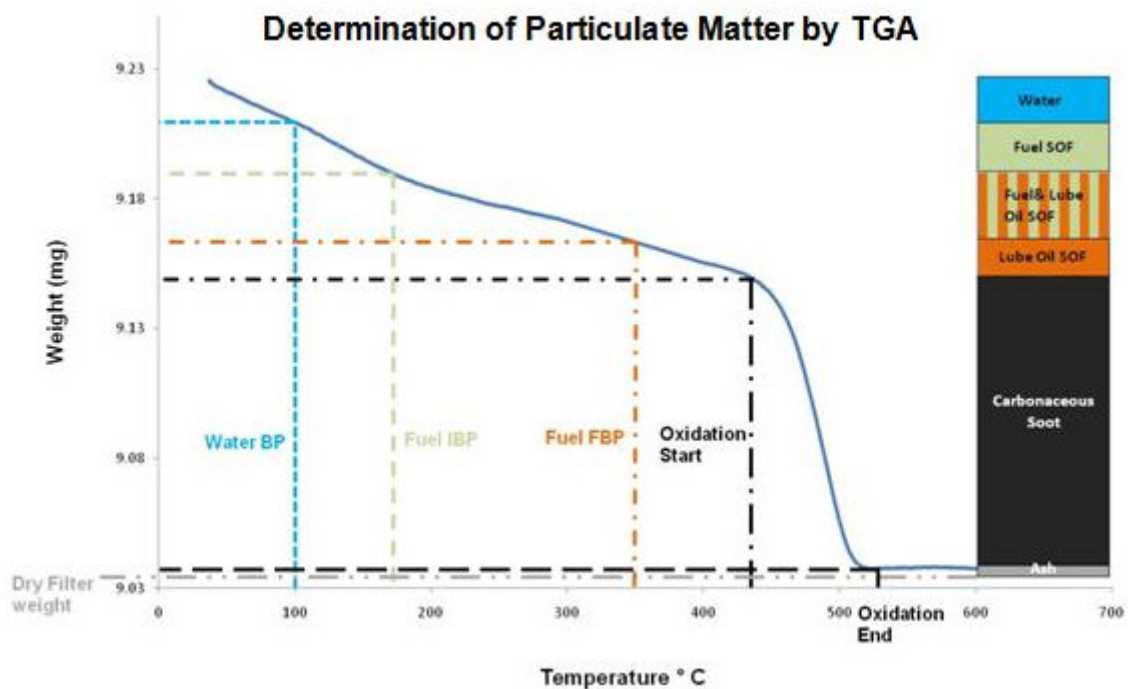
Figure 3.5. Proportional distribution of PM using TGA.

Figure 7.7 in Chapter 7 is compiled using this method however the HCs proportion of the SOF

has not been split according to its origin.

3.2.2.4 Speciation of HC $C_1 – C_7$

For a more comprehensive speciation of the composition of the smaller (harmful)

unburnt hydrocarbon emissions, a Hewlett – Packard Model 5890 Series II GC equipped with

an Agilent FID was employed. This gave the concentration in parts per million (ppm) for

carbon species from C_1 to C_7 i.e. methane (ppm) to toluene (ppm). Using this GC-FID for C_1-C_5, the minimum detectable concentration is 1ppm, for C_6 - C_7 2 ppm, the accuracy at 50 ppm is +-1 ppm. (This was checked by using a gas standard which is accurate to 0.1 ppm).

3.2.2.5 Presence of Aldeyhydes and Ketones

To determine the presence of ketone/aldeyhydes in the exhaust emission a 2,4-Dinitrophenyl hydrazine method analogous to Lipari & Swarin (1982) was utilised. Here 1 l/min of exhaust gas (flow meter controlled) was bubbled through a chilled column of 2,4-Dinitrophenyl hydrazine solution for 20 minutes. The individual aldehydes and ketones react with the acidic solution of DNPH. Presence and concentration of aldehydes are determined by injecting the sample into a high performance liquid chromatograph (HPLC Dionex Summit) and a comparison of the area under the peaks was made with a known reference standard of 15 aldehydes (See Appendix).

3.2.2.6 Determination of Fatty acid Profile for RME (Table 2.3.)

GC analysis to determine the fatty acid profile of the methyl ester fuels were carried out on a Perkin Elmer (Waltham, Massachusetts, USA) Clarius 500 GC equipped with an FID. The GC uses a 30 m x 0.25 mm Elite 5-ms Perkin Elmer capillary column (film thickness of 0.25 µm).

3.3 FUELS

The fuel mixtures used throughout the thesis (Table 3.5.) were obtained from three types of pure fuels provided by Shell Global Solutions UK: Ultra Low Sulphur Diesel (ULSD), Synthetic Diesel - a Fischer Tropsch GTL and RME.The GTL used in these tests is of a similar composition to Biomass GTL, though is only seen as a prototype (as the GTL used here was

Table 3.5. Fuels Tested

Abbreviation	% Volumetric Makeup
ULSD	100% ULSD
RME	100% RME
GTL	100% GTL
DMC	100% DMC
B30	30% RME 70% ULSD
GD30	30% GTL 70% ULSD
3-way blends	
B15G15	15% RME 15% GTL 70% ULSD
B20G10	20% RME 10% GTL 70% ULSD
B10G20	10% RME 20% GTL 70% ULSD
dimethyl carbonate blends	
1DMC	1% DMC 99% ULSD
2DMC	2% DMC 98% ULSD
4DMC	4% DMC 96% ULSD
20DMC	20.3% DMC 79.7% ULSD

synthesized from natural gas). The dimethyl carbonate was obtained from Sigma Aldridge. The fuels key properties are shown in Table 3.6.

Table 3.6. Properties of fuels and fuel blends

Properties	ULSD	GTL	RME	B30*	G30*	B20G10*	B15G15*	B10G20*	DMC	1 DMC*	2 DMC*	4 DMC*	20 DMC*
Cetane Number	53.9	80	54.7	54.1	61.7	56.7	57.9	59.2	35.5	53.7	53.5	53.2	50.2
Density at 15 °C (kg/m^3)	827.1	784.6	883.7	844.1	814.4	834.2	829.2	824.3	1075	829.6	832.1	837	877.3
Viscosity at 40 °C (cSt)	2.5	3.5	4.5	3.1	2.776	3	2.9	2.9	0.6	2.4	2.4	2.4	2.1
50% Distillation (°C)	264	295	335	-	-	-	-	-	-	-	-	-	-
90% Distillation (°C)	329	342	342	-	-	-	-	-	-	-	-	-	-
LCV (MJ/kg)	42.7	43.9	39	41.6	43.1	42.1	42.3	42.6	15.8	42.4	42.2	41.6	37.2
Sulphur (mg/kg)	46	~0	5	34	32	33	33	33	0	45.5	45.1	44.2	36.7
Total Aromatics (wt%)	24.4	0.3	~0	17.1	17.2	17.1	17.1	17.1	0	24.2	23.9	23.4	19.5
C (wt%)	86.5	85	77.2	83.7	86.1	84.5	84.9	85.3	40	86	85.6	84.6	77.1
H (wt%)	13.5	15	12	13.1	14.0.	13.4	13.5	13.7	6.7	13.4	13.4	13.2	12.1
O (wt%)	~0	~0	10.8	3.2	~0	2.2	1.6	1.1	53.3	0.5	1.1	2.1	10.8
H/C Ratio (Molar)	1.88	2.1	1.85	1.87	1.95	1.9	1.9	1.92	2	1.9	1.9	1.9	1.9

* Properties calculated based on the values of ULSD, GTL , RME and DMC (cetane numbers are approximates)

CHAPTER 4
1st GENERATION MEETS NEXT GENERATION BIODIESEL

Limits on the total future potential of biodiesel fuel due to the availability of raw materials mean that ambitious fossil fuel replacement targets will need to be met by the use of both 1st and next generation biodiesel fuels. The use of higher percentage biodiesel blends requires engine recalibration as it affects engine performance, combustion patterns and emissions. Previous work within the FPS group has shown that the combustion of 50:50 blends of biodiesel fuels (1st generation RME and 2nd generation synthetic fuel) can give diesel fuel-like performance (i.e. in-cylinder pressure, fuel injection and heat release patterns) (Tsolakis *et al.*, 2003; Theinnoi *et al.*, 2009). This means engine recalibration can be avoided plus a reduction in all the regulated emissions. Using a 30% biodiesel blend (with different 1st and 2nd generation proportions) mixed with Ultra Low Sulphur Diesel (ULSD) may be a more realistic future fuel.

Global warming concerns due to the production of greenhouse gases (GHGs, Figure 4.1) have seen the promotion of the use of biofuels. CO_2 is a major contributor to GHGs. Biofuels can be viewed as near CO_2 neutral (when the full CO_2 life cycle is considered). European Union Directive 2003/30/EC (EC, 2003) promotes the use of biofuels, additionally there is an ambitious programme as described in the Commission Green Paper (COM, 2000) which has set a target of 20% substitution of conventional fuels by alternative fuels in the road transport sector by the year 2020.
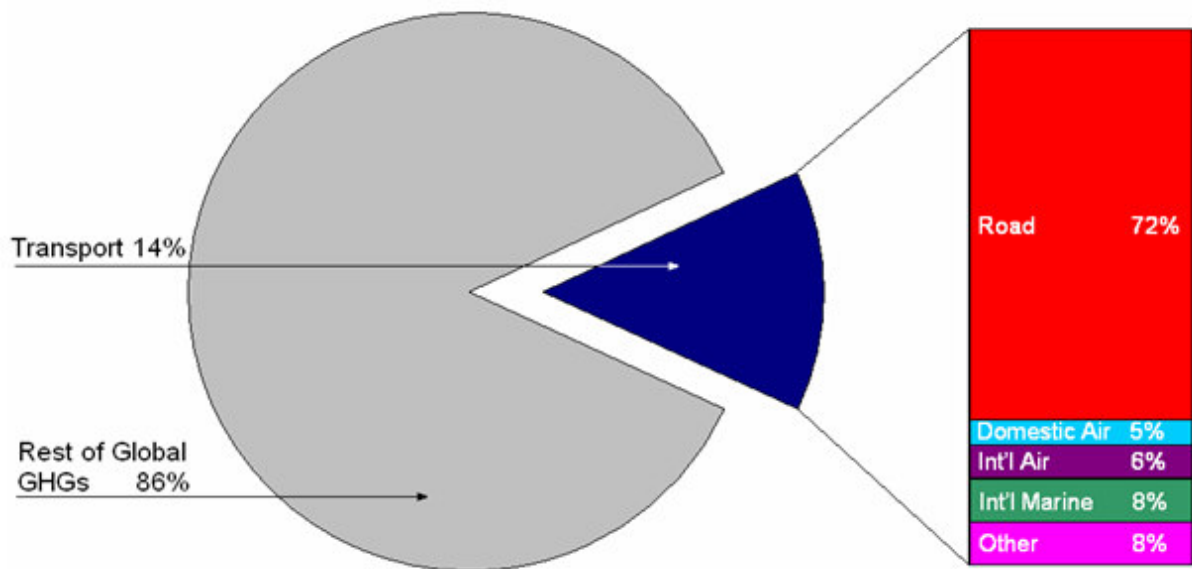
Figure 4.1. Greenhouse gases from transportation (Baumert *et al.*, 2005)

Currently many engine manufacturers only certify up to a 5% blend of biodiesel fuel and they will require convincing to certify for larger biofuel proportion blends. This implies in the short term that smaller proportion blends of biofuel with conventional fossil diesel will be the only way to achieve these targets. There may be limits on the total land available for biofuel growth. This could make ambitious 20% replacement targets difficult to meet using 1st generation biofuels alone. One potential way to achieve these levels could be by combining 1st generation biofuels such as RME with 2nd generation biofuels such as biomass to liquid (BTL). If in combination it could also be shown that the fuels complement each other and give additional emission benefits and reduce any hardware modification required, this might go some way to help engine manufacturers move forwards towards the certification of larger proportion blends.

Ideally a CI fuel would produce low emissions, be renewable, produce useable power to current diesel standards, run in both existing and newly manufactured engines and require no engine modifications.

There are several challenges with the use of first generation biofuels, these include a possible requirement for engine modifications for high proportion blends and ensuring economic viability in a world of fluctuating oil prices (Srinivasan, 2009).

In a modern diesel engine synthetic fuels can satisfy many of the above ideal fuel requirements, as recent studies have shown that synthetic fuels i.e. GTL have emission benefits in reduction of HCs, carbon monoxide (CO), NOx and PM (Oguma *et al.*, 2002; Ng *et al.*, 2008). However, due to the lower volumetric heating value of GTL, injection system hardware and injection strategy require reconfiguration (Lepperhoff *et al.,* 2006).

The primary objective of this Chapter is to show that first generation biofuels, next generation biofuels and conventional fossil diesel can be used together giving similar combustion characteristics to diesel. The secondary objective is to demonstrate that the two biofuels can complement each other. Any negatives intrinsic in one biofuel can be counteracted by the inherent positive characteristics of the other to give both emission and practical improvements.

4.0.1 Fuels, Test Conditions and Procedure (specific to Chapter 4)

Eight fuels were tested, and the basic fuel compositions are outlined in Table 4.1. Table 3.6. shows a list of fuel properties for the six tested fuels.

All steady-state test schemes were set at engine speeds of 1500 rpm and 2000 rpm. Studying the variation of the effects of blended mixtures with loads was carried out at 2 bar, 4bar and 5 bar IMEP. To

Table 4.1. Fuels Tested

Abbreviation	% Volumetric Makeup
ULSD	100% ULSD
RME	100% RME
GTL	100% GTL
B30	30%RME 70%ULSD
GD30	30%GTL 70%ULSD
3-way blends	
B15G15	15%RME 15%GTL 70%ULSD
B20G10	20%RME 10%GTL 70%ULSD
B10G20	10%RME 20%GTL 70%ULSD

study the effects of EGR, the engine was kept running at constant load with EGR variation of 0% and 30% respectively. Test conditions were determined at standard injection timing of 22 CAD before top dead centre (BTDC) as specified by the engine manufacturer. For the high cetane fuels, GTL and G30, a 2 CAD advanced injection timing (24 CAD BTDC) was employed. This was derived from earlier work, where for neat GTL, advancing the injection timing by 2 CAD gave the optimum operation point (Theinnoi *et al.*, 2009; Abu-Jrai *et al.*, 2006).

4.1 EXPERIMENTAL RESULTS AND DISCUSSION

4.1.1 Combustion- The in-cylinder pressure and heat release rate versus CAD data for the 3 source fuels over the end of compression and the early expansion strokes of the engine, are shown in Figures 4.2, 4.3, and 4.4 for engine loads of 2, 4, and 5 bar IMEP respectively. GTL has the effect of retarding the start of injection and combustion due to its reduced fuel density (Table 3.6.) and increased compressibility. On the other hand, GTL has a much larger cetane number, 80, compared to around 54 for the ULSD and RME.

This significantly reduces ignition delay (defined as the time between start of injection and start of combustion) and the fuel burnt in the 'premixed phase' (the first heat release peak (Heywood, 1988)). This can be seen in most conditions apart from the lowest speed and load.

The larger cetane number also extends the diffusion 'controlled combustion phase' (this lowers the in-cylinder peak pressure and temperature by spreading the heat release over later CAD compared to ULSD (Figures 4.3 and 4.4) (Hasegawa *et al.*, 2007).
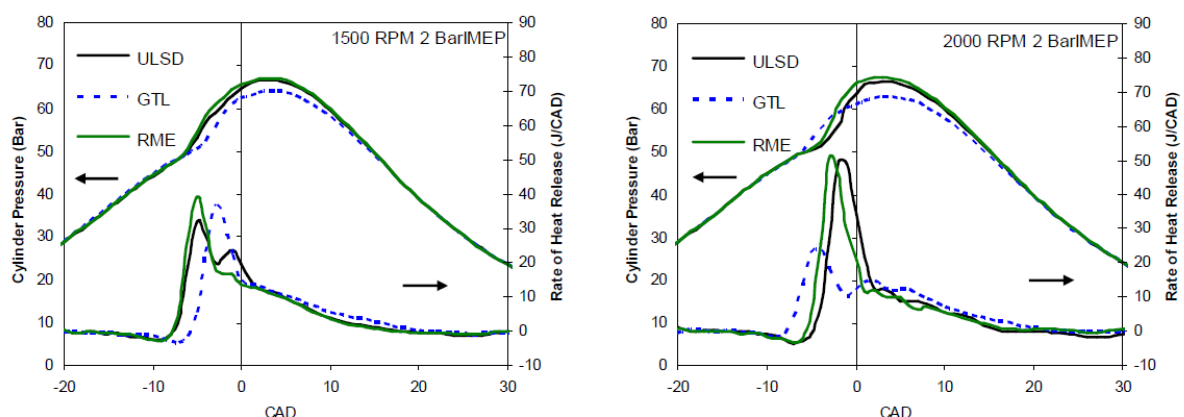
Figure 4.2. Cylinder pressure and rate of heat release for 1500 and 2000 rpm, 2 Bar IMEP, 0% EGR.
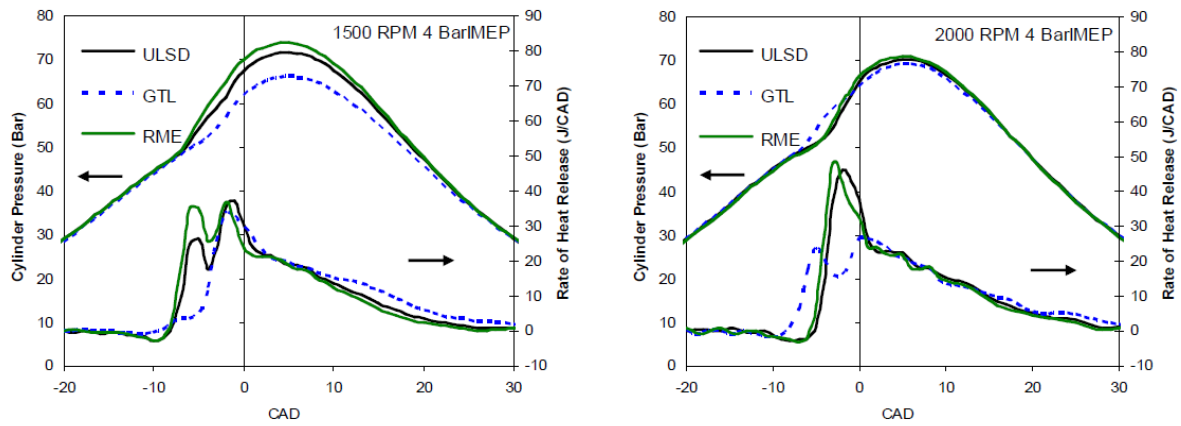
Figure 4.3. Cylinder pressure and rate of heat release for 1500 and 2000 rpm, 4 Bar IMEP, 0% EGR.
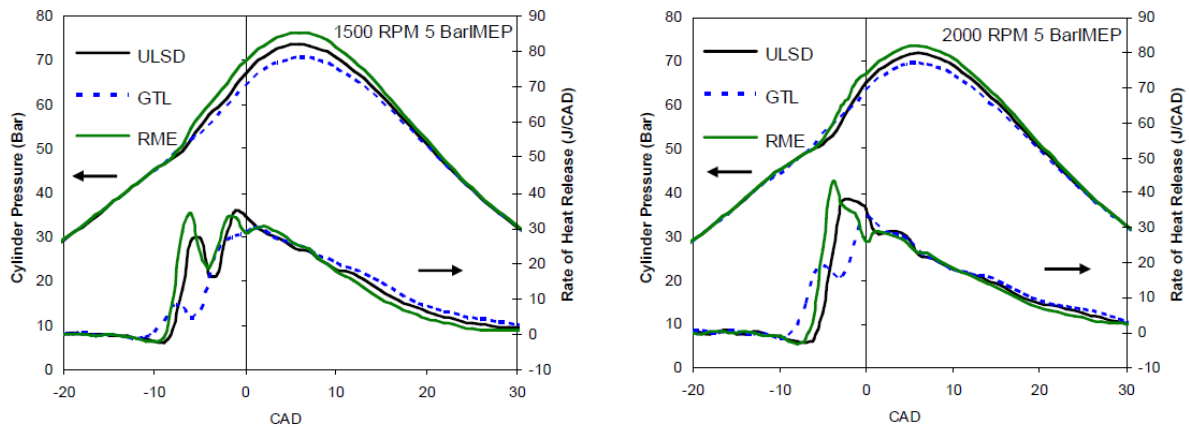
Figure 4.4. Cylinder pressure and rate of heat release for 1500 and 2000 rpm, 5 Bar IMEP, 0% EGR.

In Figures 4.2-4.4 it can also be seen that the first heat release peak for RME is larger than either ULSD or GTL. This is thought by some to be due to the oxygen content of the fuel (Table 3.6.) and again the increased rate of pressure rise (as RME has a higher density) which gives increased injection pressure and therefore, cylinder penetration. This also gives a more dispersed charge and improves the air entrainment. When the ROHR trace for RME and ULSD is compared, the opposite trend compared to GTL is observed. An ignition advance for RME is seen and this is apparent in all Figures, (the shift to the left of the RME ROHR line). It is thought to be due to its higher bulk modulus, therefore the rate of injection pressure rise of RME is much higher than that of ULSD.

Figures 4.5-4.7 show the in-cylinder pressure and heat release rate versus crank angle degree data for ULSD, B10G20, B15G15 and B20G10 over the end of compression and the early expansion strokes for engine loads of 2, 4, and 5 bar IMEP, respectively. It is immediately apparent how closely these blends match ULSD in terms of the ROHR (the fuel's combustion characteristics).

In all Figures it is possible to discern that not only is the SOC at approximately the same CAD and in phase, but also both the 'premixed phase' and the 'controlled combustion phase' are of a similar magnitude for all three blends.
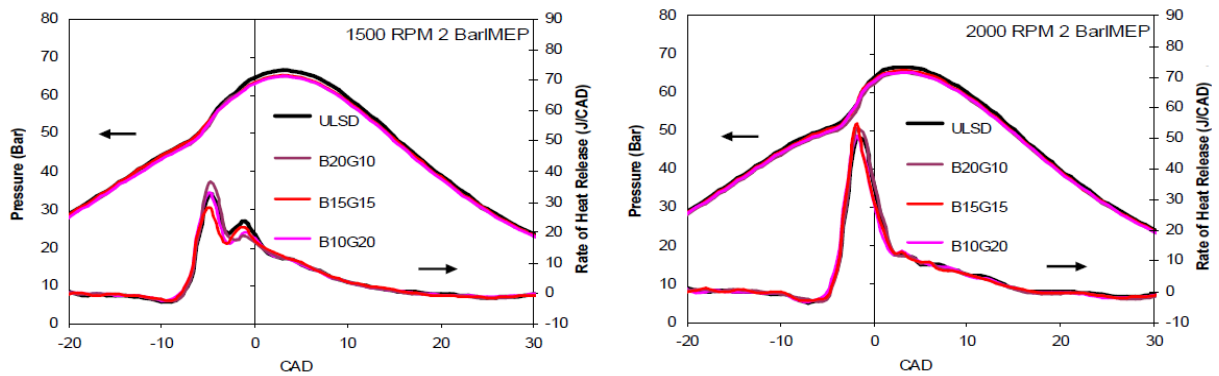

Figure 4.5. Cylinder pressure and rate of heat release for 1500 and 2000 rpm, 2 Bar IMEP, 0% EGR.
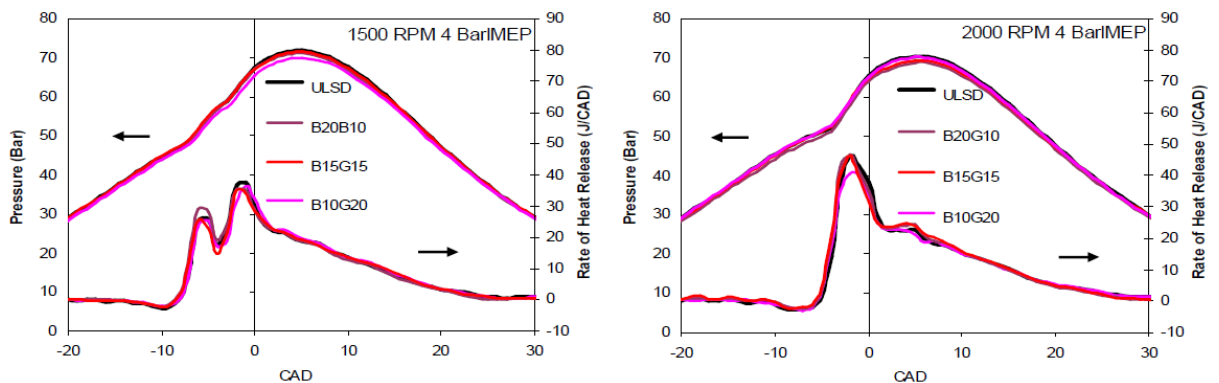
Figure 4.6. Cylinder pressure and rate of heat release for 1500 and 2000 rpm, 4 Bar IMEP, 0% EGR.
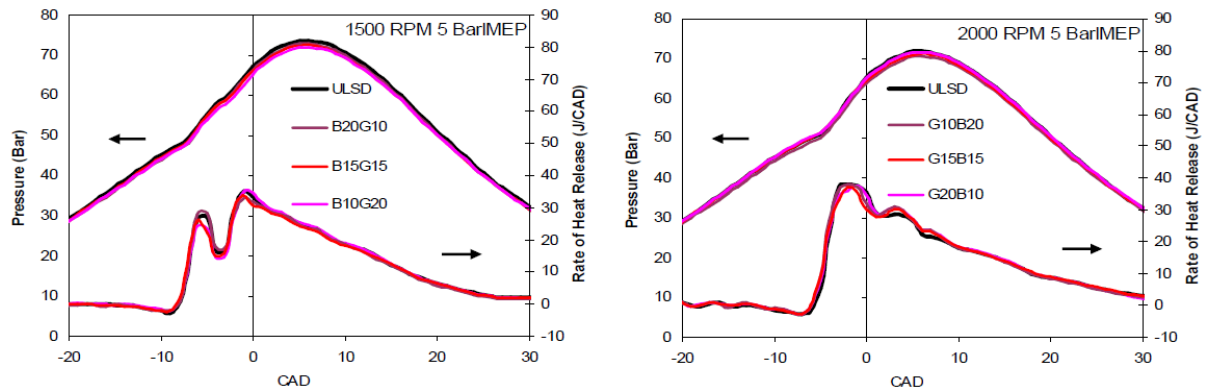
Figure 4.7. Cylinder pressure and rate of heat release for 1500 and 2000 rpm, 5 Bar IMEP, 0% EGR.

Table 4.2 shows the maximum CAD difference between SOC for the 3-way blends and SOC for ULS diesel combustion. It is thought that these small differences in CAD lie within the experimental error of the system. Therefore it is fair to say that combustion starts at the same CAD.

The combination of the increased cetane number, lower density and viscosity (Table 2.2.) of the 3-way blends when compared to RME in Figures 4.2., 4.3. and 4.4., increases the injection delay and combustion duration, whilst reducing ignition delay and fuel burnt in the 'premixed phase'.

Table 4.2. Start of Combustion

	B20G10	B15G15	B10G20
Maximum CAD difference to ULSD	-0.33*	-0.22*	-0.22*

*Taken from Figures 4-6 i.e. all tested conditions

In terms of ROHR amplitude, as might be expected, the higher proportion RME blend B20G10 sees the greatest peaks. Again this could be attributed to its increased oxygen content and higher bulk modulus than the other blends (Table 3.6.). In general B10G20 exhibits the lowest amplitude ROHR in a comparable fashion to the ROHR from GTL in Figures 4.2., 4.3. and 4.4.. The closest ROHR for the 6 conditions tested appears to be B20G10, which certainly is more adept at matching the ULSD trace at the higher engine speed of 2000 rpm (2, 4 and 5 BarIMEP). At 1500 rpm, B20G10 is again superior at the

highest load, 5 Bar. However, 1500 rpm 4 BarIMEP is most closely matched by B15G15 and at 1500 rpm 2 BarIMEP B10G20 seems more appropriate.

For many of the conditions, B15G15 is a close second, to B20G10 (in terms of ROHR match-up) with B10G20 usually the least akin to ULSD. This indicates that the optimal blend with the best match to the combustion characteristics of ULSD lies between B20G10 and B15G15. In other words, with ULSD de-coupled, the optimum ratio of RME:GTL lies between 50:50 and 66.6':33.3' and is in accordance with research conducted by Theinnoi *et al.* (2009).
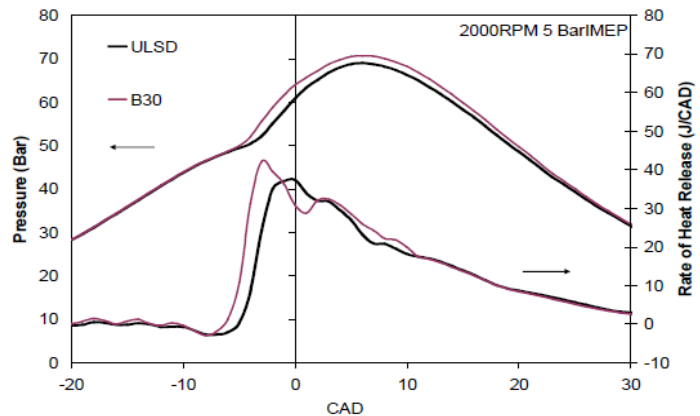
Figure 4.8. B30 compared to ULSD (indicating the need for injection system modification).

It could be argued that all these blends give a similar heat release to ULSD. As a high proportion (70% ULSD) is common to all blends this is not so surprising. However, briefly looking at B30 compared to ULSD Figure 4.8 (1 example load) which highlights how different the combustion of B30 (30% RME 70% ULSD) is to any of the combined blends of Figures 4.5. – 4.7. Figure 4.8 also highlights the potential engine re-calibration that is required to optimise the performance of larger proportion blends of biofuel. Use of any of the 3-way blends in Figures 4.5-4.7 should not entail fuel specific re-calibration.

4.2   EMISSIONS

Perhaps the most important exhaust emission is NOx, for the following reasons: its effect on human health, effect on the environment and the fact that it is difficult emission to abate especially whilst attempting to oxidise other emissions. Many other engine-out emissions

are relatively easy to treat, e.g. DOC can eliminate 90-99% of the HC's and CO and diesel particle filters (DPFs) are able to reduce PM by 95% by mass. For NOx control EGR as well as, further aftertreatment systems must be employed, such as selective catalytic reduction with urea (SCR), so the old adage "prevention is better than cure" might come into play. A fuel whose combustion produces lower emissions will also enhance the efficiency of exhaust gas aftertreatment systems due to the increased availability of active catalytic sites (Rodríguez-Fernández et al., 2009).

Figures 4.9 and 4.10 show the NOx – BSN trade-off for the 3 source fuels and the 3-way blends. Figures 4.9 and 4.10 show the relationship between PM and NOx emission. RME exhibits significantly lower amounts of smoke due to an increased premixing combustion phase and due to 10.8% O_2 within the fuel itself (compared to 0% in ULSD). A small increase in NOx is seen in Figures 4.9 and 4.10. If this is observed in conjunction with Figures 4.2-4.4, it is evident that the effect of RME fuelling is increased peak combustion pressures, due to increased premixing from a combination of inherent oxygen and increased bulk modulus. This goes some way to explain the increased NOx levels, which are highly temperature and pressure dependent, a feature that has been reported by many authors (Senatore et al., 2000; Hasegawa et al., 2007; Bielaczyc & Szczotka, 2008; Kawano et al., 2008).

GTL exhibits lower smoke due mainly to the 2 CAD advanced injection timing (though not to the same extent as RME). The significant advantage observed from GTL fuelling is the NOx reduction. The decrease is considered to occur due to lowering of the maximum heat release rate (Hasegawa et al., 2007) as this gives an indication of the maximum extent of the temperature range. The decrease of NOx emissions with GTL fuel can be linked to its

decreased modulus of compressibility, (which is related to its paraffinic nature), in effect this retards the injection timing.
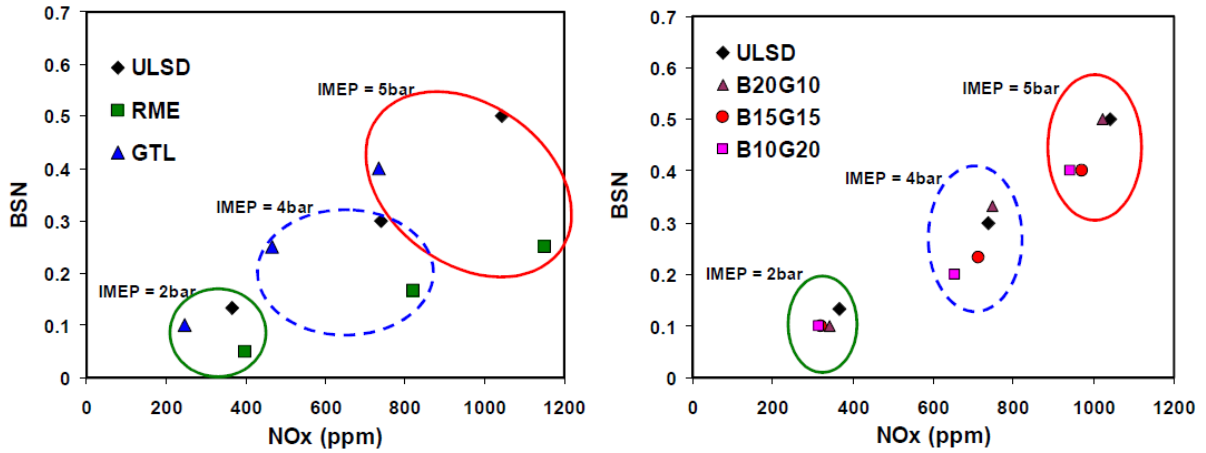
Figure 4.9. NOx – Smoke (BSN) trade-off 1500rpm.
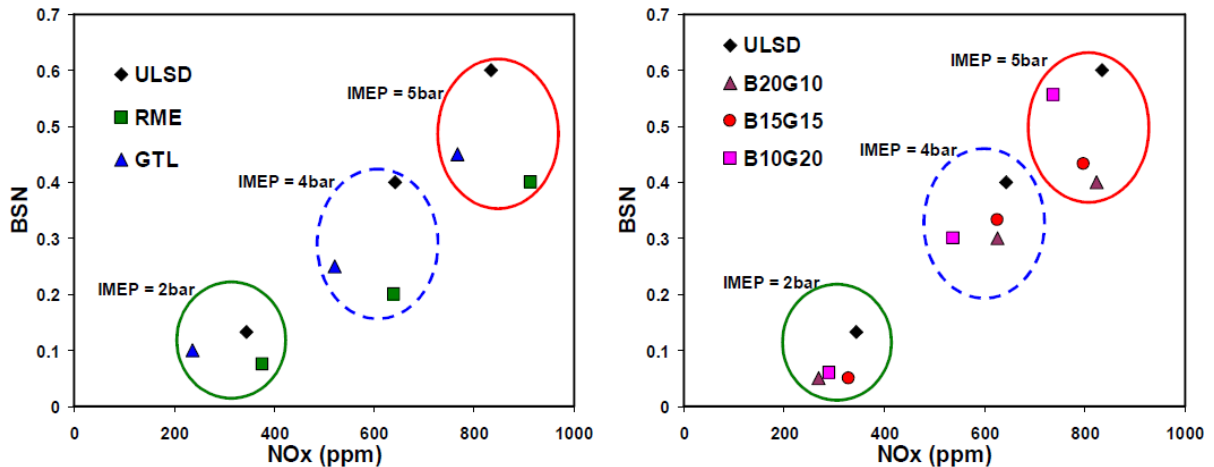
Figure 4.10. NOx – Smoke (BSN) trade-off 2000rpm.

The extent of this effect depends on the particular injection system. (This effect is exactly opposite to that observed with biodiesel, which shows an increased modulus of compressibility and increased NOx) (Boehman *et al.*, 2003).

In addition, the GTL used in these tests has a cetane number of 80. The ULSD and RME have similar cetane numbers of 53.9 and 54.7. With an increase of 10 cetane numbers, a 5% NOx reduction can be expected, in older technology engines (like the pump-line-nozzle used

in these tests). Newer engines (common rail with a modern ECU) may experience a 2% NOx reduction with the same cetane number increase (Lee *et al.*, 1998).

All of the 3-way blends exhibit lower NOx and smoke than ULSD. B10G20 and B15G15 perform best in terms of NOx and BSN. The reduction of smoke with RME, GTL and the 3-way blends compared to diesel can also be attributed to their significantly lower sulphur contents compared to ULSD. Potentially the benefits in terms of NOx control of these 3-way blends, is that with reduced engine-out smoke there is increased potential regarding EGR rate (an established lean burn NOx control mechanism). This is because re-circulating large quantities of PM can cause combustion irregularities (and in turn reduced power) as well as lubricant soiling and abrasive
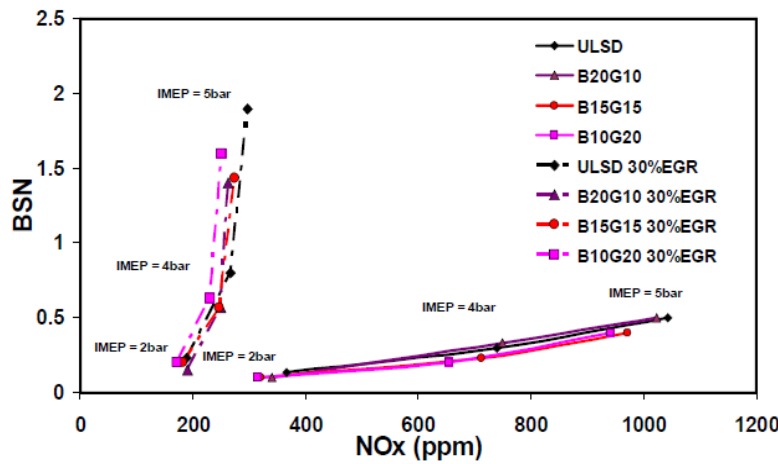
Figure 4.11. NOx - BSN trade-off for 0% and 30% EGR.

wear. So the maximum EGR rate could be increased with these 3-way blends see Figure 4.11.

Figure 4.12 was compiled using mean averaged values from all the tested conditions. The engine thermal efficiency, (the engine energy output over the fuel energy input) was dependent on the fuel type see Figure 4.12. The general trend is: GTL > G30 > B10G20 > B15G15 > B20G10 > ULSD > B30 > RME. Though, the differences are small (and the advanced injections should be considered), especially with the 3-way blends. Indeed fuel flow rates (not shown) for the 3-way blends compared to ULSD are in proportion to their heating values across all conditions.
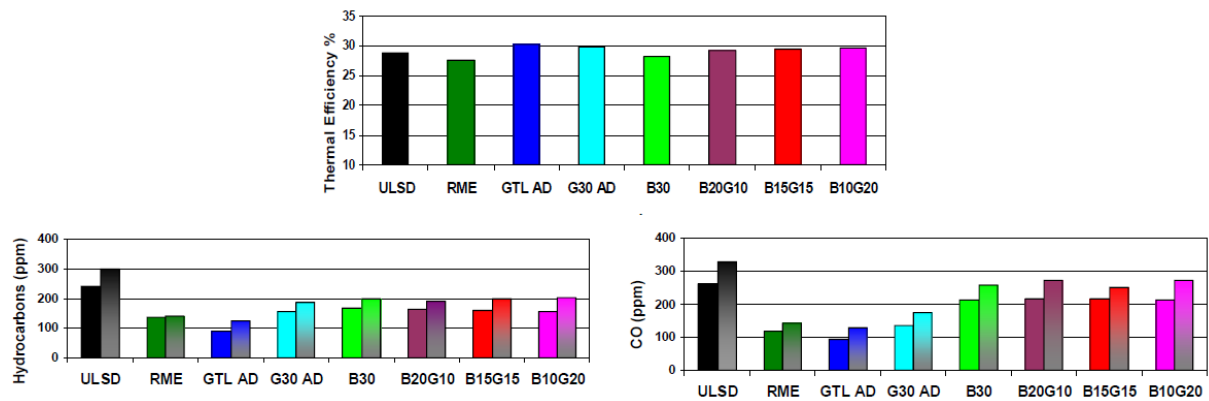
Figure 4.12. Thermal Efficiency, Hydrocarbon and CO emissions from the 8 tested fuels. For the Hydrocarbon and CO chart LHS column is 0% EGR and the RHS column is 30% EGR.

Figure 4.12 shows that hydrocarbons and CO emissions were significantly reduced for the combustion of RME, the 3-way blends and B30 compared to diesel. For RME and B30 this can be explained by the high O_2 content 10.8% wt for RME and 3.2% for B30. The oxygen contributes by improving fuel oxidation even in locally rich fuel combustion zones (Mueller *et al.*, 2003). The increased concentration of oxygen atoms in this over-rich mixture contributes to hydrocarbon and CO suppression. For the 2 fuels at advanced injection timing, the advance will no doubt be the principle reason for the more complete combustion. For blends containing GTL, its improved combustion quality (cetane number) could also be a driving mechanism.

It is feasible that proportional ULSD replacement can be achieved by blending. A ULSD:GTL:RME mix akin to the ones reported in this work could help in achieving future biofuel replacement targets. A further study to optimise the RME:GTL percentage along with the effect on a modern multi cylinder (higher injection pressure) engine is envisaged for the FPS group.

4.3   SUMMARY AND CONCLUSIONS

To assess the feasibility of a more realistic future biofuel, a comparative combustion study between ULSD, GTL (synthetic diesel), biodiesel (RME), and 3-way blends of ULSD, GTL and RME has been conducted. Blending ULSD, GTL and RME can produce a fuel with similar combustion characteristics (i.e. in-cylinder pressure, ROHR and start of combustion) to conventional ULSD with no fuel economy penalty. The optimal blend that most closely matches the combustion characteristics of ULSD lies between B20G10 and B15G15. Alternatively expressed:- with ULSD de-coupled, the optimum ratio of RME:GTL lies between 50:50 and 66.6':33.3'. Problem emissions produced by one source fuel are counteracted by inherent advantageous characteristics of the other in the blend. This creates a blend that requires no engine modifications. There are additionally simultaneous improvements in smoke-NOx trade-off and engine efficiency due to the dynamic properties of the blends, e.g. the higher cetane number due to the GTL and the increased oxygen content due to the RME proportion. In fact, all engine emissions tested were reduced. Diesel mixed with GTL and RME may be more realistic (than a blend having only two constituents) as a future fuel. It could feasibly help to reduce both emissions and reduce the need for fuel specific engine modifications. If GTL can be produced from a bio source it would also help towards GHG emission targets. Providing RME and a BioGTL can be produced economically and in sufficient quantities, Diesel replacement targets could be achieved by a blend of this type. These blends of fuel could be used in both newer and older engines and could be sold at the pump today.

CHAPTER 5

A COMPARISON OF DIESEL AND BIODIESEL EMISSIONS USING DIMETHYL CARBONATE AS AN OXYGENATED ADDITIVE

Oxygenated biodiesel fuels such as RME can be utilised in an unmodified conventional diesel engine (Chapter 4). RME combustion produces low emissions of unburnt total hydrocarbons (THCs), carbon monoxide (CO), and PM (Chapter 4). This is due in part to fuel-borne oxygen content (10.8% wt). This Chapter examines the effect of adding fuel-borne oxygen in the form of DMC (a nontoxic potentially bioderived 53.3% wt oxygenated additive) to conventional pump diesel.

Biofuels have attracted keen interest in Europe. The European road transport market alone is approximately 270 m tonnes (2004). This is projected to rise to 325 m tonnes by 2020, (Ho, 2006) when the biofuels directive 2009/28/EC should see 10% biofuel replacement. This could mean that biofuel production will have to be of the order of >30 m tonnes/y (as biofuels are often of lower heating value). The potential for oxygenated additives has been discussed in Chapter 2. Dimethyl carbonate (Figure 2.4. in Chapter 2) as an additive for ULS diesel could be counted towards biofuel replacement targets. It has been proposed as a suitable non toxic bio oxygenated additive and an explanation was given in Chapter 2.

The primary objective of Chapter 5 is to further our understanding of the role that fuel-borne oxygen can play in diesel combustion by comparing diesel combustion with diesel containing DMC and biodiesel. The secondary objective is to examine the potential of DMC as an oxygenated additive for conventional fossil diesel.

5.0.1 Fuels, Test Conditions and Procedure (specific to Chapter 5)

Six fuels were tested, and the basic fuel compositions are outlined in Table 5.1. Table 3.6. shows a list of fuel properties for the six tested fuels. 20DMC has been included, as its fuel oxygen percentage weight approximates that of RME.

Table 5.1 Fuels (Chapter 5)

Abbreviation		% Volumetric Makeup		
ULSD	100%	Ultra Low Sulphur Diesel		
RME	100%	Rapeseed Methyl Ester		
1DMC	1%	Dimethyl Carbonate	99%	ULSD
2DMC	2%	Dimethyl Carbonate	98%	ULSD
4DMC	4%	Dimethyl Carbonate	96%	ULSD
20DMC	20.30%	Dimethyl Carbonate	79.70%	ULSD

Testing Procedure. All tests were steady state and were set at engine speeds of 1500 and 2000 rpm. Studying the variation of the effects of blended mixtures was carried out at 2 bar, 4 and 5 bar IMEP. To study the effects of EGR, the engine was kept running at constant load with EGR variation of 0% and 30%, respectively.

5.1 EXPERIMENTAL RESULTS AND DISCUSSION

5.1.1 Combustion- An interesting observation was that during the fuel blending stage it was noticed that small introductions of DMC in ultra low sulphur (ULS) diesel (ULSD) dissolve and disperse readily. However the largest blend of DMC in ULS diesel (20DMC) did not disperse readily and certainly some agitation was required to achieve an apparent continuous single phase liquid. The implication of this might be that in time the DMC might separate from the diesel and perhaps some sort of surfactant might be required. A rudimentary investigation revealed that in 1 month at room temperature around half of the

20DMC had separated from the ULS diesel. All the other blends appear to have no visual separation.

The larger blend 20DMC also presented a problem during combustion. Peak cylinder pressures were much higher than ULS diesel combustion (Figure 5.1), especially in the initial premixed combustion phase. This is attributed to its reduced cetane number and high oxygen content. The injection timing is set at a fixed point, however, much of the energy produced is created before top dead centre (TDC), i.e. during the compression stroke, where it is counterproductive. For this reason, the largest IMEP of 5 bar became unattainable when this fuel was used, as the injection system hardware was unable to deliver the amount of fuel required. Figure 5.1 represents a typical cylinder pressure (top) and rate of heat release (ROHR) (bottom) across a range of CAD. The 20DMC series has been omitted from Figures 5.2 and 5.3 for the previously mentioned fuelling problems.
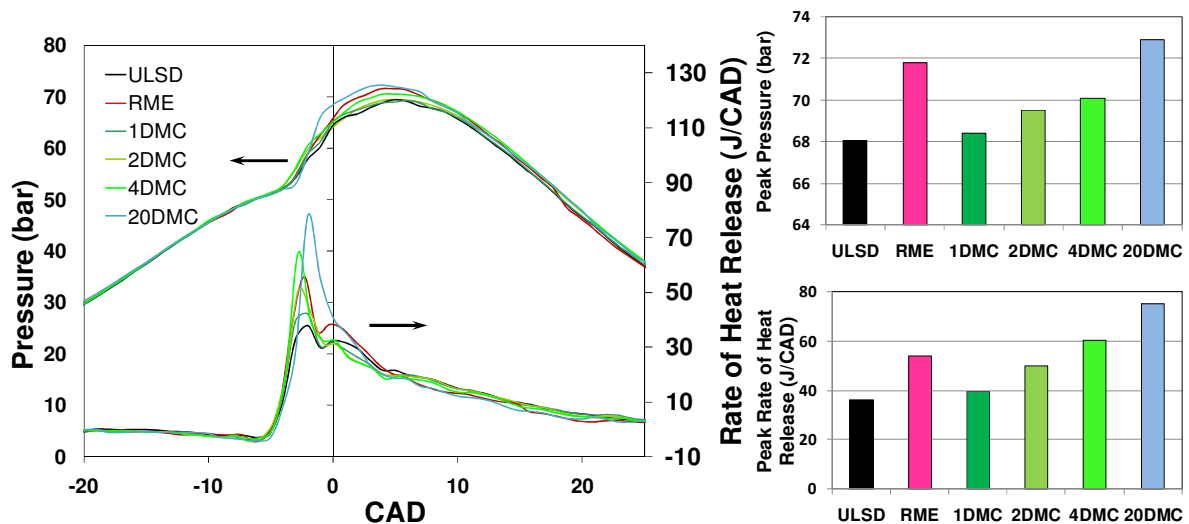
Figure 5.1. Cylinder pressure and rate of heat release 2000rpm, 4 bar IMEP 0% EGR.

When considering cylinder pressure, it is apparent that higher peak pressures are achieved for the blended fuel. In fact, the peak increases in line with the increased proportion of DMC i.e. the peak pressures increase as oxygen content increases. This is an

indication that an increased premixed (close to TDC) combustion has occurred. If the cylinder pressure just prior to TDC is considered, it is seen that the initial pressure rise is also greater for the oxygen containing blends. Again as oxygen in the blend increases, so does the pressure rise (this is most clearly seen for 4DMC in Figure 5.1) and the pressure rise rate (not shown).

On ROHR analysis (Figure 5.1), it can immediately be seen that there is an apparent difference in the initial peak rates of heat release for all the DMC containing blends. It can also be seen that this peak value is related to the quantity of DMC, i.e. more DMC gives a higher initial peak rate of heat release. This indicates that an increased proportion of the fuel is used during the premixed or rapid combustion phase with fuel-borne oxygen. This would appear logical, as with fuel-borne oxygen, more fuel will be in contact with oxygen to within the flammability limits during the ignition delay period (point of injection to start of combustion, i.e. positive ROHR)(Heywood, 1988).

Additionally, cetane number and density are not significantly influenced by small additions of DMC (Table 3.6.). The start of combustion for all fuels was maintained at approximately -6 CAD. Taking a further look at the ROHR in Figure 5.1, it can be gleaned that during the mixing controlled combustion and late combustion phase, the blends containing DMC are at, or below, the base heat release of ULS diesel. One likely reason for this is that during ULS diesel combustion, cylinder pressures are lower than for the oxygenated blends. Therefore, an increased fraction of the fuel has remained unburnt and is still available for combustion. The increase of the oxygen concentration going into the spray does not significantly affect the lift-off length (i.e., as the gas temperature was not significantly altered), and soot oxidation is improved without considerably increasing NOx (Benajes *et al.*,

2010). Another possibility is that without fuel-borne oxygen there will be a larger proportion of soot (incomplete combustion) which can still (temperature dependently) react to release heat in this later expansion stroke.

Similar combustion trends to the aforementioned were seen for all load conditions and at both engine speeds (1500 and 2000 rpm). The principal differences were the extent of the variance between loads i.e. less noticeable at lower loads. These trends were also seen for both EGR rates of 0% and 30%.

Comparing biodiesel to conventional diesel (Table 3.6.), it is possible to see that peak pressures are higher for biodiesel and that the pressure ramps up slightly earlier. Perhaps more interesting is the distinct difference noticed from the ROHR, where it is clear that combustion has commenced earlier and also the increase in the premixed peak (first peak). On consideration, it is thought that the advance in combustion will be due principally to the increased bulk modulus, i.e. density of the biodiesel, which causes the rate of pressure rise within the fuel to ramp up faster and in turn inject earlier into the cylinder. This trend has been observed by many researchers (Mcdonald *et al.*, 1995; Szybist *et al.*, 2003 Szybist & Boehman, 2003; Hassaneen, 2008; Zhang *et al.*, 2008). The premixed ROHR peak for biodiesel is at both an earlier CAD and is larger than for ULS diesel.

Biodiesel has both increased density and fuel-borne oxygen at 10.8% wt in the case of RME (Table 3.6.). It follows that with increased density, there is potential for increased cylinder penetration during fuel injection. This should enhance the mixing process, as increased penetration will spread the mixture over a larger area. Following on from this, premixed combustion should increase with an increase in fuel density. So this density increase combined with a large proportion of fuel-borne oxygen should see a fairly large

increase in the extent of the premixed combustion. The biodiesel in this case has a lower caloric value (LCV) of 39 MJ/kg compared to diesel of 42.7 MJ/kg. As a percentage, biodiesel contains around 92% of the energy of diesel by mass. It becomes apparent that the many differences in chemical and physical properties between biodiesel and diesel make it particularly difficult to isolate the effect of the just one component, in this case oxygen.

For the DMC blends, the fuel's physical properties, density, viscosity, compressibility, cetane number, and heating value, are approximately equal to diesel. The significant difference is that they range from 0.5 to 2.1% wt oxygen (Table 3.6.). The picture is therefore much clearer and it becomes slightly easier to attribute differences more specifically to the oxygen weight percentage.

Since the principal fuel's physical properties do not vary significantly for these DMC blends, it stands to reason that the SOC will not be significantly affected by the DMC. This is noticed in Figure 5.1. where it is possible to see that SOC, i.e. positive ROHR, is at the same CAD for diesel and the DMC blends.

Significantly, the extent of the premixed peaks for all the DMC blends is noticed. Indeed, on further examination of Figure 5.1, it is discernible that the first premixed ROHR peak for biodiesel is not as large as that of either 2DMC or 4DMC. This first premixed peak for biodiesel is generally either lower than or similar in value to 2DMC and always beneath 4DMC. A blend containing only 2.1% wt oxygen (4DMC) can produce a larger amount of premixed ROHR than biodiesel which contains 10.8% wt. The reason for this lies within the many differences between biodiesel and ULS diesel (some of which have been discussed) such as, different structures with various functional groups and the reduced LCV of biodiesel.

Clearly explanations for enhancement of premixing for biodiesel combustion must be careful to avoid attributing improved premixed combustion to oxygen content alone.

5.2   EMISSIONS

Figure 5.2 represents the NOx emissions at 2, 4, and 5 bar IMEP, with and without EGR. For all the EGR off conditions, the most apparent observation was that all the oxygenated fuels produced higher NOx emissions when compared to the source ULS diesel fuel. This can be explained by the oxygenated fuels having increased cylinder pressures (with higher temperatures) and indeed increased period of time at these higher pressures (Stone, 1999) (Figure 5.1). NOx emissions for 20 DMC are large, which makes it an impractical fuel for standard injection parameters in this engine.
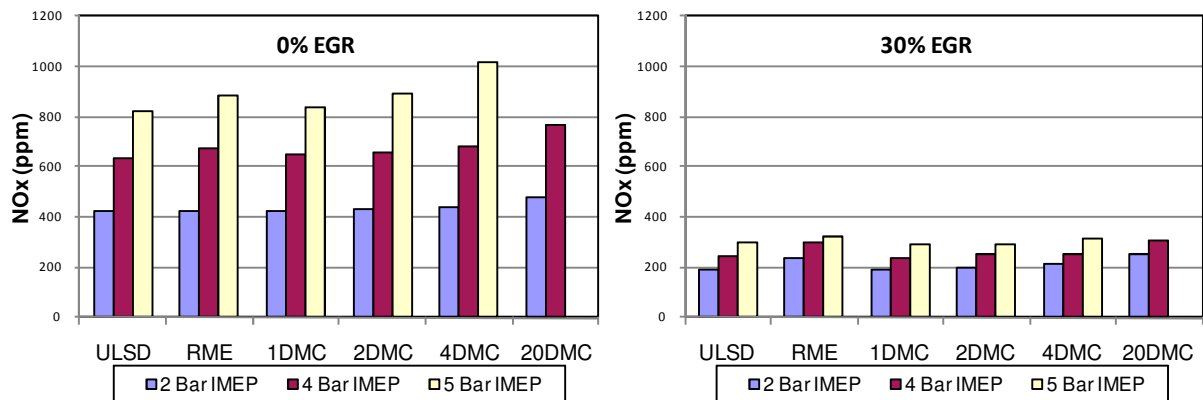
Figure 5.2. Total nitrogen oxides emissions for 3 engine loads (2, 4 and 5 bar IMEP) at 2000 rpm for both with and without EGR.
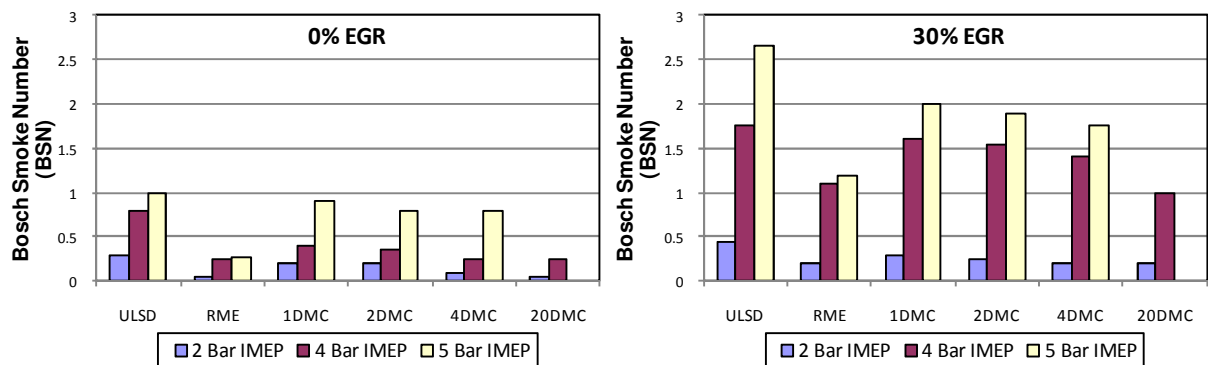
Figure 5.3: Smoke levels at 2000 rpm.

When EGR is applied at 30% (volumetric), the oxygenated fuelled NOx emissions are reduced to the approximate level of NOx emissions for standard ULS diesel combustion at 30% EGR. Since the NOx base emissions (0% EGR) were higher for the oxygenated fuels, it seems that EGR NOx suppression is greater with oxygenated fuels. Reductions in peak cylinder pressures and temperatures during EGR are due principally to oxygen intake reduction (which will be in proportion for each fuel) (Ladommatos *et al.*, 2000). For oxygenated fuel combustion, there will also be an increase in the specific heat capacity (C_p) for EGR conditions. This is due to more complete (due to fuel-borne oxygen and any changes in H/C ratio) combustion yielding a greater proportion of increased C_p CO_2 and H_2O (Ladommatos *et al.*, 1996).

A problem with high EGR rates is that combustion can become unstable at high load due in part to high levels of smoke (Ladommatos *et al.*, 1996; Abd-Alla, 2002; Zheng *et al.*, 2004). Fuel-borne oxygen can help by extending the EGR limits for these high load (smoke limited) conditions, this in turn can further reduce NOx levels [e.g., Theinnoi *et al.* (2008)].

Smoke or PM emissions are of concern for health, environmental, legislative, and aesthetic reasons. Figure 5.4 shows typical smoke levels for various engine loads with and without EGR. It is possible to see that all the oxygenated fuels produce lower smoke levels than their diesel (ULS DIESEL) counterparts for corresponding speed load conditions. Comparing the DMC blends, it is also plausible that as fuel-borne oxygen levels increase, smoke levels go down. In view of the increased cylinder pressures (Figure 5.1) associated with the oxygenated fuels, this might be expected. Smoke or PM is made up of carbon soot particles, VOCs, water, a small amount of metallic compounds, and ash (Kittelson *et al.*, 1999).
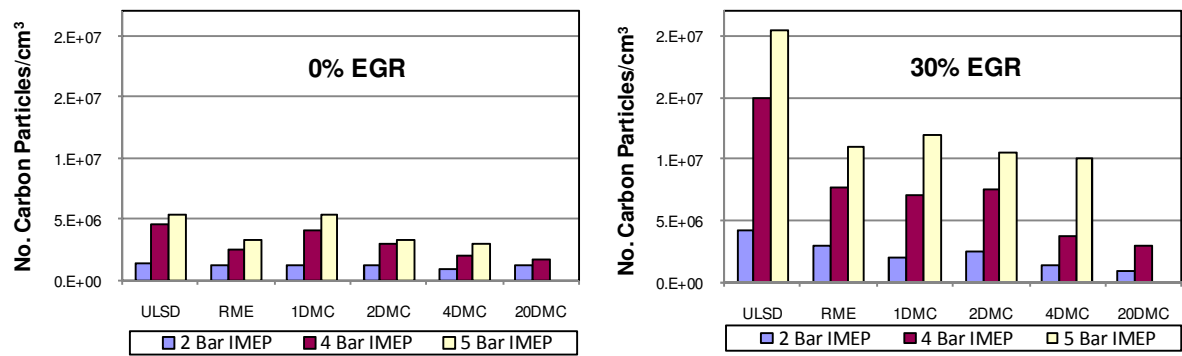
Figure 5.4. Soot particle number at 2000 rpm.
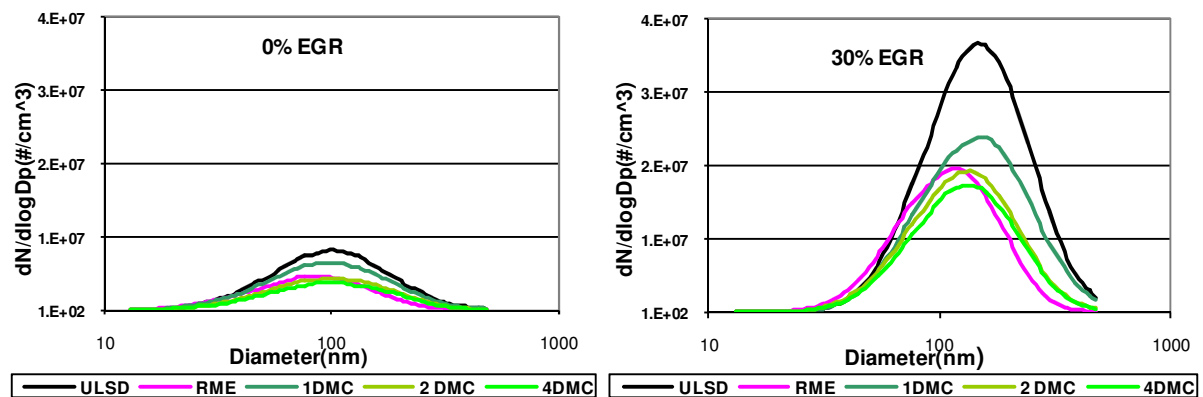
Figure 5.5: Soot particle size distribution at 2000 rpm and 5 bar IMEP.

A SMPS was employed to determine a detailed size distribution of the carbon and carbon agglomerated particles specifically. This was achieved by thermally driving off the VOCs and water using a thermodilution system set at 573 K, prior to the particle spectrometer.

All the oxygenated fuels gave lower total number emissions of carbon particles (Figure 5.4). Indeed, during EGR conditions, the total number of carbon particles was reduced by as much as 50% for the oxygenated fuels. Figure 5.5 shows typical carbon particle size distributions for EGR on and EGR off at 5 bar IMEP and 2000 rpm. All the oxygenated fuels produced a reduced size distribution, with a shift toward a smaller mean carbon particle size. For the DMC blends, in terms of the mean particle size, the DMC blends were slightly less than diesel (ULS diesel). This is thought to be due in part to suppression of soot nuclei

growth at the core of fuel droplets, due to the fuel-borne oxygen (Miyamoto *et al.,* 1998). Biodiesel (RME) has a more significantly reduced mean particle size compared to ULS diesel. This is thought to be due to both a reduced formation rate of particulate and proportion of carbon particles coagulating together to form larger mean diameter carbon agglomerated particles. One explanation for this phenomenon might be that the formation and coagulation is stunted by the increased cylinder pressures. These cylinder pressures in turn are due to fuel-borne oxygen and the increased density (which induces increased penetration and dispersal) of biodiesel fuelling. This same argument could be used to explain the increased proportion of small nuclei mode carbon particles for biodiesel combustion in Figure 5.5.

In general, Figures 5.4 & 5.5 confirm that oxygenation reduces the total amount of smoke and by a more significant margin, reduces the total number of carbon particles. In fact, substitution of ULS diesel with DMC at just 2% in this engine, can achieve a total number of carbon particles reduction equivalent to biodiesel (RME) fuelling.

Taking into account that smoke measurements (Figure 5.3) encompass the proportions of not only carbon particles but also VOCs PM and water PM, it is interesting that reductions in smoke levels for the DMC blends were not as large as the reductions in carbon soot particles noticed in Figures 5.4 and 5.5. It is thought that this is attributed to the inclusion of the SOF in the smoke measurements.

In ideal combustion, air is mixed completely with the atomised fuel. The reality is different; there are zones that are deficient in oxygen. Nevertheless, these zones undergo the heating of combustion, which leads to thermal decomposition (Schulz *et al.*, 1999). This decomposition can create shorter hydrocarbon chain lengths and potentially toxic VOCs.

Fuel-borne oxygen aids the reduction of hydrocarbon emissions. As the proportion of oxygen is increased, the reduction in THCs increases (due to the DMC increase within the blend (Figure 5.6a)).

a)   b)
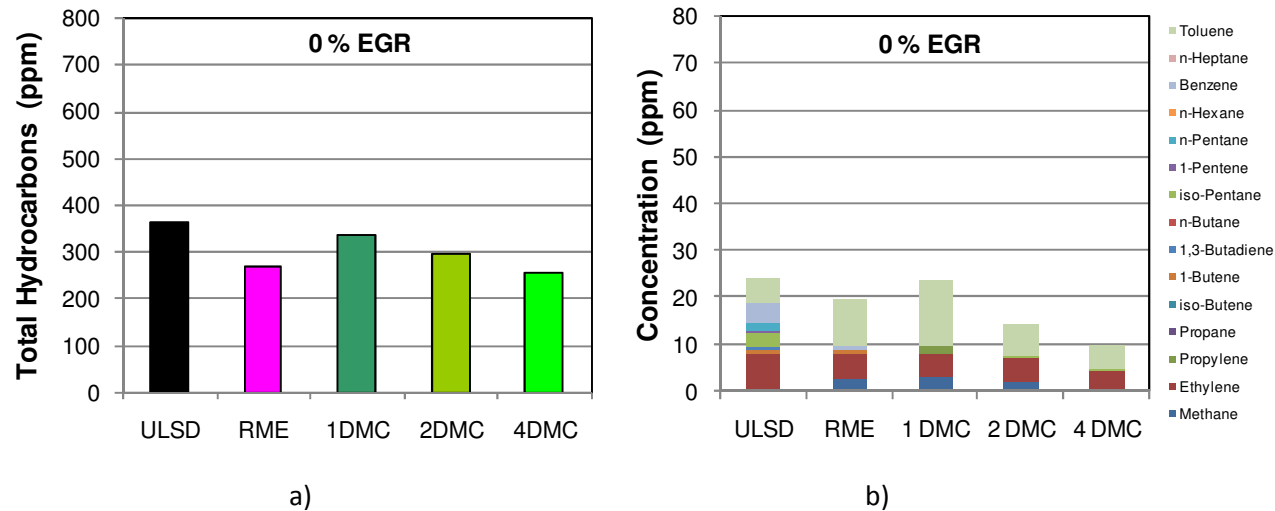
Figure 5.6. a) Unburnt total hydrocarbons (methane C_1) and b) gas chromatograph hydrocarbon speciation 0% EGR (C_1-C_7) 2000 rpm 5 bar IMEP.

a)   b)
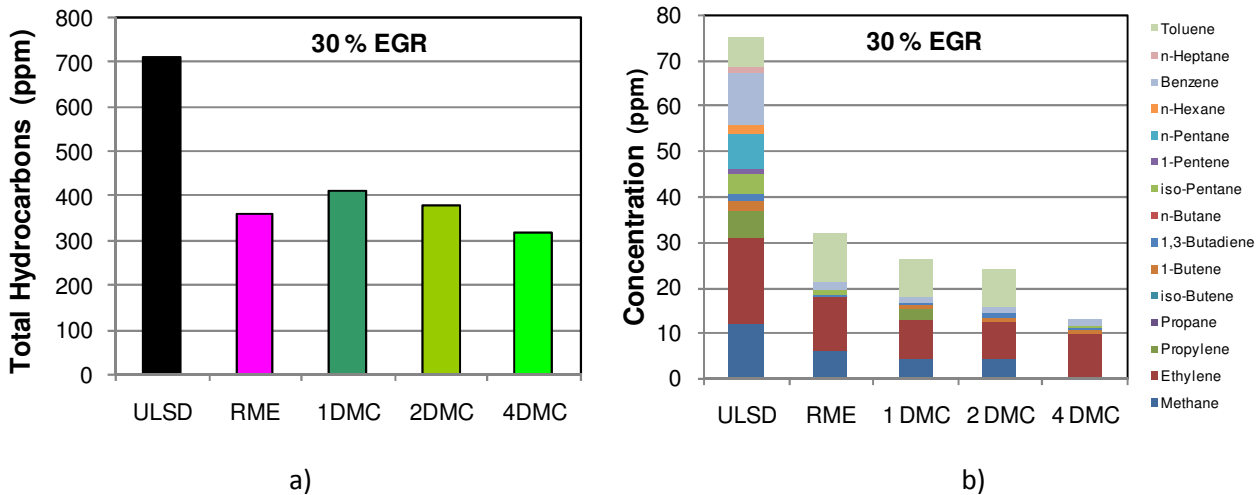
Figure 5.7. a) Unburnt total hydrocarbons (methane C1) and b) gas chromatograph hydrocarbon speciation 30% EGR (C_1-C_7) 2000 rpm 5 bar IMEP.
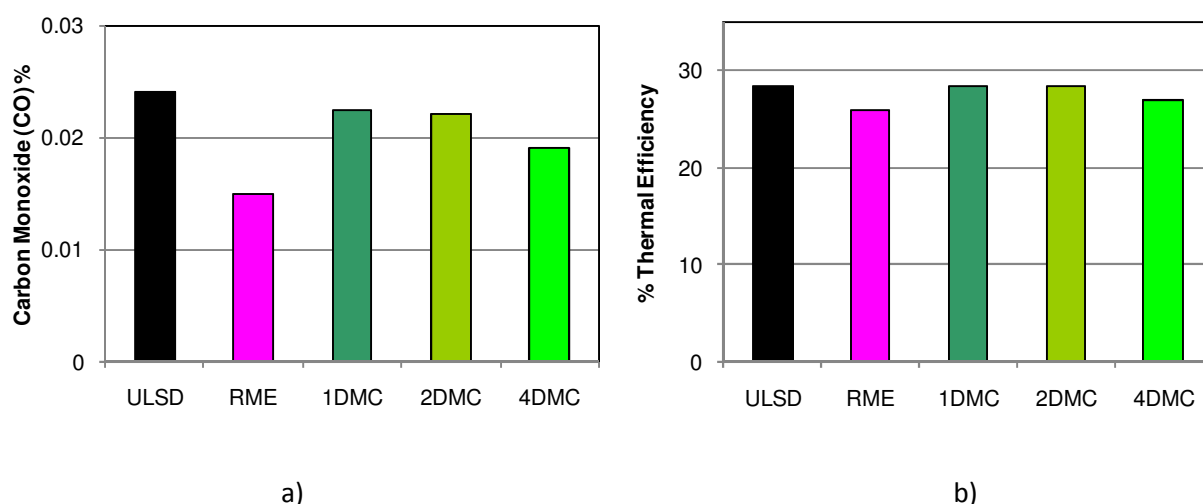
Figure 5.8 a) Carbon monoxide (CO) emissions and b) % thermal efficiency.

Figure 5.6b details the composition of hydrocarbon (HC) compounds (C_1-C_7) and was quantified using a GC-FID. Some VOCs in Figure 5.6b are of specific interest, as compounds such as benzene and 1,3-butadiene are known carcinogens that are harmful to human health (US DHHS, 2005). Interestingly both benzene and 1,3-butadiene emissions were present during ULS diesel combustion; however for the DMC blends, these compounds were not detected. RME showed no 1,3-butadiene and a reduced level of benzene. Fuel-borne oxygen appears to not only reduce the level of VOCs, but also reduce the variety of VOCs within this (C_1-C_7) range.

Again there is a large reduction in VOCs for the oxygenated fuels (Figure 5.7a), with total levels up to 50% reduced compared to ULS diesel fuelling. This shows that during EGR, when inlet oxygen levels are reduced, fuel-borne oxygen has an even larger effect upon the engine out emission of both THCs and the smaller C_1-C_7 compounds (Figure 5.7b). It also appears that the fuel-borne oxygen has largely reduced the formation of benzene and suppressed formation of 1,3-butadiene (carcinogens) to below detectable levels.

Figure 5.8a shows that carbon monoxide emissions reduced in proportion with the increase in level of oxygenation of the fuel. Thermal efficiency data was compiled using mean values from all the tested conditions. The engine thermal efficiency (the engine energy output over the fuel energy input) was dependent on the fuel type (Figure 5.8b). The general trend is: ULSD > 1DMC > 2DMC > 4DMC > RME though, the differences are small. Indeed fuel flow rates (not shown) for the DMC blends compared to ULS diesel were in proportion to their heating values across all conditions.

Benefits in smoke, PM, and HC were seen for DMC as an additive in ULS diesel. This could be used to help expand EGR limits (i.e., higher NOx reduction) and could also benefit the aftertreatment system's performance, longevity, and cost.

5.3   SUMMARY AND CONCLUSIONS

To assess the role that fuel-borne oxygen plays in combustion and to test the feasibility of DMC as a diesel additive, a comparative combustion study has been conducted between diesel (ULS diesel), biodiesel (RME), and 4 blends of the oxygenated DMC additive in diesel. DMC at 53% wt oxygen can be mixed neat with diesel at low levels and utilised as a combustion fuel in a standard diesel engine. However, larger proportion DMC blends such as 20DMC (20.3% DMC in diesel) were not practicable. Fuel-borne oxygen can help to improve engine out emissions of THCs, CO, and PM. Even low level additions of DMC (2 and 4DMC) can reduce carbon PM (soot) by as much as 50% in this engine. Emissions of NOx were slightly increased due to an enhanced, more premixed combustion for all the oxygenated fuels. An interesting observation is that 2% DMC in diesel can generate comparable particulate, THCs, and CO emissions to RME combustion, even though it has only 1.1% wt oxygen. It is thought that 2DMC is a blend of merit for further study. DMC addition in diesel

may also have potential to reduce the smaller potentially carcinogenic VOCs such as benzene and 1,3-butadiene, during EGR conditions this quality is especially apparent. Fuel-borne oxygen reduces the level of VOCs emitted and also reduces the variety of VOCs within the tested (C_1-C_7) range.

Several potential emissions benefits with dimethyl carbonate as a diesel additive have been observed. There may be challenges, such as, potential water contamination issues not observed in this laboratory based work (using clean fuel tanks in a controlled environment) and this should be investigated. A more thorough miscibility study would also be advantageous. An optical study on DMC combustion and the use of a modern multicylinder (higher injection pressure) engine are envisaged for the FPS group.

CHAPTER 6

ACTIVITY OF PROTOTYPE CATALYSTS ON EXHAUST EMISSIONS FROM BIODIESEL FUELLED ENGINES

In this Chapter a prototype catalyst has been integrated into the exhaust system of the Lister-Petter TR1 engine. This Chapter attempts to detail some of the similarities and differences between the aftertreatment of diesel and 1st generation biodiesel (RME). The catalyst used here, and integrated within the aftertreatment exhaust system to control the HC, CO, PM and potentially NOx emissions from diesel exhaust gas, was developed by Johnson Matthey (JM). The catalyst activity in removing HC and nanoparticles is examined for RME combustion and emissions.

Simultaneous control of PM and NOx emission is a challenging task (Chapter 1). Advances in diesel engine design (e.g. multiple injections, EGR), fuels (e.g. biofuels, synthetic fuels) and aftertreatment (e.g. DOC, DPF) technologies are required in order to fulfil future emission regulations (Tsolakis, 2006; Furuhata *et al.*, 2007).

Particulate composition (for ULS diesel) is generally made up of agglomerated solid carbonaceous material, volatile organics, ash and sulphur (Dec, 1997; Kittelson, 1998). The particle size distribution can be divided into three categories as nano or nuclei-mode (5-50nm diameter range), accumulation mode (50-1000 nm diameter range) and coarse mode (diameter larger than 1000 nm) (Kittelson, 1998). Most particles from ULS diesel combustion have diameters less than 100 nm (PM_{10}). Nano-particles are reported to be one of the most harmful causes of lung injury and cancer. When inhaled they get trapped in cavities in the lungs causing damage (Lakkireddy *et al.*, 2006).

Literature shows that, RME combustion produces particle emissions with significantly lower solid (soot/carbon) fraction and considerably higher unburned fuel portion in the SOF when compared with diesel PM (Schroder *et al.*, 1999; Krahl *et al.*, 2003).

The DOC catalyst has several tasks:

1) Reduce C-containing emissions

2) Protect the DPF from excessive PM (mainly organic carbon) and unburned fuel

2) Achieve an exotherm to heat the DPF and oxidise the soot (for active regeneration)

3) Produce NO_2 (to continuously oxidise the soot trapped on the DPF at reduced temperature (for passive regeneration) [e.g. Allansson *et al.* (2002)].

Although standard precious metal (i.e. platinum - Pt and palladium – Pd) catalytic converters are able to reduce PM emission due to oxidation of the organic carbon, they are reported to be unsuitable in oxidising elementary carbon (soot), as the oxidation reaction of soot proceeds much more slowly that the reactions of gaseous species and organic carbon (Hosoya *et al.*, 1996; Mayer *et al.*, 1998).

However, it has been proposed that oxidation catalysts can be effective in controlling PM (mass and number), as well as HC and CO, when biodiesel fuel, such as RME, is used for combustion (Stein, 1996). In a recent study by Johnson Matthey (Chatterjee *et al.*, 2008) using older and new technology diesel engines fuelled with ULS diesel (ULSD), it was demonstrated that a PM reduction of 38% and 47%, respectively, was achieved over the DOC.

In an earlier work in the FPS group it was reported that a significant reduction of NOx and smoke (PM) emissions can be achieved by the engine operating with RME and EGR (Tsolakis, 2006; Tsolakis *et al.*, 2007). Besides this, further reduction of NOx emissions can be achieved by including in the DOC or combining with the DOC, Selective Catalytic Reduction catalysts.

With this arrangement four way (CO, HC, PM and NOx) control can be achieved (Chatterjee *et al.*, 2008).

A bi-functional prototype catalyst (designed by JM), that will act as a NOx adsorber (control NOx emissions (HC-SCR)) and oxidise C containing species (e.g. HC, CO and PM) is tested in this Chapter. As the tests were carried out at steady state operating conditions without active control, the results in this Chapter are mainly focused on the impact of the prototype catalyst on the reduction of C-containing species from the combustion of biodiesel RME with and without EGR. The combination of the biodiesel fuelled engines use of EGR and prototype catalyst, may unlock potential performance synergies between the three technologies and benefit engine performance and emissions.

6.0.1 Fuels, Test Conditions and Procedure (specific to Chapter 6)

Two fuels were tested, ULS diesel and RME, the basic fuel properties are outlined in Table 3.6.. The prototype low loading supported Pt based catalyst was coated onto a cordierite honeycomb monolith substrate (diameter of 115mm and length 75mm) with a high cell density (600 cpsi). The engine conditions (speed-load) used in this study, are shown in Table 6.1. Cooled EGR 20% by volume was used.

Table 6.1 Engine conditions

Engine condition	SPEED (rpm)	IMEP (bar)	EGR (% vol.)	ULSD $T_{EXHAUST\ GAS}$ (^{o}C)	RME $T_{EXHAUST\ GAS}$ (^{o}C)
1	1200	4	0%	241	261
			20%	220	242
2	1500	2	0%	183	200
			20%	167	185
3	1500	4	0%	237	248
			20%	210	230
4	1500	5	0%	283	303
			20%	257	276
5	2000	4	0%	225	240
			20%	204	221

6.1 EXPERIMENTAL RESULTS AND DISCUSSION

Table 6.2 Engine conditions and exhaust gas compositions with 0% EGR.

Engine Condition	Diesel (ppm)			Biodiesel (ppm)		
	HC	NOx	CO	HC	NOx	CO
1	189	694	120	28	746	360
2	199	309	200	142	429	190
3	205	669	100	114	735	100
4	198	873	100	44	1045	100
5	110	527	167	20	531	100

Combustion parameters for ULS diesel and RME at 1500 and 2000 rpm can be seen in Figures 4.2-4.4 in Chapter 4.

6.1.1 Effect of Fuel at Various Engine Operating Conditions

The catalyst effect on the HC and NOx emissions from the engine operation with diesel and RME at five engine speed and load conditions (Table 6.1 and 6.2) with no EGR are shown in Figure 6.1.

Biodiesel is less compressible and has a higher viscosity and density than diesel, as well as inherent oxygen (Rakopoulos & Hountalas, 1996; Graboski & McCormick, 1998; Senatore *et al.*, 2000; Szybist & Boehman, 2003; Boehman

Figure 6.1 Catalyst effects on the HC, NOx and CO Emissions for diesel and biodiesel with no EGR.

et al. (2004). These differences in fuel properties can significantly affect engine performance

and emissions, as has been reported in numerous experimental and modelling combustion studies. Biodiesel combustion, such as with RME, is reported to affect injection characteristics (i.e. increased injection pressure and rate, reduced ignition delay) and combustion phasing (i.e. advanced combustion, increasing premixed combustion phase Figures 4.2-4.4).
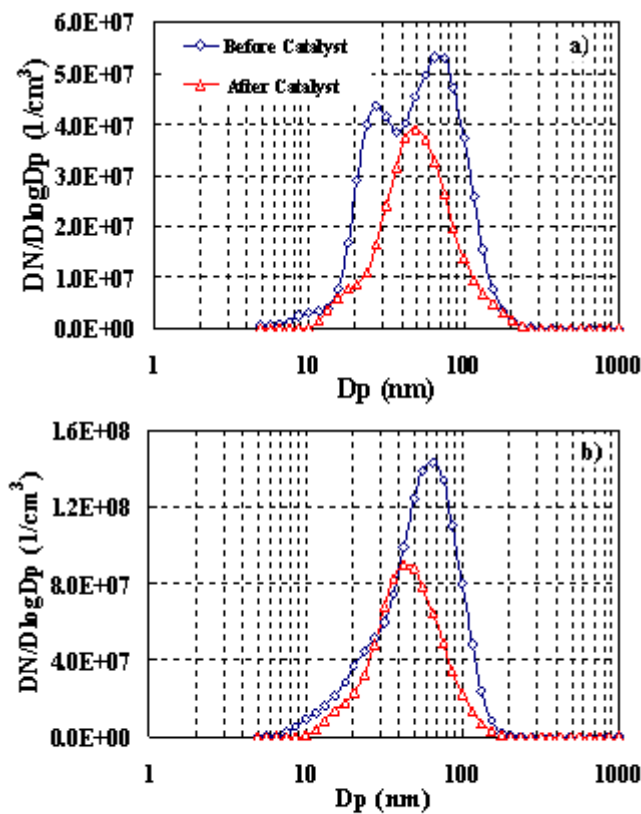
Figure 6.2. Catalyst effect on particle number Distribution with biodiesel fuelling. Engine speed: a) 1500rpm   b) 2000rpm.

In addition, the advanced combustion seen with the engine operating on RME may induce a higher heat release rate, and therefore increased NOx and reduced HC and CO (Figure 6.1). However, it has also reported that lower solid (soot/carbon) particle formation, with a considerably higher portion of un-burnt fuel in the SOF, is present for the RME fuelled engine exhaust gas, compared to diesel fuels (Krahl *et al.*, 2003; Mueller *et al.*, 2003; Schroder *et al.*, 1999).

The amount of HC (ppm) removal over the prototype catalyst was similar for both fuels, but in the case of RME fuelling the HCs conversion (%) was higher over the catalyst due to lower HC concentration in the untreated exhaust gas and the slightly higher exhaust gas temperatures (Table 6.1). The maximum hydrocarbon reduction for RME over the prototype

catalysts was approximately 90%. At steady state (catalytic) converter operation, there was insignificant NOx reduction (less than 25%).

6.1.2 Catalyst Performance in Reducing PM, for RME

Results from the effects of the catalyst on the particulates distribution from the combustion of biodiesel are only shown for engine conditions 3 and 5. The differences between the PM from the combustion of diesel fuel and biodiesel have been previously reported [e.g. Tsolakis (2006), Krahl *et al.* (2003)]. The higher engine speed for a given engine load (IMEP 4 bar) increased the injection pressure (comparison of conditions 3 and 5).

The higher fuel injection pressure in the case of 2000rpm engine speed, and better fuel atomisation (increased in number but smaller in size fuel droplets) and air-fuel mixing in the combustion chamber, resulting in higher production of smaller diameter particles, due to nucleation within the locally supersaturated zones, and increased particle number (Tsolakis 2006). The better mixing of the air and fuel in the combustion chamber results also in reduced unburnt hydrocarbons (Figure 6.1) and hence lower rate of the gas-to-particulate conversion due to the condensation process. It is also reported that increased fuel injection pressure and improved air/fuel mixture can substantially reduce the solid fraction of the PM to a point that can be oxidised over the catalyst (Kresco *et al.*, 1998; Pegan, 1999).

The prototype catalyst reduces the particles along the measured range, with more significant PM reduction seen at the nuclei mode (Figure 6.2 and 6.3), as at that range the PM are mainly liquid fuel droplets. Preliminary analysis, as well as an earlier study using Johnson Matthey DOC technology, has revealed that the converter can significantly modify PM size and composition by effectively removing organic carbon, such as SOF (soluble organic fraction), but has almost no effect on elementary carbon (soot) (Sumlya & Yokota, 2004).
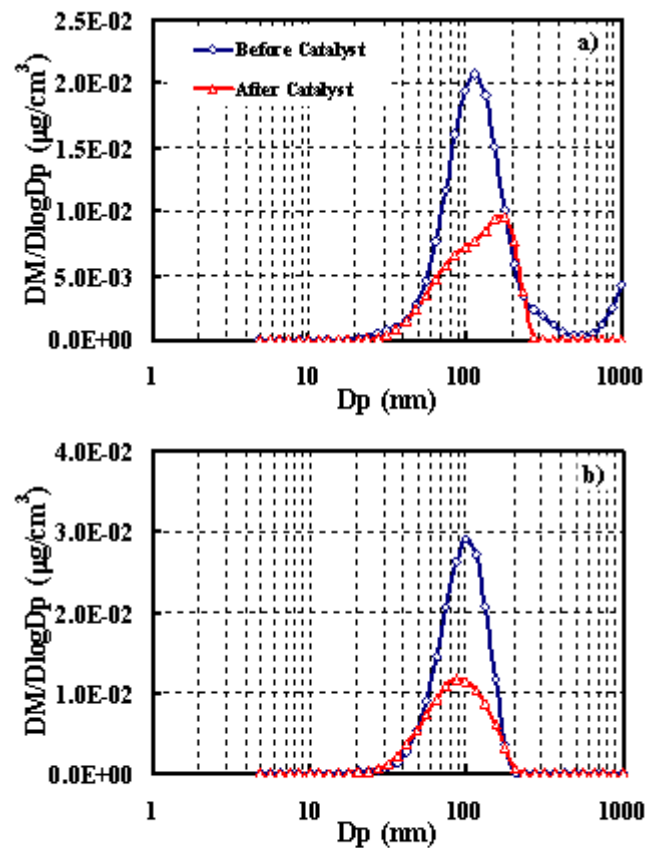
Figure 6.3. Catalyst effects on particle mass distribution with biodiesel fuelling. Engine speed: a) 1500rpm b) 2000rpm.

Figure 6.4 shows the effects of the catalyst on the total number and mass concentration from the engine operation at 4 bar IMEP at 1500rpm and 2000rpm engine speeds, respectively. Particulate Matter that are consisting mainly of volatile organic materials (i.e. low diameter) are easier to oxidise over the catalyst, while there is no noticeable difference in the catalyst performance at the different engine operating conditions.
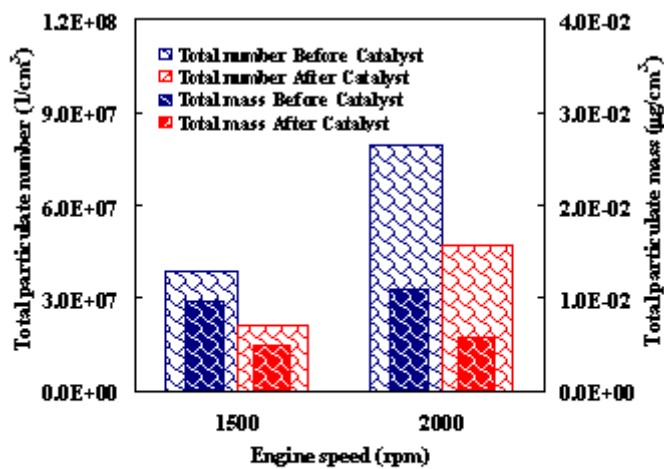
Figure 6.4. Effects of engine speed on total particle number and mass over the catalyst. Biodiesel fuelling, engine load IMEP 4 bar, EGR = 0% vol.

6.1.3 Catalyst Performance in Reducing PM, for RME with EGR

The EGR reduces NOx by lowering combustion temperature through reduced oxygen concentration in the combustion chamber, as well as through heat absorption (Ladommatos *et al.*, 1998). The EGR also retards the start of the combustion and this leads to the increased level of HC and reduced NOx level as illustrated in Table 6.3 and Figure 6.5. The HC concentration in the engine exhaust gas from the combustion of RME was dramatically reduced over the catalyst at these relatively high exhaust gas temperatures. On the other hand, the catalyst did not affect significantly the removal of NOx, as can be seen in Table 6.3, Figures 6.1 and 6.5.
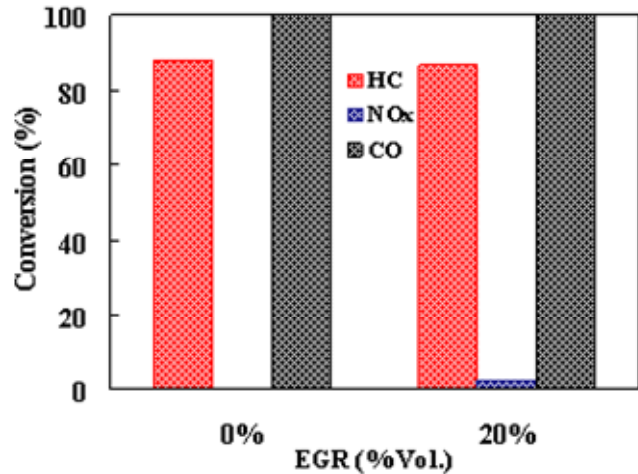
Figure 6.5. Catalyst effects on the HC and NOx emissions for biodiesel with and without EGR engine speed 1500 rpm IMEP 4 bar.

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Table 6.3. Engine conditions and exhaust gas compositions with 20% EGR, 1500rpm, Engine load 4 bar IMEP (condition 3).

EGR (% vol.)	Before DOC (ppm)			After DOC (ppm)		
	HC	NOx	CO	HC	NOx	CO
0%	114	735	100	14	733	0
20%	155	419	200	21	408	0

EGR addition is associated with incomplete combustion due to the lack of oxygen availability in the combustion zones. The lower combustion temperature from the use of EGR also causes an increase in the PM formation rate from unsaturated species such as acetylene and ethylene (Mueller *et al.*, 2003). The combustion of oxygenated fuel such as RME can reduce the PM formation precursors and allow engine operation with higher EGR additions. EGR addition increases the number of accumulation mode particles and reduces the number of nucleation mode (size < 10nm) particles. With the use of EGR the maximum peak number (Figure 6.6) and mass (Figure 6.7) of the particles are also shifted towards higher sizes.

The retarded start of combustion with the use of EGR (results are not shown) (Tsolakis, 2006; Tsolakis *et al.*, 2007) gives less time for PM oxidation and, in conjunction with the increased fuel consumption and hence increased fuel droplets concentration in the combustion chamber, results in the increased incomplete combustion products. These conditions can promote particle size growth due to condensation of the increased volatile materials. It is also suggested by other researchers that the increase of the total particulate number in conjunction with increased size particles may be due to the coexistence of coagulation with homogeneous nucleation of metallic ash particles, and heterogeneous nucleation of PAH and carbon soot on the metallic ash particle (Ristovski *et al.*, 2000; Graskow *et al.*, 1998).

It is clear that the PM emissions were dramatically reduced over the catalyst from the engine operation on biodiesel with EGR, however the particles size distribution has been affected by the catalyst and under these conditions it seems to be dependent on the engine operating condition. For the engine condition 3 (Engine speed 1500rpm, Figures 6.6a and 6.7a) with EGR, there was a reduction of particles over the catalyst at all sizes (diameters), however for the engine condition 5 (Engine speed 2000rpm, Figures 6.6b and 6.7b) there was an increase in the concentration of the nuclei mode particles.
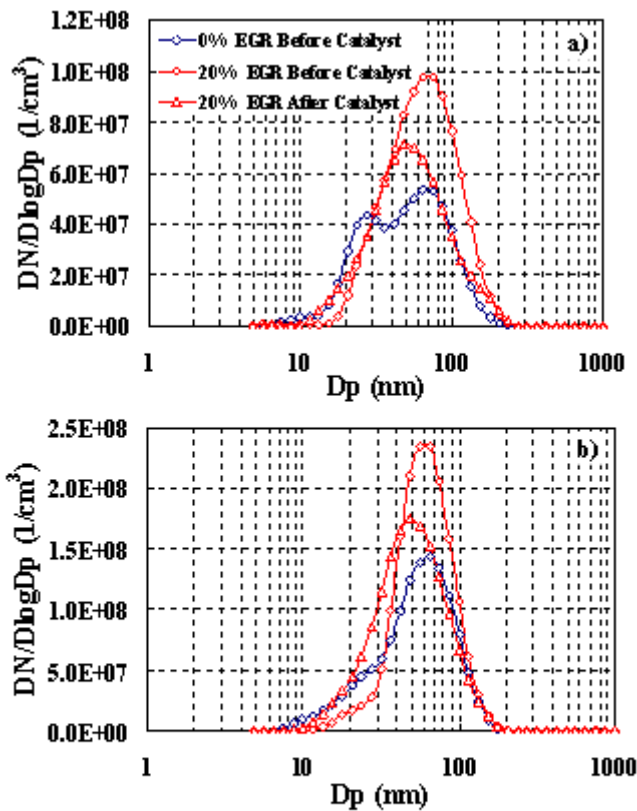
Figure 6.6. Catalyst effects on particle number with biodiesel fuelling with and without 20% EGR. Engine speed: a) 1500 rpm b) 2000rpm.
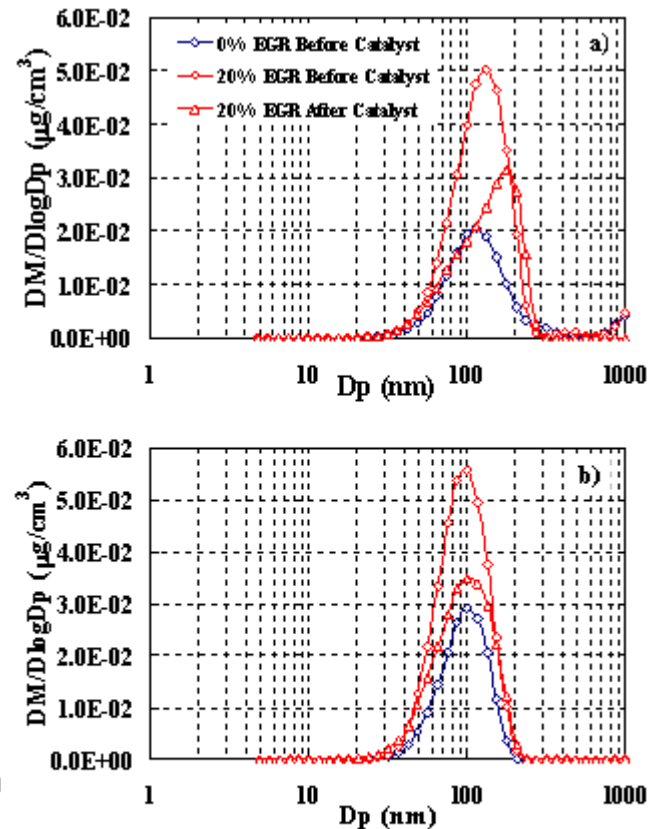
Figure 6.7. Catalyst effects on particle mass distribution for biodiesel fuelling with and without 20% EGR. Engine speed: a) 1500 rpm b) 2000 rpm.

The prototype catalyst does not produce new particles but rather reduces the larger size particles by burning off the organic carbon and leaving behind only the core of the PM (soot) and this results in the increased concentration of the nuclei mode particles mainly consisting

of solid carbon. This can also be supported by analysis of the particulate samples carried out by several researchers [e.g. Khair (1997)] and indicated that the SOF remained constant with the use of EGR, however the elemental carbon fraction (soot/carbon) of the particulate increased as EGR rates increased.

The increased number of nuclei mode liquid droplets (soot free) particles seen from the biodiesel combustion and were able to reduced over the oxidation catalyst (Figures 6.2-6.4) were converted to larger diameter particles with the use of EGR, while their composition was also changed. The catalyst still reduces particulate organic carbon (SOF), however, does not curb the soot fraction. DPFs are a very effective aftertreatment alternative to control the insoluble PM fraction on EGR equipped engines in applications where very low PM emission levels are required (Khair, 1997).

EGR favours particle formation as the peak in-cylinder pressure is reduced, hence the rate of soot burn-off reduces when compared to the rate of soot formation. This allows larger accumulation mode particulates to form (where before many of these particulates would have been in nucleation mode). As a result the total particle number and mass levels were increased as illustrated in Figure 6.8a and 6.8b.
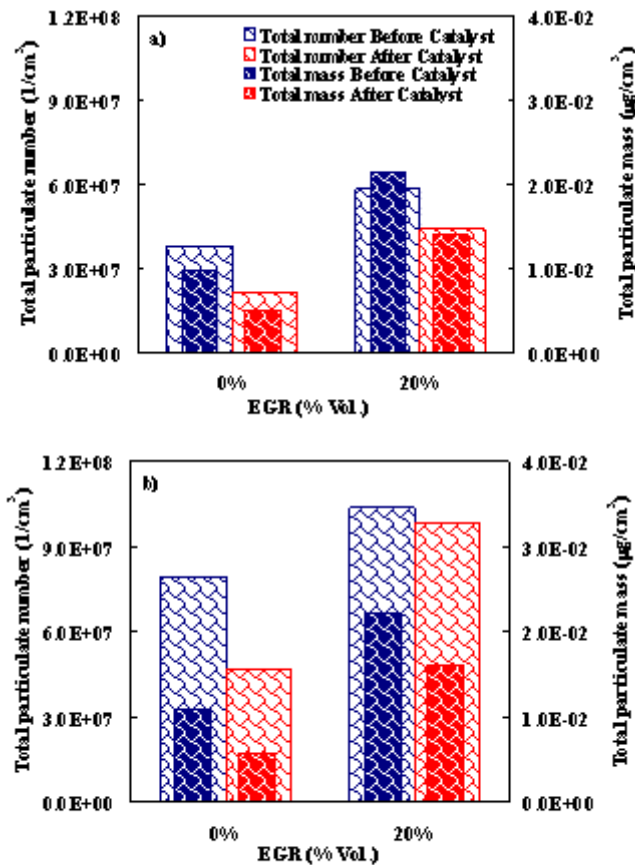
Figure 6.8. Effects of catalyst on total particle number and mass for RME biodiesel fuelling with and without 20% EGR engine speed: a) 1500 rpm b) 2000 rpm.

Figure 6.9 shows the influence of the catalyst activity under EGR on the total particle number and mass reduction for various engine conditions. In earlier studies (Hosoya *et al.*, 1996; Stein, 1996) it was reported that a DOC can increase the PM mass and PM concentration at all sizes due to SO_2 to SO_3 formation and thus the formation of sulphate particulates and sulphuric acid aerosol at temperatures higher than 250°C. Fuel free of sulphur and aromatic hydrocarbons, such as biodiesel, are able to reduce significantly PM emissions in the engine exhaust and enhance aftertreatment performance.

As seen in Figure 6.9, for the tests without EGR addition a considerable improvement of up to 50% and 30% was seen for PM total number and mass for both engine speed, respectively, together with significant HC and CO conversion (Figures 6.1 and 6.5). The use of EGR deteriorates the catalyst performance in reducing PM and especially the total number. For the engine condition of 2000rpm, where
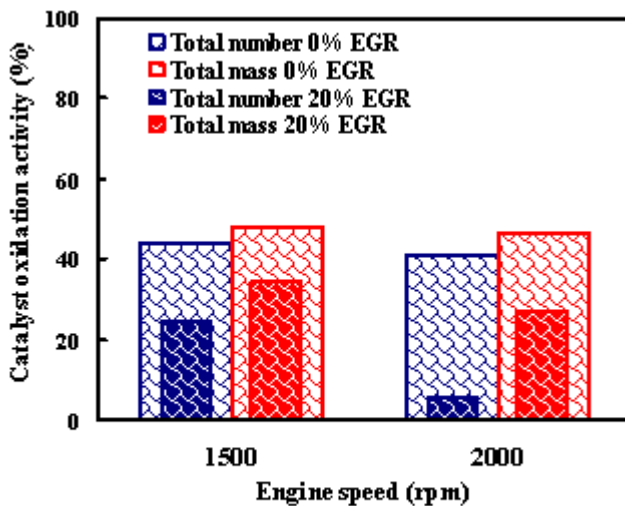
Figure 6.9. The catalyst oxidation activity on total particle number and mass for RME biodiesel fuelling.

increase of smaller diameter particles was seen over the prototype catalyst, there was significant reduction in PM mass (<30%) but the reduction in total PM number was only up to 5%. A trend that further support the argument that the catalyst does not produce new particles but the EGR increases the size of particles in the combustion chamber and exhaust while the prototype catalyst burn-off the organic carbon and reduces the PM size.

6.2   SUMMARY AND CONCLUSIONS

A prototype catalyst was assessed for RME emissions aftertreatment performance. The oxygenated low aromatic and very low sulphur content biodiesel fuel (RME) improved the engine HC, CO and PM exhaust emissions with some increase in NOx emissions.

The investigation of the RME fuelling with the prototype catalyst established that it reduces not only the amount of HC, but also the total particulate concentration. However, the catalyst did not have a large affect upon the NOx reduction.

The novel prototype catalysts can effectively reduce particle mass and unregulated hydrocarbons emitted from RME combustion. Up to 50% and 30% reduction in PM number and mass was seen, respectively over the prototype catalyst. The reduction of PM concentration over the catalyst is expected to enhance the performance of other aftertreatment devices such as diesel particulate filter (i.e. reduce regeneration frequency) and lean NOx catalysts (i.e. enhance NOx adsorption or protect the catalyst active sites from coking) integrated in the exhaust and located downstream the prototype catalyst. EGR addition in the combustion process of biodiesel reduces the soot free nuclei mode particles and increases the larger diameter particles (accumulation mode). Depending on the engine and catalyst operating conditions, the SOF of the accumulation mode particles is burnt-off over the catalyst and leaves behind smaller diameter soot.

CHAPTER 7

SPECIATION OF PARTICULATE MATTER FROM BIODIESEL COMBUSTION AND ITS REDUCTION BY AFTERTREATMENT

It is worthwhile to determine the nature of PM produced from diesel fuels, especially those derived from biodiesel, and also to ascertain whether current technology is suitable for PM exhaust removal for biodiesel. In this Chapter ULS diesel and biodiesel (RME) were tested for combustion and emissions, with no aftertreatment and then with aftertreatment (DOC and DPF). A host of online and offline PM analytical techniques were then used to quantify the PM emission.

Many of the dangers of PM were highlighted in Chapter 1. For RME combustion in Chapters 5 & 6 it was seen that PM formation is less likely, due both to the increased temperatures of the premixed flame and the availability of oxygen even at the core of injected fuel droplets and this is in accordance with (Ito *et al.*, 2003; Rakopoulos *et al.*, 2004; Xu & Chia-fon, 2006; Hribernik & Kegl, 2007; Treea & Svenson, 2007). Conversely, there is an emission penalty that has been observed by many for RME fuelling, i.e. NOx emissions increase Chapter 4, also seen by (Graboski & McCormick, 1998; US EPA, 2002b; Babu & Devaradjane, 2003; Cheng *et al.*, 2006; Lapuerta *et al.*, 2008; Robbins *et al.*, 2009). This is thought to be due to these increased cylinder temperatures and increased time period at high temperature due to the injection advance for RME (Figures 4.2-4.4) and this is substantiated by many (Graboski & McCormick, 1998; Monyem *et al.*, 2001; US EPA, 2002b; Babu & Devaradjane, 2003; Szybist & Boehman, 2003; Alam *et al.*, 2004; Cheng *et al.*, 2006; Lapuerta *et al.*, 2008; Robbins *et al.*, 2009; Tormos *et al.*, 2010). Some studies have shown that PM for biodiesel is not only reduced, but also of a different nature (Chapter 5). The

mean particle size and total number are reduced compared to diesel combustion. This is believed to be due to soot formation and agglomeration suppression, due to reductions in soot precursors and the increased cylinder pressures exhibited during biodiesel combustion (Bagley *et al.*, 1998; Boehman *et al.*, 2005; Jung *et al.*, 2006; Treea & Svenson, 2007; Lapuerta *et al.*, 2008; Klein-Douwel *et al.*, 2009; Lee *et al.*, 2009; Robbins *et al.*, 2009). PM from biodiesel combustion has been shown to have an increased proportion of small nano particulate compared to diesel. This is thought to be due to the enhanced fuel spray characteristics creating an increased proportion of SOF (liquid PM). Health studies to date have focused upon the damage caused by solid particulate, damage caused by liquid particulate is less clear (Chapter 1).

Since PM consists of a variety of both solid (e.g. carbon) and liquid (e.g. water) constituents. Liquid PM can often be gaseous at early stages of the exhaust and aftertreatment process and this is highly dependent on the local exhaust gas temperature. Clearly to treat these two phases of PM emissions, both gaseous fluid interaction and physical filtration are required. In this Chapter a DOC (Section 1.6.9) is employed to remove exhaust gaseous proportions of PM from CI exhaust. To achieve physical filtration a wall flow monolith DPF (Chapter 1) is utilised to remove soot (and other solid PM) from the CI engines emission.

The aims of this Chapter are to highlight similarities and differences between PM produced from biodiesel (RME) and diesel combustion and to assess two filtration technologies (DOC and DPF) for ULS diesel and biodiesel exhaust.

7.0.1 Fuels, Test Conditions and Procedure (specific to Chapter 7)

Two fuels were tested, ULS diesel and RME, the basic fuel properties are outlined in Table 3.6. All tests were steady state and were set at an engine speed of 1500 rpm. Tests were carried out at 2 bar, 4 bar and 5 bar IMEP. A schematic diagram of the engine and aftertreatment system is displayed in Figure 7.1. (radiator design indicates cooled EGR).
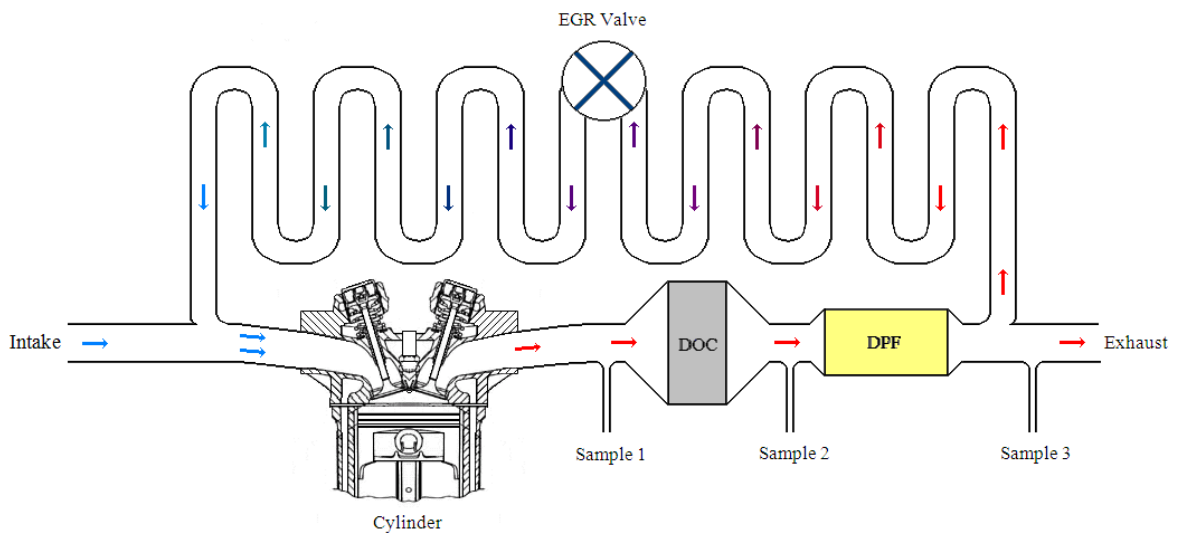
Figure 7.1. Diesel engine schematic with aftertreatment and EGR.

The DOC utilised was a prototype low loading supported Pt based catalyst that was coated onto a cordierite honeycomb monolith substrate (diameter of 115mm and length 75mm) with a cell density of 600 cpsi.

The DPF (Figure 7.1) was cordierite (diameter of 58mm and length 153mm) with a channel density of 300 cpsi.

7.1   EXPERIMENTAL RESULTS AND DISCUSSION

The in-cylinder pressure and heat release rate versus CAD data for ULSD and RME over the end of compression and the early expansion strokes of the engine, are shown in Figure 7.2, for a representative engine load of 4Bar IMEP 0% EGR at 1500 rpm. This same speed and load condition is used for all the combustions and emissions analysis.

Cylinder Pressure & ROHR
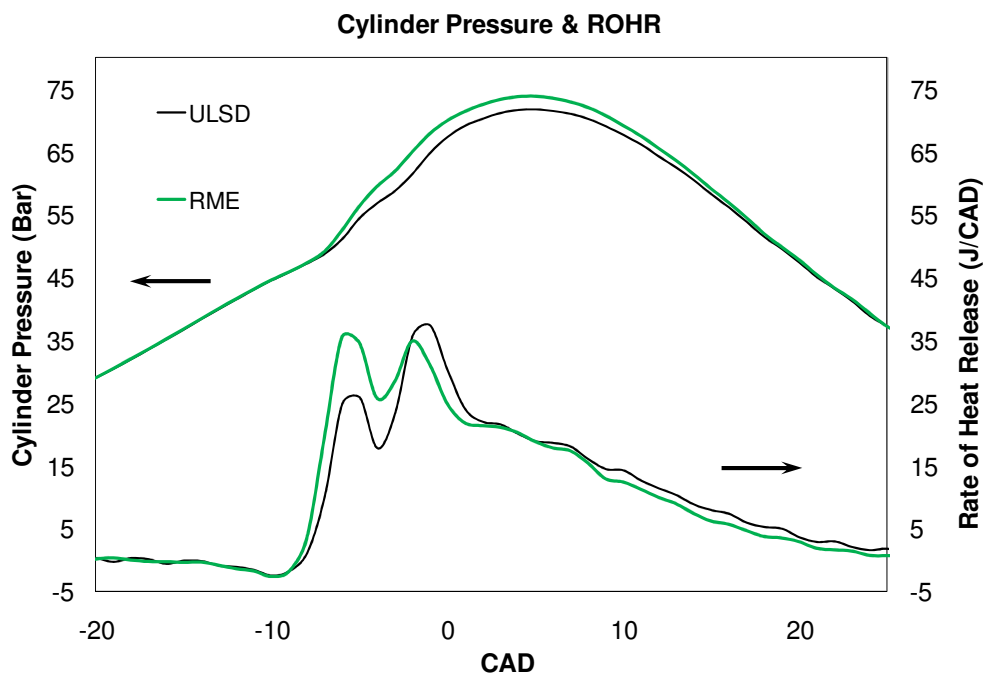
Figure 7.2. Cylinder pressure & ROHR, 1500 rpm 4 Bar IMEP.

RME combustion (green line) exhibits a slightly advanced and increased peak pressure seen at the top of Figure 7.2. This can be explained more clearly on consideration of the ROHR curves seen at the bottom of Figure 7.2. It is visualised that the start of combustion (+ve ROHR) is advanced slightly for RME, thought to be due primarily to its physical properties; increased density, decreased compressibility and increased viscosity (Lapuerta *et al.*, 2008). The first 'premixed' heat release peak for RME is larger than ULSD. This is thought by many to be due to both fuel-borne oxygen and the increased injection pressure due to RME's higher density and bulk modulus of compressibility. RME effectively has improved fuel

air entrainment due to fuel-borne oxygen, especially at the core of fuel droplets, so a larger proportion of the fuel is effectively 'premixed'. The increased density of RME also provides increased injection pressure (Table 3.6.) and again the increased rate of pressure rise (as RME has a higher density) which gives increased injection pressure and therefore, cylinder penetration. This also gives a more dispersed charge improving the air entrainment. The amount of RME burnt is also a factor that increases peak cylinder pressure, as the advanced premixed combustion is before TDC in the compression stroke and so is slightly out of phase compared to the manufacturer's injection parameters which are optimised for diesel. The result of this is that a larger injection (on top of that due to its lower calorific value) of biodiesel is required. It is conceivable that the difference between RME and ULSD peak pressures would be somewhat reduced for a fuel specific optimised injection strategy i.e. retarded injection for biodiesel.

7.2   EMISSIONS

It is widely accepted that harmful NOx emissions from biodiesel fuelling are higher than for diesel. Figure 7.3 is no exception, detailing the NOx – Bosch smoke number trade-off for RME and ULS diesel from this engine.

The square marker points on the trendlines in Figure 7.3 represent the load conditions of 2, 4 and 5 Bar IMEP. It is possible to see that at each condition RME has significantly lower smoke emissions but also has increased NOx emissions when compared with ULS diesel. On consideration of the NOx emissions for RME the increase can be attributed to the increased cylinder pressures, injection advance and amount of injected fuel, for all the aforementioned reasons.
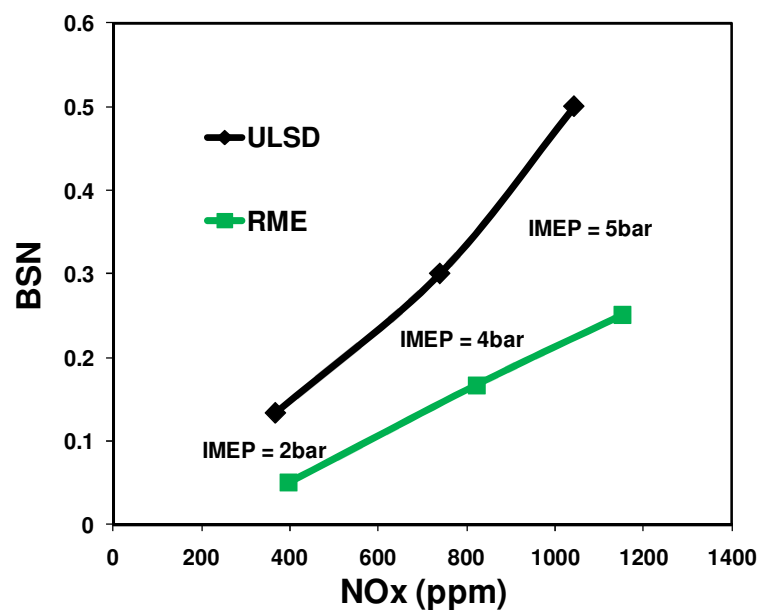
Figure 7.3. NOx – Smoke (BSN) trade-off 1500rpm.

This result concurs with those of many researchers looking at NOx formation in combustion, where the principle factors are high temperatures and the time period at extreme temperature, (Graboski & McCormick, 1998; Monyem *et al.*, 2001; US EPA, 2002b; Babu & Devaradjane, 2003; Ito *et al.*, 2003; Szybist & Boehman, 2003; Alam *et al.*, 2004;

Rakopoulos *et al,.* 2004; Boehman *et al.*, 2005; Jung *et al.*, 2006; Xu & Chia-fon, 2006; Hribernik & Kegl, 2007; Treea & Svenson, 2007; Lapuerta *et al.*, 2008; Klein-Douwel *et al.*, 2009Robbins *et al.*, 2009; Tormos *et al.*, 2010).

PM measured using the Bosch smoke number (light reflectance from a soiled filter paper) is considered as a measure of the total PM emission i.e. it includes; soot, HC SOF, water SOF and ash. To explain the low Bosch smoke number emissions levels for RME again Figure 7.2 is considered, it shows that the injection was advanced and that peak cylinder pressures were higher for RME. Increased cylinder pressures make the formation of solid carbonaceous (soot) particulate less likely as complete combustion is promoted.

A more complete combustion due to fuel-borne oxygen additionally makes the combustion of the constituents of the fuel more likely, so a reduction in unburnt HCs also results (Figure 7.4). There are additionally several more potential factors that can explain reduced HC emissions. These include; higher cetane number for RME, lower final distillation point for RME, the advanced injection for RME, FIDs may have a lower sensitivity when detecting the oxygenated compounds from RME combustion and heavy hydrocarbons from RME combustion may condense in the heated lines of the Horiba analyser (Lapuerta *et al.*, 2008).
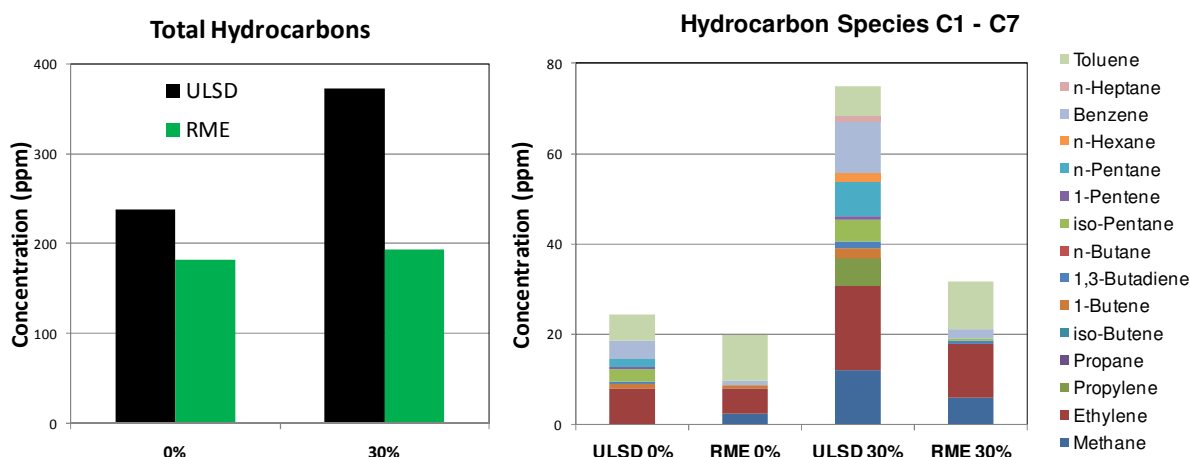
Figure 7.4. Total hydrocarbons and small unregulated hydrocarbons for ULS diesel and RME for 0 and 30% EGR.

To meet current and proposed future NOx legislation EGR is employed as an effective NOx control strategy (Heywood, 1988; Ladommatos *et al.*, 2000). On examination of Figure 7.4 it is possible to see that when EGR is applied at 30% the net rise in THC emissions is somewhat less for RME than for ULS diesel. In fact, RME is less susceptible to the low oxygen conditions of EGR and this is attributed to the oxygenated structure of RME. The implication of this when combined with lower engine out soot levels, might be that EGR limits could be extended for a NOx emissions optimised RME combustion strategy. Of course any underestimates due to the sensitivity of the test medium (FID) would also need to be considered as they may be exaggerating this benefit of RME fuelling.

Future emissions legislation may attempt to consider dangerous hydrocarbon species individually, in an analogous fashion to the introduction of particulate number (PN) limits that were introduced for Euro V. For example acetaldehyde, formaldehyde, benzene, and 1,3-butadiene are known carcinogens (US DHHS, 2005). On examination of Figure 7.4 it is possible to discern that both benzene and 1,3-butadiene are present in small quantities for ULS diesel combustion, and that when EGR is applied at 30% the quantities of these species

(and indeed all the measured species) grow significantly. This is a fairly apparent demonstration of the need for a DOC, most especially with the increased use of EGR for NOx control. Benzene levels were significantly reduced for RME combustion when compared to ULS diesel. Interestingly 1,3-butadiene was not detected for RME combustion at all the tested load conditions until EGR was applied.
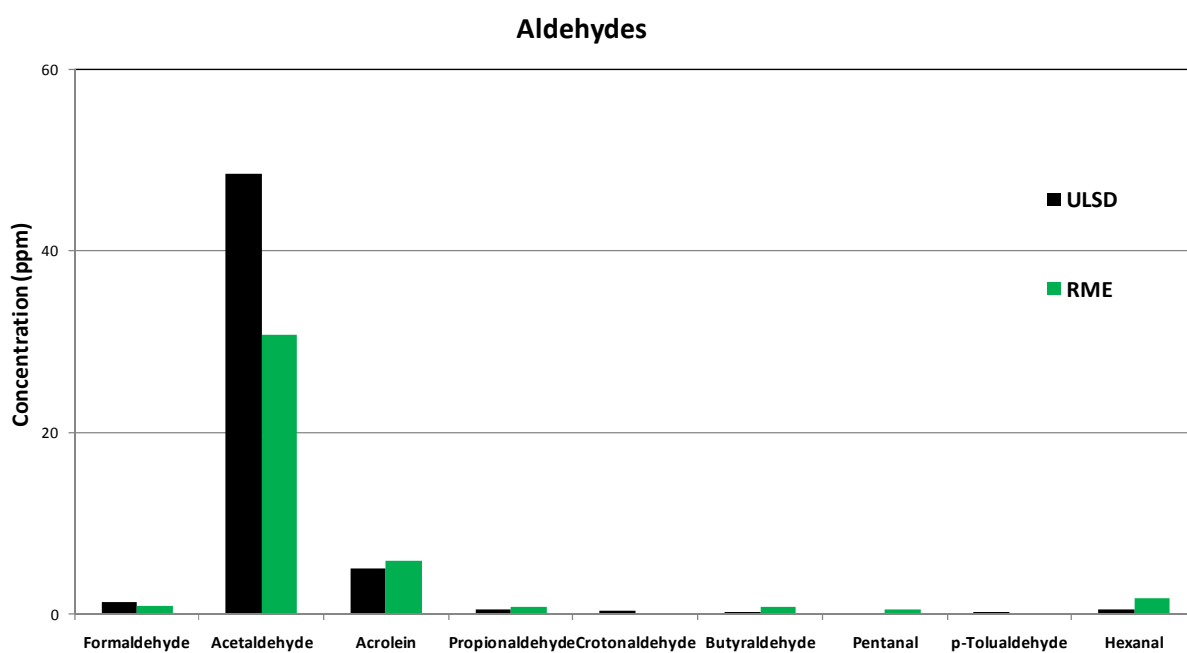
Figure 7.5. Nine detected aldehydes & ketones.

To look for the presence of aldehydes and ketones, an offline DNPH method was used (see Chapter 3). Of the fifteen aldehydes and ketones tested (see appendix) nine were found to be present (Figure 7.5.). The presence of the two carcinogenic aldehydes formaldehyde and acetaldehyde were detected during both ULS diesel and RME combustion (Figure 7.5.). RME combustion for the 3 tested conditions appeared to produce reduced amounts of these carcinogens. This would appear to fit with the reduced overall THC emissions observed in Figure 7.4. Figure 7.6 shows THC and CO emissions for the ULS diesel and RME, with and

without aftertreatment. At this condition (300 °C local exhaust gas) THCs are reduced by around 80% over the DOC for both ULS diesel and RME and CO is almost eliminated.
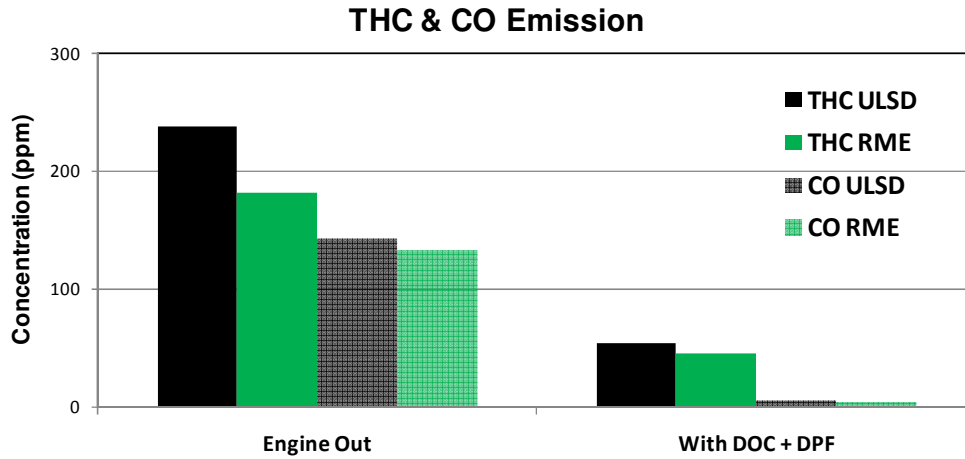
THC & CO Emission

Figure 7.6. THC & CO emissions without and with aftertreatment.

The engine thermal efficiency (the engine energy output over the fuel energy input) was 28.5% for ULS diesel and 27% for RME (taken here as an average of the 3 load conditions at 0% EGR). It is thought that the thermal efficiency difference is primarily due to the phase difference of RME combustion (Figure 7.2), and that if optimised for RME, i.e. for a retarded injection, 28.5% could be maintained. The fuel flow rates were in proportion to the fuels heating values (not shown).

Figure 7.7 details the compositional makeup of the particulate matter in the exhaust when running with ULS diesel and RME, without and with aftertreatment. The y-axis of Figure 7.7 represents the PM mass collected on a central portion of a glass fibre filter. The results are therefore proportionally related to each other, but are not total PM emissions like those given in Figure 7.8.
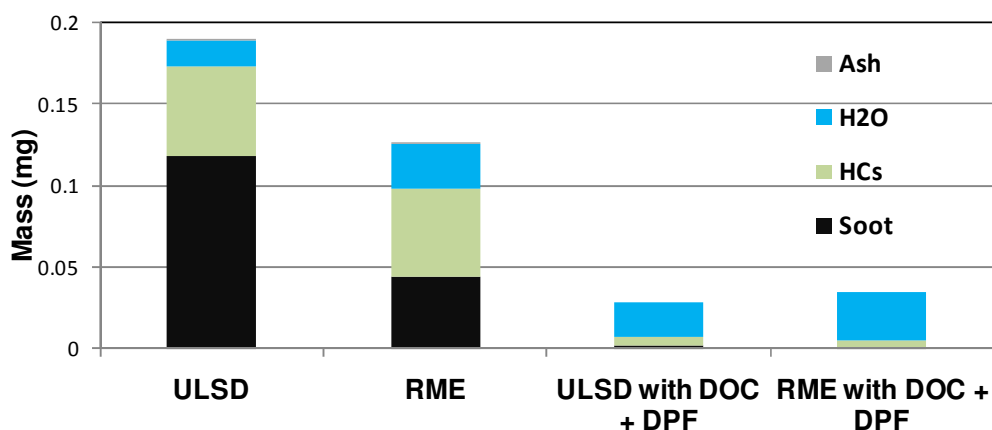
Figure 7.7. Exhaust particulate matter classified by TGA.

Considering base PM emissions it is observed that ULS diesel produces more soot than RME. At this condition more than double. This trend was true for all the tested conditions. RME combustion appears to produce larger amounts of harmless water PM and this is attributed to the more complete combustion for RME previously observed. The gravimetric method used to compile Figure 7.7 clearly illustrates the effectiveness of the DPF for soot and metallic ash removal. As a relative percentage a minimum of 98% of the soot was removed at all the tested conditions by this method. The DOC is able to oxidise many of the SOF hydrocarbons and Figure 7.7 is reinforced by Figure 7.6 which details HCs emissions with and without aftertreatment for this condition. Interestingly it is also seen that when the aftertreatment is employed the proportion and amount of harmless water PM increases. This may evidence HC oxidation over the DOC. It was also noticed that the max rate of weight loss (achieved during the soot oxidation Figure 3.5.) during the TGA temperature ramps, was at lower temperature for RME than ULS diesel at this condition 480° C RME 510° C ULS diesel. This trend was true for all the tested conditions. It is possible to interpret this as an indication of soot oxidation activity i.e. soots produced from RME combustion are more active in oxidation. Caution is taken in converting this data to reaction energies, as the collection medium is dissimilar to soot caught in a cordierite DPF. This is however

interpreted as a potential positive for RME combustion as soots that are more active are easier to burn off during regeneration.
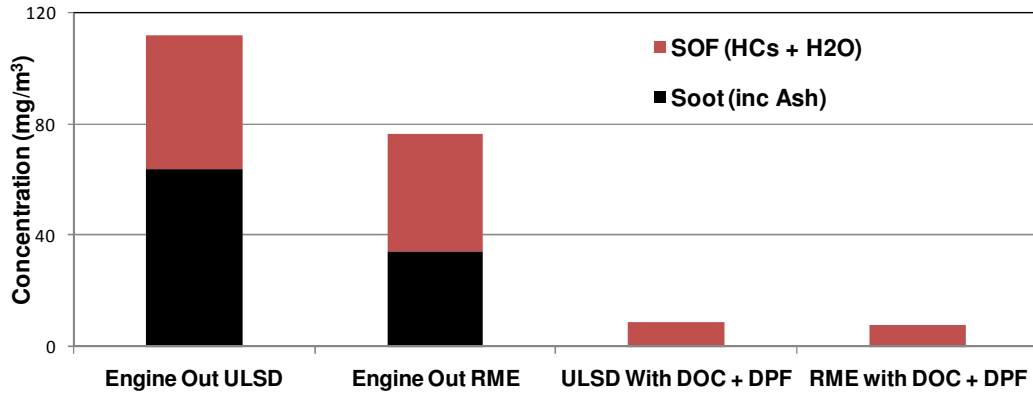
Figure 7.8. Particulate matter emission Horiba Mexa 1230PM.

Figure 7.8 details real time measured PM using a new diffusion charging detector by Horiba Instruments. Comparison between Figures 7.8 and 7.7 shows some correlation. Again RME has a lower base emission of soot and a similar amount of SOF to ULS diesel combustion. Almost complete elimination of soot and ash by the DPF is seen and the DOC eliminates most of the HCs SOF. It is known that the SOF remaining after the filtration is predominantly water due to the low THC emissions observed from the duel FIDs of the Mexa 1230PM.

To give a clearer picture of the nature of PM produced during combustion, a TSI SMPS was employed to measure engine out PM particle size distribution. The particle size classifier counts the number of particles across a range of particle sizes by classifying each size individually, so this type of test is only really suitable for steady state tests. Figure 7.9 details the particulate size distribution for ULS diesel, RME and RME with aftertreatment for a room temperature dilution. At this temperature SOF liquid PM components are included as well as solid PM such as soot and ash. On consideration of the engine out emission, it is observed

that the ULS diesel PM emission is larger at nearly all particle diameters. However, at the lowest (nano-particulate) sizes the emission from RME combustion is larger. The mean average particle size is reduced for RME compared to ULS diesel Figure 7.9 and Table 7.1.
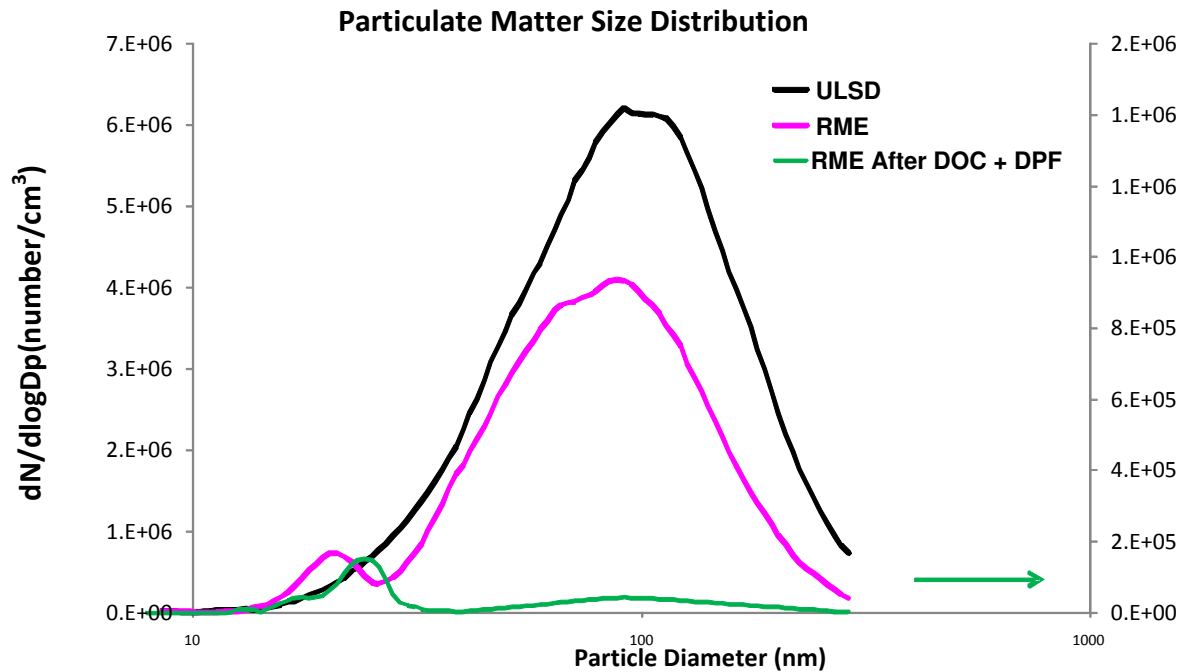
Figure 7.9. Particulate matter distribution low temp dilution.

When aftertreatment is also considered it can be gleaned that PM number is reduced significantly across all particle diameters tested.

Table 7.1. Cold dilution	ULSD	RME	ULSD Treated	RME Treated
			(with DOC + DPF)	(with DOC + DPF)
Median(nm)	80.1	72.9	45.3	39.2
Mean(nm)	91.2	82.4	69.1	60.2
Geo. Mean(nm)	77.8	71.6	43.7	36.8
Mode(nm)	88.2	76.4	16.8	8.3
Geo. Std. Dev.	1.8	1.7	2.8	2.7
Total Concentration(No./cm^3)	2.9E+08	1.7E+08	2.8E+06	2.1E+06

Table 7.1 shows details about the average particulate sizes for the data shown in Figure 7.9. Table 7.1 also includes details for ULS diesel with aftertreatment (not shown in Figure

7.9). To summarise, Table 7.1 RME combustion produces particulate of smaller median, mean and mode average size than ULS diesel. When the aftertreatment system is utilised, the median, mean and mode average size of the particulate is reduced. This data showing a shift towards smaller average particulate sizes emitted is an indication that the filter trap has increased efficiency when trapping larger size particulate. This seems logical as the DPF is predominantly a physical filtration mechanism and it stands to reason that larger particulate are more likely to become trapped within the DPF. It is remembered that filtration does occur for the smaller particulate, it's just more efficient when filtering larger PM.

To gain a clearer understanding of the solid PM, i.e. soot and ash, engine conditions were retested with the SMPS with the thermodiluter employed. The thermodiluter is set at 300 °C in order to drive off the bulk of the SOF, leaving just carbon and ash (solid particulate). Figure 7.10 shows the same conditions as Figure 7.9 and for proportional comparison the Y-axis has been fixed to that of Figure 7.9.

Figure 7.10 shows the PM emission now without the SOF fraction. It is possible to see that the quantity of PM is reduced, and that most apparently for RME, the first peak is absent. This is an indication that these smaller nano particulate are mainly made up of SOF liquid particulate. Summarising, RME combustion yields an increased proportion of small nano-particulate compared to ULS diesel, but the particulate is of SOF nature i.e. liquid particulate. This is particularly interesting, as health studies have shown that nano-particulate are a concern, due to their damaging nature (Gordon *et al.*, 1998; Pope, 2000; Samet *et al.*, 2000; Peters *et al.*, 2001; Pope *et al.*, 2002; Hartogg *et al.*, 2003; Krzyzanowski, 2005; Helfenstein *et al.*, 2008). However, these health studies have considered solid particulate only and implications of the damaging affect of liquid particulate remain unclear. From Figure 7.10 it

is possible to discern that RME combustion actually produces less solid particulate than ULS diesel combustion across all particulate diameters. Distinguishing between liquid and solid PM may become an important parameter for future legislation as the health effects of these distinct constituents becomes more apparent. An interesting example of this might be water PM, as this (clean) is known to be harmless. It has been shown that RME combustion produces larger amounts of water PM (Figures 7.7 & 7.8). Current legislation adds water PM to the total PM count and this may indicate certain fuels as larger polluters than they effectively are. This is a matter requiring accurate resolution. Improved future legislation might take this into account.
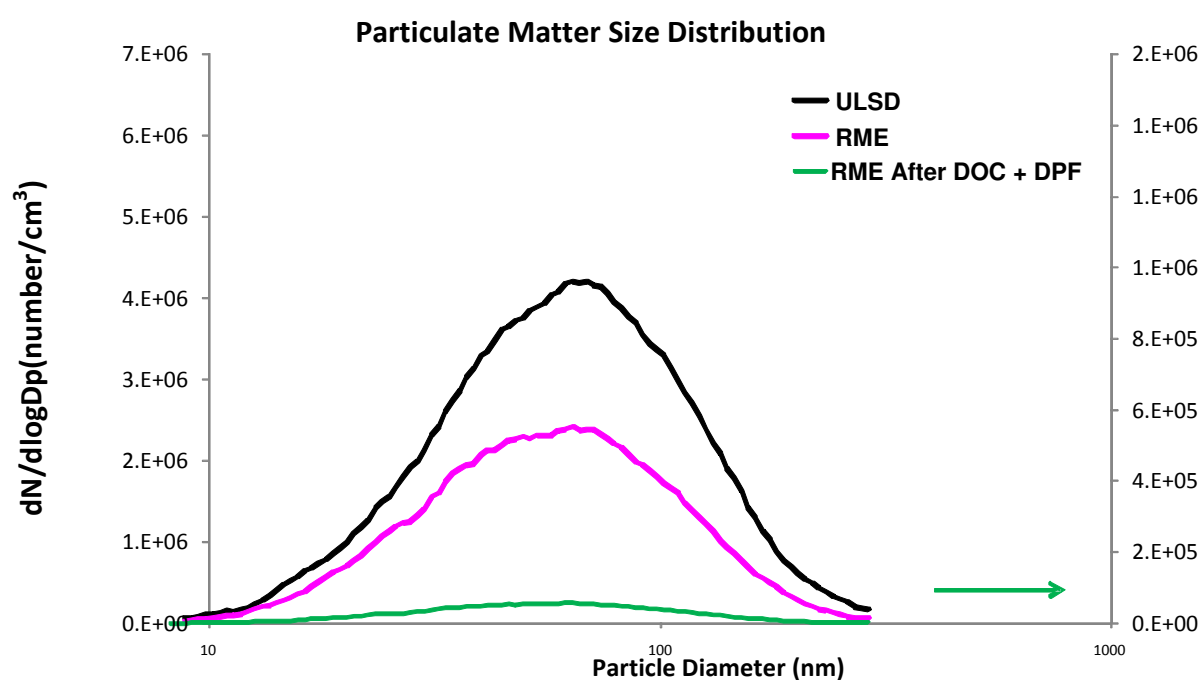
Figure 7.10. Particulate matter distribution high temperature dilution.

Table 7.2 details average particle size information for the hot dilution. If a comparison is made with Table 7.1 (cold dilution) it is possible to see that median, mean and mode average increases for both fuels for the hot dilution, i.e. when the SOF is removed, the average

particle size is larger. This indicates that the SOF particulate is of smaller average size, a fact

reinforced by the removal of the SOF peak for RME seen in Figure 7.10.

Table 7.2. Hot dilution	ULSD	RME	ULSD Treated	RME Treated
			(with DOC + DPF)	(with DOC + DPF)
Median(nm)	84.0	77.7	47.5	41.8
Mean(nm)	99.0	92.0	75.0	67.2
Geo. Mean(nm)	81.8	76.3	45.9	39.2
Mode(nm)	93.1	91.4	17.7	9.9
Geo. Std. Dev.	1.9	1.9	2.9	2.9
Total Concentration(No./cm^3)	2.4E+08	1.1E+08	2.3E+06	1.3E+06

Table 7.3 shows a summarized breakdown of the PM filtration efficiency for the PM

sampling techniques employed (again at 1500RPM 4 Bar IMEP 0% EGR) for ULS diesel and

RME. Briefly from Table 7.3, around 99% of solid PM was filtered for both ULS diesel and

RME by mass and by number. Liquid PM is filtered more than 80% for ULS diesel and RME by

mass and more than 95% by number. This can be explained by the nature of liquid PM as

liquid PM is defined at ambient temperatures. Whereas, in the exhaust where the

temperatures are higher, liquid PM would be in the gaseous phase. Combining the

efficiencies in Table 7.3 with the results in Figures 7.7 and 7.8 it can be seen that the

remaining PM was mainly water. So the majority of the hydrocarbons are oxidised over the

catalyst, but the water vapour continues through the aftertreatment system and remains in

the gaseous phase passing through the DPF. It only becomes liquid again when the gas is

cooled during the dilution process for analysis. Logically, the aftertreatment efficiency for

liquid PM produced from RME is less than that of ULS diesel. This is due to the lower engine

out levels of hydrocarbons and relatively large engine out amounts of water PM (Figure 7.7).

Table 7.3. AFTERTREATMENT EFFICIENCY

PM Type	PM Sampling Technique	ULS Diesel	RME	
Solid PM	Horiba Mexa 1230PM	99.28	99.49	% Mass
Solid PM	TSI SMPS 3080 Hot	99.25	99.09	% Mass
Solid PM	TSI SMPS 3080 Hot	99.07	99.06	% Number
Liquid PM	Horiba Mexa 1230PM	89.45	82.73	% Mass
Liquid PM	TSI SMPS 3080	88.10	85.55	% Mass
Liquid PM	TSI SMPS 3080	96.22	95.78	% Number
Solid & Liquid PM	Bosch Smoke Meter	95.02	92.93	% Mass
Solid & Liquid PM	Horiba Mexa 1230PM	95.07	90.25	% Mass
Solid & Liquid PM	TSI SMPS 3080 Cold	94.50	91.47	% Mass
Solid & Liquid PM	TSI SMPS 3080 Cold	98.36	98.03	% Number

In terms of total PM filtration (solid & liquid PM) at this condition it is noticed that each of the three PM mass measurement systems places ULS diesel aftertreatment at more than 94% efficiency by mass and 98% by number. When considering total PM filtration for RME combustion and this aftertreatment system more than 90% filtration by mass and 98% by number is seen.

To attain a clear direct comparison for the aftertreatment system efficiency for each fuel, efficiencies of the aftertreatment system should be measured using comparable engine out PM load conditions i.e. (higher engine load for the RME). It is also important not to lose sight of the fact that only one representative engine condition is assessed in Table 7.3.

7.3   SUMMARY AND CONCLUSIONS

In Chapter 7, ULS diesel and RME were combusted by CI both with and without aftertreatment. The combustion and emissions were then characterised for a range of regulated and unregulated emissions, with particular emphasis upon the PM produced and its suppression by the aftertreatment system.

It was found that:

RME combustion is slightly advanced, has a larger proportion of premixed phase combustion and higher cylinder pressures arise in order to produce an equivalent load to ULS diesel. Emissions of NOx are increased for RME. Increased cylinder pressures suppress soot formation and make complete combustion more likely. Emissions of soot HCs and CO are reduced for RME combustion and a slight reduction in thermal efficiency was observed.

Using an online GCFID and an offline DNPH method, dangerous unregulated carcinogenic compounds; acetaldehyde, formaldehyde, benzene, and 1,3-butadiene were found in ULS diesel exhaust for 0% EGR. Acetaldehyde, formaldehyde and benzene were observed in exhaust from RME combustion for 0% EGR though the concentrations are reduced compared to ULS diesel. When EGR is applied at 30% for both fuels, the levels of these carcinogens increased significantly and 1,3-butadiene was also observed in RME exhaust.

Offline TGA analysis and online PM analysis using a diffusion charging process revealed that RME combustion produces significantly less solid PM (less than half) compared to ULS diesel combustion. However, it produces slightly more liquid PM, with an increased proportion of water PM.

SMPS analysis of PM size distribution at two temperatures revealed that ULS diesel PM is increased at nearly all PM sizes. Nevertheless, at the small nano particulate size RME combustion produces an increased proportion of this particulate. These nano particulates were revealed to be SOF (liquid PM).

PM removal was assessed for ULS diesel and RME combustion using a platinum coated cordierite based oxidation catalyst and a wall flow cordierite diesel particulate filter.

THC emissions were reduced by at least 80% for both ULS diesel and RME combustion at all tested conditions. CO was almost eliminated for both ULS diesel and RME combustion at all tested conditions. The oxidation catalyst appeared to function equally efficiently for both ULS diesel and RME.

TGA and diffusion charge PM analysis revealed that solid PM was severely reduced by the DPF and that the DOC removed much of the SOF in HC form. The SOF PM that remained was found to be predominantly water for both ULS diesel and RME combustion. There are indications from TGA analysis that soot created during RME combustion is more reactive in oxidation than soot created during ULS diesel combustion.

SMPS PM measurements showed that PM was reduced at all particulate sizes for both ULS diesel and RME. Total PM filtration levels for the aftertreatment system are more than 94% by mass and 98% by number for ULS diesel. For RME total PM filtration is more than 90% by mass and 98% by number.

CHAPTER 8

NEAR FUTURE GREEN CI FUELS AND ASSOCIATED PM AFTERTREATMENT

In Chapter 4 a combustion and emissions study was conducted. The study compared ULS diesel, 1st Generation biodiesel (RME), 2nd generation biodiesel (GTL) and 3-way blends of ULSD, GTL and RME. It was found that the three-way blend (B20G10) could match diesel fuel performance and give reduced engine out emissions for all the regulated emissions. B20G10 could realistically meet future green legislation (EC, 2009) and it is identified as a promising near future fuel for the unmodified CI engine.

In Chapter 5 the role that fuel-borne oxygen plays in combustion is examined. Dimethyl carbonate (DMC) as a diesel additive is evaluated through comparative combustion studies of diesel (ULS diesel), biodiesel (RME), and four blends of the oxygenated DMC additive in diesel. 2DMC (2% DMC in diesel) can generate lower NOx and comparable particulate, THCs, CO compared to RME combustion, even though it has only 1.1% wt oxygen. 2DMC is proposed as a promising near future fuel for the unmodified CI engine.

In Chapters 6 and 7 prototype catalysts and a DPF were evaluated for their performance with ULS diesel and 1st generation biodiesel. In the near future it is thought that 2nd generation biofuels that have reduced impact upon the 'food vs. fuel' debate, as well as potentially increased efficiencies in production (see section 2.4) will become commonly available. Bio-mass GTL is also proposed as a potential near future fuel for the unmodified CI engine.

Determination of the nature of PM is of paramount importance. It has been demonstrated in Chapters 5, 6 and 7 that PM produced from different fuels can be of a

different nature. This may have implication for future aftertreatment system design and/or legislation.

It is worthwhile to determine the nature of PM produced from near future fuels. This is particularly relevant to fuels derived from green sources, as they can give both low GHG and local clean air emissions benefits (see Tables 2, 3 and the introduction to Chapter 4). As more is understood about the nature of PM produced from near future fuels, it will become easier to determine the viability of current aftertreatment technology, or whether new aftertreatment solutions will be needed.

In this Chapter ULS diesel and 1st generation biodiesel (RME) are used as reference fuels to compare and contrast 3 near future fuels; B20G10, 2DMC and 2nd generation biomass (GTL). The fuels were tested for combustion and emissions, with no aftertreatment and then with aftertreatment (DOC and DPF). Online and offline PM analytical techniques were then used to quantify the PM emission.

8.0.1   Fuels, Test Conditions and Procedure (specific to Chapter 8)

Five fuels were tested (Table 8.1.), the basic fuel properties are outlined in Table 3.6. All tests were steady state and were set at an engine speed of 1500 rpm. Tests were carried out at 2 bar, 4 bar and 5 bar IMEP and 0% EGR. Details of the catalyst and DPF can be found in Chapter 7. A schematic diagram of the engine and aftertreatment system is displayed in Figure 7.1.

Table 8.1. Fuels Tested

Abbreviation	% Volumetric Makeup
ULSD	100% ULSD
RME	100% RME
B20G10D	20% RME 10% GTL 70% ULSD
2DMC	2% DMC 98% ULSD
Biomass (GTL)	100% GTL

8.1   EXPERIMENTAL RESULTS AND DISCUSSION

The in-cylinder pressure and heat release rate versus CAD data for the 5 fuels over the end of compression and the early expansion strokes of the engine, are shown in Figure 8.1, for a representative engine load of 4Bar IMEP 0% EGR at 1500 rpm. This same speed and load condition is used for all the combustions and emissions analysis.
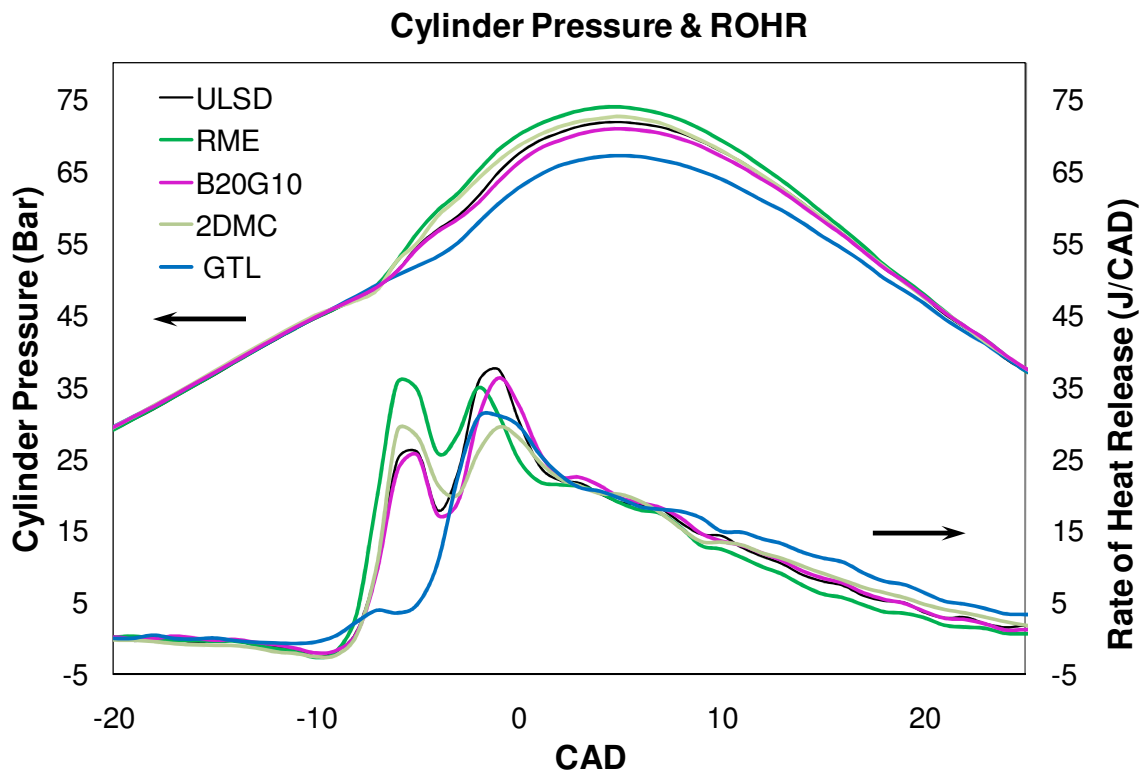
Figure 8.1. Cylinder pressure & ROHR, 1500 rpm 4 Bar IMEP.

Figure 8.1 presents for the first time the near future fuels ensemble. A comprehensive combustion analysis for each of these fuels was performed in Chapters 4 and 5. In brief:

For 1st generation RME and 2DMC the first heat release peak is larger than ULS diesel. This is thought to be due to the oxygen content of the fuels (Table 3.6.) which makes an increased proportion of the fuel spray effectively a pre-mixture of fuel and oxygen. For RME

the pre-mixture is also amplified due to the bulk modulus effects for this engine. For 2DMC there will be an increase to the premixed phase, as it has a slightly reduced cetane number (Figure 1.11.) compared to ULS diesel and RME. Increased cetane number (a measure of the quality of auto ignition) significantly reduces ignition delay (defined as the time between start of injection and SOC) and the fuel burnt in the 'premixed phase' (the first heat release peak (Heywood, 1988)).

2nd Generation GTL is unique and this is a function of its formation and alkane (long hydrocarbon chains) structure (section 2.4.2). The properties of 2nd gen (GTL) have the effect of retarding the start of injection and combustion due to reduced fuel density (Table 3.6.) and increased compressibility. For 2nd gen GTL this property has been counteracted by a 2 CAD advanced injection timing (see Chapter 4). 2nd gen GTL and G20B10 have a cetane number of 80 and 57 compared to around 54 for the ULSD and RME. So the presence of 2nd gen GTL reduces the premixed phase of combustion allowing a larger proportion of the fuel to be burnt in the mixing controlled combustion phase (diffusion burning) (Figure 1.3.).

For B20G10 which contains both 1st gen (RME) and 2nd gen (GTL) the increased bulk modulus effects of RME are largely offset by the reduced bulk modulus effects of 2nd gen (GTL). This gives similar injection characteristics to ULS diesel injection, but with both fuel-borne oxygen (which increases the proportion of the premixed phase) and increased cetane number (which reduces the proportion of premixed). Overall the premixed phase is slightly reduced compared to ULS diesel and the combustion duration overall increases. This increase in duration will have positive emissions consequences.

For peak cylinder pressure comparison, it is noticed that 2DMC has peak cylinder pressures (an indication to peak temperatures) that are slightly higher than ULS diesel, though significantly lower than 1st gen RME. B20G10 has significantly lower peak cylinder pressures than RME and slightly lower peak pressures than ULS diesel. Appreciably, 2nd gen (GTL) has significantly lower peak combustion pressures than the other fuels and this is believed to be due to the notably reduced extent of the premixed combustion phase

8.2   EMISSIONS

Figure 8.2 depicts the NOx – Bosch smoke number trade-off for the three near future fuels, RME and ULS diesel.
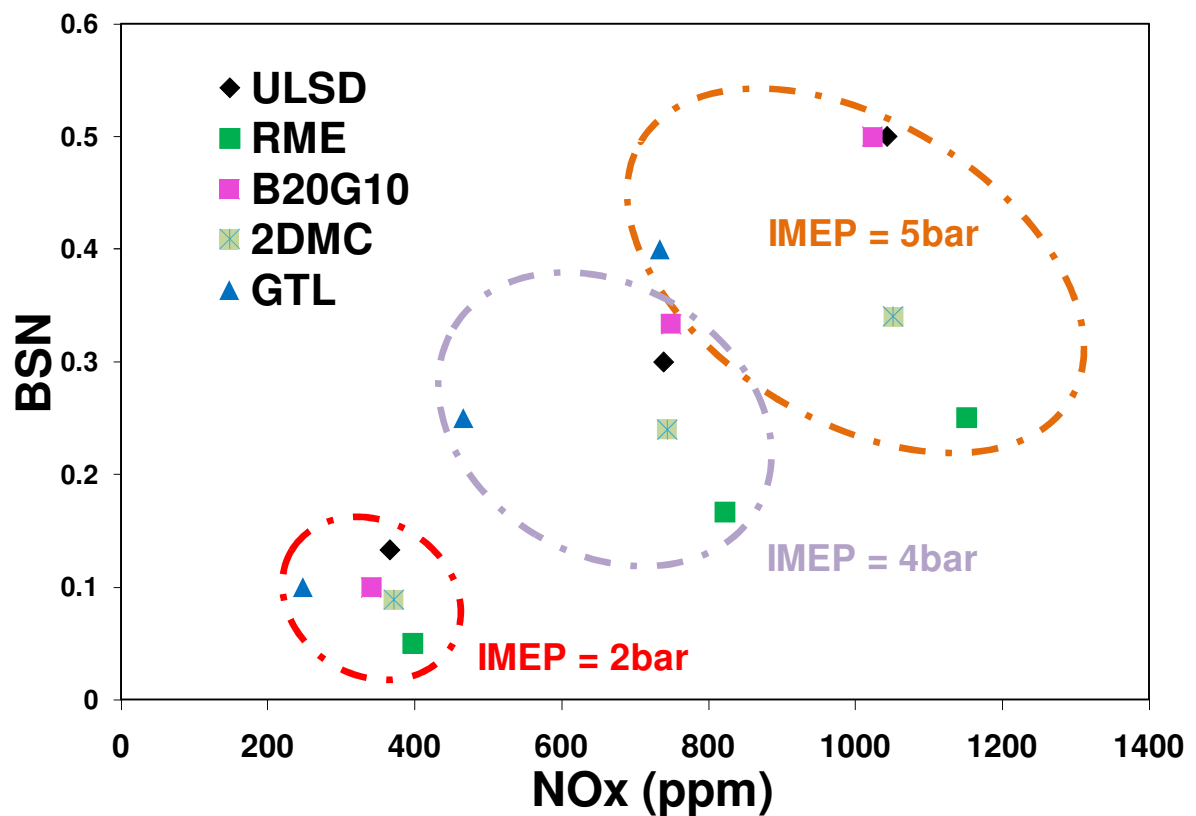
Figure 8.2. NOx – Smoke (BSN) trade-off 1500rpm.

The marker points in Figure 8.2 represent the load conditions of 2, 4 and 5 Bar IMEP. Analysis of this trade-off is found in Chapters 4 and 7. NOx benefits are apparent for GTL and

in most conditions for B20G10. Figure 8.2 also includes 2DMC which was not previously shown in this manner (Figures 4.9 & 4.10). Interestingly, 2DMC combustion gives BSN smoke values that are evidently higher than the values for RME combustion at all loads. This seems to conflict with the findings in Chapter 5, where it was concluded that 2DMC and RME combustion generate comparable particulate. This requires resolution. It is postulated that this difference may be due to the shortcomings of the BSN light reflectance technique, as it can only detect the darkening due to black smoke. Smoke that would appear white would not affect the BSN signal. It is known that in terms of overall PM number and PM mass (Chapter 5) that 2DMC and RME are comparable, so it is theorised that RME smoke must contain a larger proportion of white smoke (non soot PM) to make up this difference.

When the aftertreatment system was employed, as expected, there was no real effect on NOx emissions for any of the fuels tested (the prototype catalyst employed in Chapters 7 & 8 is a DOC, not a bi-functional DOC & NOx adsorber type catalyst like the one employed in Chapter 6). BSN was significantly influenced by the aftertreatment system, so much so, that for all the fuels at all conditions the reading was below the detectable limits of the BSM (i.e. < 0.04 BSN).

Figure 8.3 shows THC and CO emissions for ULSD, RME and the 3 near future fuels B29G10, 2DMC and GTLAD with and without aftertreatment. Explanation for the engine out emissions of THC and CO can be found in Chapters 4 & 5. It is also believed that the advanced injection for GTL should not be forgotten, as it is thought that this might exaggerate the emissions benefit of GTL. The unmodified injection timing PM level for GTL is actually higher than ULS diesel for this engine type (Abu-Jrai *et al.,* 2006) and perhaps 2 CAD

advance represents overcompensation for the bulk modulus effects, see Figure 8.1. SOC is earlier for GTL than ULS diesel.
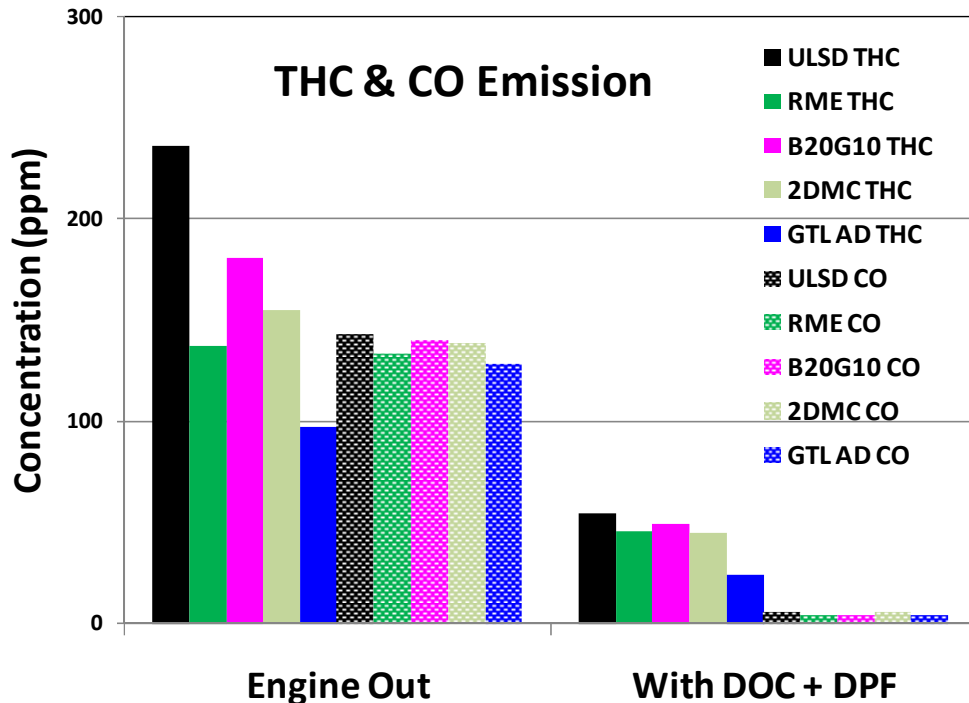
Figure 8.3. THC & CO emissions without and with aftertreatment.

At this condition (300 °C local exhaust gas) THCs are reduced by around 80% over the DOC and CO is almost eliminated for all the fuels. It is thought that the DOC is able to function well with all the near future fuels, as each of the new fuels has reduced engine out emissions of THC and CO when compared to ULS diesel. Therefore it is less likely that the active catalytic sites would be blocked, as the catalyst is far from its saturation point (i.e. well within its capability limits for HC and CO reduction). The general trend for thermal efficiency (the engine energy output over the fuel energy input) is: GTL > B20G10 > ULSD = 2DMC > RME (see Chapter 4). Though, the differences are small (and the advanced injection of GTL should be considered). Fuel flow rates (not shown) compared to ULS diesel were in proportion to their heating values across all conditions.
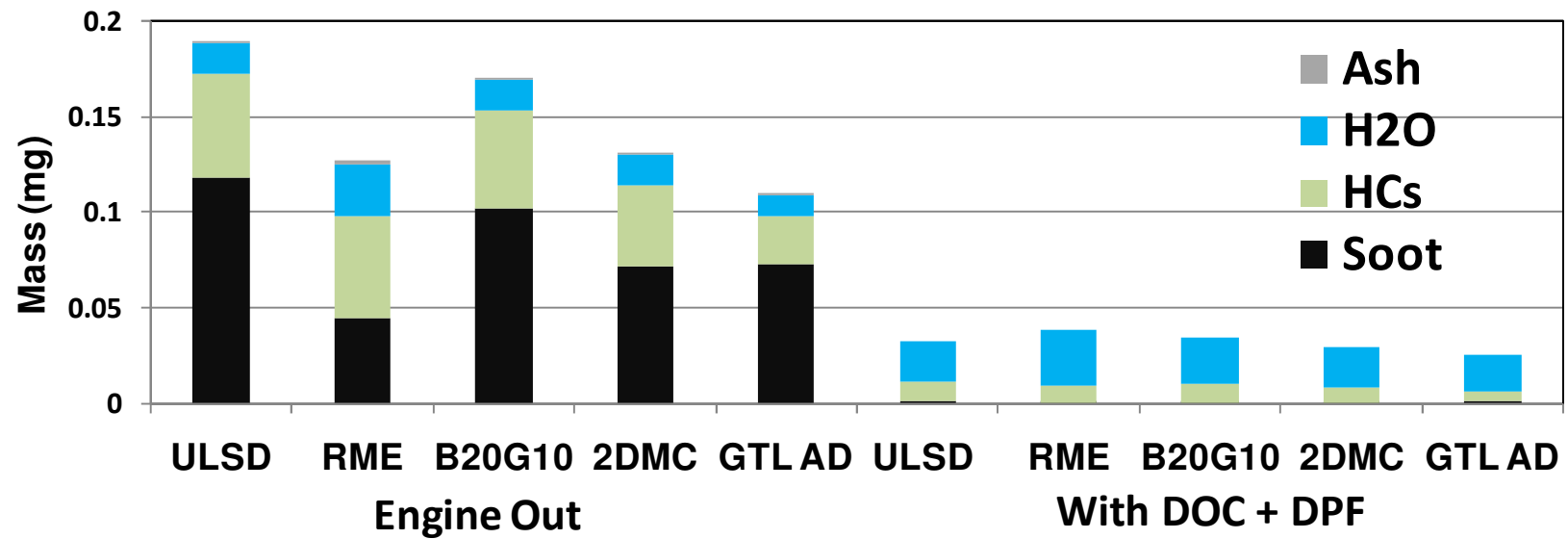
Figure 8.4. Exhaust particulate matter classified by TGA.
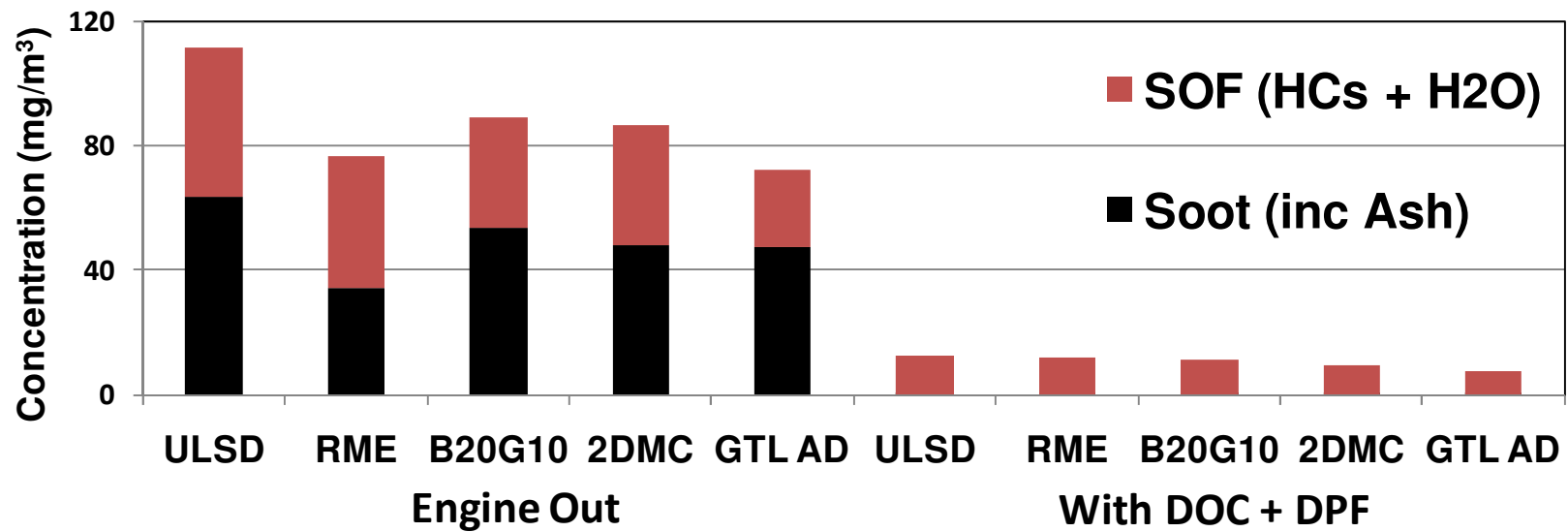
Figure 8.5. Particulate matter emission Horiba Mexa 1230PM.

Figure 8.4 details the PM compositional makeup according to the offline TGA method (Chapter 3) when running with ULSD, RME and the 3 near future fuels B29G10, 2DMC and GTLAD without and with aftertreatment. Figure 8.5 depicts SOF and Soot for the same conditions and fuels using a new online Horiba Mexa 1230PM analyser (Chapter 3).

Correlation between the 2 methods is apparent, it can also be seen that the aftertreatment solution is very effective (99%+) for solid PM (soot & ash) for all fuels. The DOC is particularly efficient at around 80% for HCs for all fuels. Evidence of the oxidation of HCs and CO is also shown by the slight increase in water PM following the aftertreatment system (Figure 8.4).

Overall PM is reduced for B20G10 and more significantly for 2DMC and GTL compared to ULS diesel by both methods, Figures 8.4 & 8.5. In Chapter 7 the overall PM and profile differences between RME and ULSD were discussed. The PM profile produced by B20G10 and 2DMC combustion does not appear significantly different to the PM profile of ULS diesel. For 2nd gen GTL however, the profile does appear to be different. Proportionally, soot produced from GTL combustion is about 68% of the total PM, compared to 60% for ULS diesel and 40% for RME. This is interesting, though not necessarily a problem (as overall the PM level is still reduced compared to ULS diesel). This trend is perhaps also evidenced by the discussion relating to the BSN (Figure 8.2) where it is noticed that in terms of BSN at 4 Bar IMEP (the condition of Figures 8.4 & 8.5) GTL has a BSN of 0.25 and RME has a reduced BSN 0.18. It is known from Figure 8.5 that total PM levels for GTL are lower and yet the BSN is higher. It is thought that Figures 8.4 & 8.5 show the possibilities of the shortcomings of BSN in exhaust measurements referred to earlier.
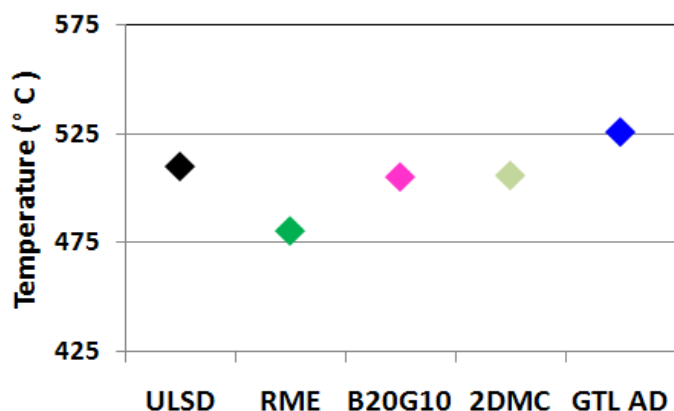
Figure 8.6. TGA max rate soot oxidation temps.

Figure 8.6 shows the max rate of weight loss temperature (achieved during the soot oxidation Figure 3.5.) for the TGA. The general trend depicted was true for all the tested conditions. It is possible to interpret this as an indication of soot oxidation activity i.e. soots with a lower temperature max rate of soot oxidation are more active in oxidation. Caution is taken in converting this data into reaction energies for the soot (this had been the intention), as the collection medium is dissimilar to soot caught in a cordierite DPF. Soot oxidation activity may evidence soot compositional differences in the microstructure of the soot. For example, a more compact microstructure (containing fewer gaps/voids) has been shown to be less active in oxidation and soots with more voids are more active (Song *et al.*, 2009). The microstructure will probably be largely due to the degree of saturation of the soot particulate as they agglomerate with volatile organic matter (VOM) (liquid PM). Williams *et al*. (2006) suggest the soot microstructure makes it possible for a 'capsule type oxidation' at reduced temperatures, or put more simply, the soot with voids has increased surface area.

Potentially this finding is positive for RME, B20G10 and 2DMC combustion, as soots that are more active are easier to burn off during DPF regeneration, an advantage in the regeneration process. Conversely this result could be interpreted as a (not widely reported) negative for GTL fuels. It is thought that GTL soot contains less voids because fuel-borne oxygen is not present (Song et al., 2009) and there is reduced relative VOM during agglomeration. A recent study demonstrated to the author by Liebig *et al.* (2009) showed

that GTL combustion actually aids the aftertreatment regeneration strategy as the period between regenerations can be increased. This is credible because the overall PM level produced from GTL is lower. The result in Figure 8.6 indicates that when the filter warrants regeneration it will require a bit more energy than ULS diesel combustion for the same PM loading. It is unclear if this could have significant implications for aftertreatment systems. Passive regeneration systems for example, might have more difficulty in regeneration (though regeneration would be required less often).

8.3   SUMMARY AND CONCLUSIONS

In Chapter 8, 3 promising near future fuels (B20G10, 2DMC and GTL) were combusted by CI both with and without aftertreatment. The combustion and emissions were then characterised for a range of regulated emissions, with particular emphasis upon the makeup of the PM produced and its suppression by the aftertreatment system.

It was found that:

8.3.1   FUELS

B20G10 (a blend of ULSD, 1st gen RME and 2nd gen GTL) is a fuel with similar combustion characteristics (i.e. in-cylinder pressure, ROHR and start of combustion) to conventional ULS diesel. All the regulated emissions from B20G10 are reduced compared to ULS diesel. The PM produced is of a similar profile (proportional makeup) to ULS diesel. B20G10 soot is more active in oxidation (positive) than ULS diesel soot.

2DMC (a blend of ULSD, and DMC) is a diesel fuel which is enhanced by a small amount of oxygenation from the green additive DMC. Regulated emissions of THC, CO (>30% reduction) and PM (50% reduction) from 2DMC combustion are reduced compared to diesel

but there is a small NOx penalty. The PM produced is of a similar profile (proportional makeup) to ULS diesel. 2DMC soot is more active in oxidation (positive) than ULS diesel soot.

2nd gen GTL (a proposed biomass 2nd gen GTL) has an alkane (long hydrocarbon chains) structure (section 2.4.2). This high cetane petroleum diesel substitute has a significantly reduced proportion of pre-mixed combustion. Combustion is cooler, occurring predominantly in the mixing controlled combustion phase (diffusion burning). All the regulated emissions from 2nd gen GTL combustion are reduced when compared to diesel. The PM produced has a dissimilar profile (proportional makeup) to that of ULS diesel. It contains proportionally more soot and less SOF than ULS diesel. 2nd gen GTL soot is less active in oxidation (negative) than ULS diesel soot. The implication of this result may affect the DPF regeneration strategy.

8.3.2 AFTERTREATMENT

The **DPF** is very effective (99%+) for solid PM (soot & ash) for all fuels (2 techniques). The **DOC** is particularly efficient at around 80% for HCs for all fuels for the tested condition (3 techniques). Levels of emissions after the aftertreatment system for THC, CO and PM for the 3 near future fuels are reduced compared to ULS diesel. The system (DOC + DPF) is believed to be a capable combination to help future fuel powered CI engines meet emission targets.

CHAPTER **9**

ENGINE PERFORMANCE AND PM SPECIATION FOR COMPRESSION IGNITION ENGINES WITH A RANGE OF FOSSIL AND BIOFUELS

The effect that realistic near future fuels have on combustion and emissions has been examined with a particular emphasis upon PM. New green source fuels can give both low GHG and local clean air emissions benefits. Aftertreatment systems were designed to deal with fossil diesel PM. It is important to understand the nature of PM produced by near future fuels in order to determine the viability of current aftertreatment technology and the path for future development. The following is a summarised account of the main findings of this research thesis.

9.1   CONCLUSIONS AND SUMMARY

Chapter 4 **Diesel Engine Performance and Emissions when 1st Generation Meets 2nd Generation Biodiesel**

To assess the feasibility of a realistic future biofuel, a comparative combustion study between ULSD, GTL (synthetic diesel), biodiesel (RME), and 3-way blends of ULSD, GTL and RME was conducted. Blending ULSD, GTL and RME can produce a fuel with similar combustion characteristics (i.e. in-cylinder pressure, ROHR and start of combustion) to conventional ULSD, with no fuel economy penalty. B20G10 (20% RME, 10% GTL 70% ULSD) was found to be a promising 3-way blend. Problem emissions produced by one source fuel are counteracted by inherent advantageous characteristics of the other in the blend. This creates a blend that requires no engine modifications. All regulated emissions are improved, as well as engine efficiency. This is attributable to the dynamic properties of the blends, e.g. the higher cetane number due to the GTL and the increased oxygen content due to the RME

proportion. Diesel mixed with GTL and RME may be more rational (than a blend having only two constituents) as a future fuel.

Chapter 5 **A Comparison of Diesel and Biodiesel Emissions Using Dimethyl Carbonate as an Oxygenated Additive**

To assess the role that fuel-borne oxygen plays in combustion and to test the feasibility of DMC as a diesel additive, a comparative combustion study was conducted between diesel (ULS diesel), biodiesel (RME), and 4 blends of the oxygenated DMC additive in diesel. DMC at 53% wt oxygen can be mixed neat with diesel at low levels. Fuel-borne oxygen can help to improve engine out emissions of THCs, CO, and PM. Even low level additions of DMC (2% or 4% DMC) can reduce carbon PM (soot) by as much as 50%. Emissions of NOx were slightly increased due to enhanced premixed combustion for oxygenated fuels. 2DMC can generate comparable particulate, THCs, and CO emissions to RME combustion, even though it has only 1.1% wt oxygen. 2DMC was merited as a promising fuel for further study.

Chapter 6 **Activity of Prototype Catalysts on Exhaust Emissions from Biodiesel Fuelled Engines**

A prototype catalyst was assessed for RME emissions and aftertreatment performance. The catalyst reduces not only the amount of HC, but also the total particulate concentration. However, the catalyst did not have a large effect upon the NOx reduction.

The prototype catalyst effectively reduces PM mass and unregulated hydrocarbons emitted by RME combustion. Up to 50% reduction in PM number and 30% reduction in mass was recorded. Employing EGR in the biodiesel combustion process reduces the soot free nuclei (nano) mode particles and increases the larger diameter particles (accumulation

mode). Subject to certain engine and catalyst operating conditions, the SOF of the accumulation mode particles is burnt-off over the catalyst and this leaves behind soot of smaller mean diameter.

Chapter 7 **Speciation of Particulate Matter from Biodiesel Combustion and it's Reduction by Aftertreatment**

A comprehensive, 1st generation biodiesel (RME) and ULS diesel CI combustion and emissions study was performed, both with and without aftertreatment. The combustion and emissions were characterised for a range of regulated and unregulated emissions, with particular emphasis upon the PM produced and its suppression by aftertreatment.

RME combustion is considered advanced, with a larger proportion of premixed phase combustion and higher cylinder pressures than for ULS diesel. Emissions of soot HCs and CO are reduced for RME combustion. Emissions of NOx are increased for RME. Emission concentrations of dangerous unregulated carcinogenic compounds; acetaldehyde, formaldehyde, benzene, and 1,3-butadiene are reduced for RME when compared to ULS diesel combustion. RME combustion produces significantly less solid PM (less than half) compared to ULS diesel combustion. However, it produces slightly more liquid PM, with an increased proportion of water PM.

Analysis of PM size distribution at two temperatures revealed that ULS diesel PM number is increased at nearly all PM sizes. Nevertheless, RME combustion produces an increased number of small nano particulate. These nano particulates were revealed to be SOF (liquid PM).

Aftertreatment: The efficiency of the oxidation catalyst was comparable for both ULS diesel and RME. The SOF PM that remained was found to be predominantly water for both

ULS diesel and RME combustion. PM measurements showed that PM matter was reduced by the aftertreatment at all particulate sizes for both ULS diesel and RME. Total PM filtration levels for the aftertreatment system are more than 90% by mass and 98% by number, for both RME and ULS diesel (solid & liquid PM).

Chapter 8 **Near Future Green CI Fuels and Associated PM Aftertreatment**

Three promising near future fuels were selected from the research outlined in earlier Chapters, (B20G10, 2DMC and GTL).

B20G10 (a blend of ULSD, 1st gen RME and 2nd gen GTL) is a fuel with similar combustion characteristics (i.e. in-cylinder pressure, ROHR and start of combustion) to conventional ULS diesel. All the regulated emissions from B20G10 are reduced compared to ULS diesel. The PM produced is of a similar profile (proportional makeup) to ULS diesel and the soot is more active in oxidation (positive).

2DMC (a blend of ULSD, and DMC) is a green oxygenate additive enhanced diesel fuel. Regulated emissions of THC, CO and PM from 2DMC combustion are reduced compared to diesel but there is a small NOx penalty. The PM produced is of a similar profile to ULS diesel and the soot is more active in oxidation (positive).

2nd gen GTL (a proposed biomass 2nd gen GTL) is a high cetane petroleum diesel substitute. All the regulated emissions from 2nd gen GTL combustion are reduced when compared to diesel. The profile of PM produced is not the same as ULS diesel. It contains proportionally more soot and less SOF than ULS diesel. 2nd gen GTL soot is less active in oxidation (negative) than ULS diesel soot. This may influence DPF regeneration strategy.

The **DPF** is effective (99%+) for solid PM (soot & ash, solid) for all fuels evaluated. The **DOC** is efficient at around 80% for HCs for all fuels for the tested condition.

9.2   CLOSING REMARKS

The history of the emissions from combustion can be traced back over the centuries. Recently, serious concern about GHG emissions and local clean air has increased the focus on all emissions. The automotive industry (a key contributor to atmospheric pollution) has responded by minimizing and aftertreating fossil fuel emissions. Use of non-renewable fossil fuels is the largest man-made contributor to global warming. To move directly to zero emission fuel sources is not currently feasible. Biodiesels have potential as renewable alternatives to fossil diesel. Biodiesels have reduced GHG emissions with scope for reduction in other key emissions like PM, THC and CO.

Bio-alternatives to fossil diesel have been explored in this thesis. It was seen that CI combustion and emissions formation is complex. The source fuel has a significant effect upon CI engine performance and emissions formation processes. Carefully selected blends like B20G10 can make all round regulated emission improvements. PM produced from the combustion of bio alternatives diesel fuels is indeed different to fossil diesel created PM. For example RME has an increased proportion of SOF especially in the nano-sized range. There is a case for more research into the health effects of nano-sized SOF material. Fuel-borne oxygen and emission SOF has a bearing upon the microstructure and structure of agglomerated PM. For alternate fuels with fuel-borne oxygen it seems that current PM aftertreatment systems will be aided by these fuels. For synthetically produced 2nd generation GTL fuels there are potentially DPF regeneration implications.

It seems that (tentatively) providing the overall level of PM is reduced compared to fossil diesel combustion current aftertreatment solutions are as effective for bio alternatives as they are for fossil diesel.

9.2.1 Subsequent Work and Future Work

This thesis has explored 1st generation RME as a diesel substitute. All biodiesels are made from a limited amount of FAMEs. To further understand the influence **constituents of FAME** fuels have on combustion and emissions, a follow-on study to this thesis was devised (now completed). The study investigated the effect that the chemical structures (number of double bonds and chain length) of biodiesel fuels have on combustion and emissions, in view of future emissions reduction by tailoring the fatty acid profile and/or the processing of bio-feedstock. The resulting recommendation is that shorter chain, saturated FAME fuels would be preferable. This paper will shortly be published in *Fuel*.

The FPS group should extend the unregulated hydrocarbon speciation in chapter 7 to include aftertreatment effects (C_1-C_7 and the aldehydes). The author would also like the FPS group to extend the works of this thesis to more modern engines such as a **common rail multi-cylinder** and the new **common rail single cylinder.** To date this has only been achieved for RME and GTL by colleagues and the author on a multi-cylinder common rail engine.

For the near future it would advantageous for the FPS group to look at some of the interesting future green fuels that were merited for study, but were simply not available to test. These include **algae methyl ester, Shell HTU diesel** (Chapter 2) and the potentially promising oxygenative additive (other than DMC) **2-methoxyethyl acetate.** Cetane improver **2-Ethylhexyl nitrate** (EHN) addition in FAME fuels was also highlighted as a prospect for addition in FAME fuels.

Aftertreatment continuously develops, catalysts can now be held within the DPF and these new **catalytic DPFs** should be assessed for the future fuels of this thesis.

9.3   APPENDIX

Tested Aldehydes:

Restek Aldehydes/Ketones DNPH Stock Standard No. 31808

1	Formaldehyde-DNPH
2	Acetaldehyde-DNPH
3	Acrolein-DNPH
4	Acetone-DNPH
5	Propionaldehyde-DNPH
6	Crotonaldehyde-DNPH
7	Butyraldehyde-DNPH
8	Benzaldehyde-DNPH
9	Isovaleraldehyde-DNPH
10	Pentanal-DNPH
11	o-Tolualdehyde-DNPH
12	m-Tolualdehyde-DNPH
13	p-Tolualdehyde-DNPH
14	Hexanal-DNPH
15	2,5-Dimethylbenzaldehyde-DNPH

HPLC
Specification
Dionex Summit with chromeleon software

Pump: Summit P580 quaternary low pressure gradient pump with a built-in vacuum degasser.

Detector: Summit UVD 170s UV/VIS multi-channel detector with analytical flow cell.
Autosampler: Summit Gina 50 electronically actuated
variable volume
autosampler.

9.3.1 AUTHOR PUBLICATIONS

Rounce, P., Rodríguez-Fernández, J., Tsolakis, A., York, A.P.E., Cracknell, R.F., Clark, R.H. (2009) Diesel Engine Performance and Emissions when First Generation Meets Next Generation Biodiesel. **SAE Paper**, 2009-01-1935. *Presented by the author at a Fuels and Lubricants meeting in Florence 2009.*

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Rounce, P., Tsolakis, A., York, A.P.E. (2011) Speciation of Particulate Matter from Biodiesel Combustion and its Reduction by Aftertreatment. Submitted to **Fuel.**

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9.3.2 Awards

1. David Brewster Cobb prize for Best Research Paper by a student in engineering in 2009.

2. Best Research Poster and Presentation by a 2nd year PhD student at the Johnson Matthey Academic Conference in 2009.

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