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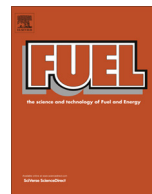
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Influence of the addition of LPG-reformate and H₂ on an engine dually fuelled with LPG–diesel, –RME and –GTL Fuels



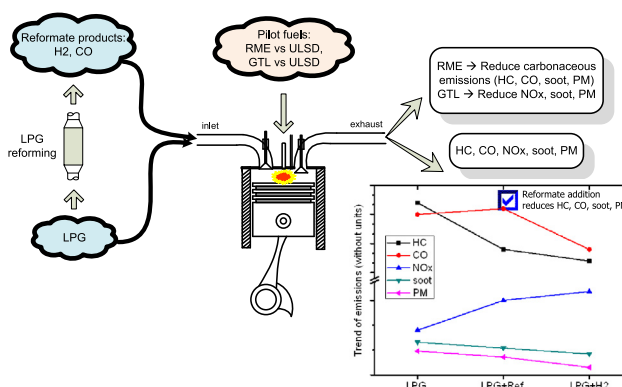
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HIGHLIGHTS

- Reformed gas enhances the LPG–diesel dual fuelled engine thermal efficiency.
- Reformed gas in LPG–diesel dual fuelling reduces regulated/unregulated emissions.
- Replacement of Diesel with RME in dual fuelling reduces THC, CO, soot and PM.
- Replacement of Diesel or RME with GTL in dual fuelling improves smoke–NO_x trade-off.

GRAPHICAL ABSTRACT



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ABSTRACT

Dual fuel compression ignition engine has been proposed as one approach to reduce diesel engine regulated emissions (NO_x and Soot) and to also allow the utilisation of other non-traditional fuels in transportation, in order to improve fuel security and CO₂ emissions. In an attempt to improve the combustion characteristics of the LPG–diesel dual fuelled engine the influence of the (a) hydrogen and reformat (H₂ and CO) additions and (b) properties of the in-cylinder injected diesel fuel, in this case diesel, biodiesel and synthetic diesel fuel were investigated.

Improvements on engine thermal efficiency and HC (including particular HC species) emissions with the reformat and further improvements on CO, soot and particulate matter with hydrogen with respect to LPG–diesel dual fuel combustion were obtained. However, an increase in NO_x was obtained due to the high in-cylinder temperature as a result of the shorter advanced premixed combustion. Moreover, the RME's oxygen content, different injection (i.e. different high bulk modulus) and combustion characteristics as a result of its properties modified the combustion process and hence produced even lower HC, CO, soot and PM emissions. On the other hand, the lower density of GTL has changed the diesel fuel injection and combustion characteristics in dual fuelling mode which resulted in the increased regulated (HC and CO) and unregulated emissions. However, LPG–GTL dual fuelling with reformat and H₂ addition showed better smoke–NO_x trade-off compared to that of ULSD and RME.

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1. Introduction

Dual fuel system in compression ignition (CI) engines has been proposed as one of the approaches to overcome the diesel engine

emission issues such as particulate matter and NO_x in order to meet the stringent future emission legislations [1]. The emission benefits of dual fuel CI engine operation are mainly based on a more homogeneous air–fuel mixture and low temperature combustion operation than in the case of conventional CI engine combustion [2,3].

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One of the gaseous fuels used in dual fuel system is liquefied petroleum gas (LPG). Currently LPG is a gaseous fuel attracting considerable attention as an alternative fuel [4]. In addition, LPG–diesel dual fuel operation could reduce soot and NO_x simultaneously [4,5]. However, increasing LPG substitution level leads to the increased ignition delay and can potentially produce a high proportion of unburned mixture in the exhaust and deterioration in the engine thermal efficiency. Additionally, at high engine load conditions engine durability problems can be experienced as a result of the uncontrolled combustion reaction rate or premature ignition and knocking [6,7]. The use of hydrogen addition and optimization of the diesel fuel properties can provide solutions to the above mentioned problems. A number of researches have reported the benefits of the utilisation of hydrogen in dual fuel engine [2,3,6,8]. They have presented improvements in terms of brake thermal efficiency, HC, CO and particulate matter (PM) emissions. All the beneficial effects are due to the hydrogen characteristics such as: absence of carbon, high flame speed, higher diffusivity and broad flammability limits [9,10].

Hydrogen and CO are the main component of synthesis gas which can be produced by reformed exhaust gas recirculation (REGR) technique. This technique involves catalytic reaction of hydrocarbon fuel with part of the engine exhaust gas. The synthesis gas which is also called reformat is then fed back to the engine combustion chamber [2,11].

The combustion of oxygenated free of aromatics HC fuels such as rapeseed methyl ester (RME) and fuels with high cetane number (CN) and free of aromatics such as gas-to-liquid (GTL) improve HC, CO and soot/PM emissions. However, RME combustion increases

NO_x emissions, while those are reduced with GTL fuelling [12]. The differences in the physical and chemical properties (e.g. density, viscosity, cetane number) of these fuels and hence different injection and combustion characteristics in addition to the advantages in terms of emissions described above may provide a solution to the problems associated with dual fuelling without significant changes in engine control.

Therefore, the objective of this study is to further our understanding of the influence of the reformat and H_2 in the LPG–diesel combustion process and emissions when the injected diesel fuels have different properties.

2. Experimental

2.1. Engine specifications and instrumentation

The engine is a single cylinder research diesel engine, and described in Table 1 while a schematic diagram of the test rig is shown in Fig. 1. The engine instrumentation has been previously described [8]. An electric dynamometer with a motor and a load cell was used to load and motor the engine. The in-cylinder pressure was recorded using a Kistler 6125B pressure transducer connected via a Kistler 5011 charge amplifier to a National Instruments data acquisition board. A digital shaft encoder was used to measure the crankshaft position. Data acquisition and combustion analysis were carried out using in-house developed LabVIEW-based software.

The test rig includes other standard engine instrumentation, such as thermocouples to measure oil, air, inlet manifold and exhaust temperatures and pressure gauges mounted at relevant points. Engine test bed safety features were also included. Atmospheric conditions (humidity, temperature, pressure) were monitored during the tests. Output from the analysis of consecutive engine cycles included peak engine cylinder pressure, values of indicated mean effective pressure (IMEP), percentage coefficient of variation (%COV) of IMEP and rate of heat release (ROHR). The COV of IMEP was used as criteria for combustion stability from a minimum of 200 cycles.

2.2. Exhaust gas emissions analysis

An Horiba MEXA 7100DEGR emissions analyser was used to measure carbon dioxide and carbon monoxide by non-disperse

Table 1
Engine specifications.

Engine specification	Data
Number of cylinders	1
Bore/stroke	98.4 mm/101.6 mm
Connecting rod length	165 mm
Displacement volume	773 cm ³
Compression ratio	15.5:1
Rated power (kW)	8.6 @ 2500 rpm
Peak torque (Nm)	39.2 @ 1800 rpm
Injection system	Three hole direct injection
Engine piston	Bowl-in-piston

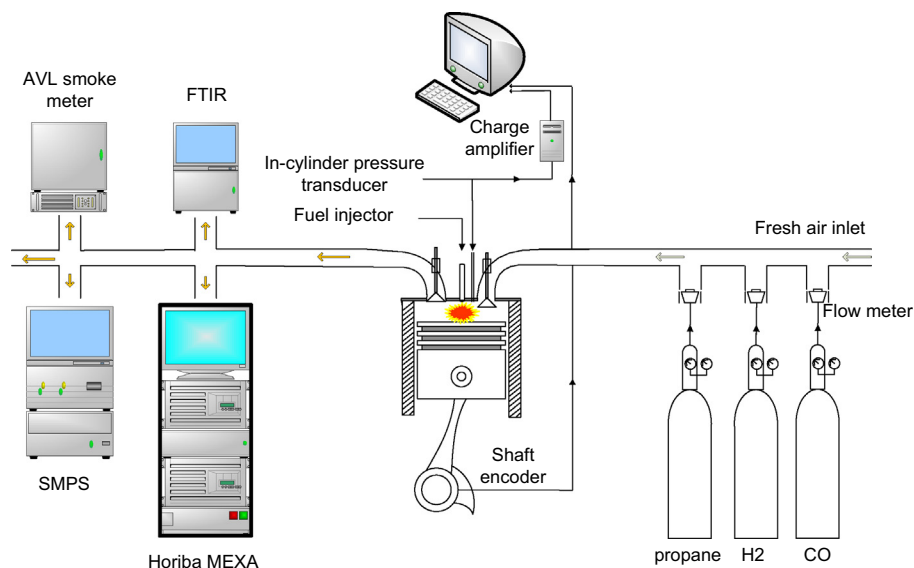


Fig. 1. Schematic diagram of experimental setup.

infrared (NDIR), oxygen using a magneto-pneumatic detection, oxides of nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$) by chemiluminescence detection (CLD), and total hydrocarbons (HC) by flame ionization detector (FID).

A multigas 2030, FTIR (Fourier transform infrared spectroscopy) analyser was also used for measurement of different hydrocarbon species.

An AVL 415S smoke meter was used for measuring the soot content in the exhaust gas of the engine. The result was displayed as filter smoke number (FSN) conforming to ISO 10054.

An SMPS (scanning mobility particle sizer) unit was used to measure the particle size distribution by classifying particles based on their electrical mobility which is related to particle size. The sample was previously diluted using a TSI 379020 thermodiluter (dilution ratio 200:1 and dilution temperature 150 °C).

2.3. Fuels

The liquid fuels used in this study were ultra low sulphur diesel (ULSD), rapeseed methyl ester (RME) and gas-to-liquid (GTL) provided by Shell Global Solutions UK (Table 2). Bottled gaseous fuels (i.e. LPG, H_2 , and CO) were used to simulate LPG-reformed gas. The LPG composition used was 100% propane (C_3H_8) (Table 3).

2.4. Engine operating conditions

The combustion studies and emissions analysis was carried out at two different engine loads, 3 and 5 bar IMEP at 1500 rpm engine speed. LPG fed into the engine inlet manifold at three different concentrations of 0.2, 0.5 and 1% of the total volumetric intake charge air flow rate. Hydrogen and carbon monoxide concentrations were selected, assuming complete fuel reforming of half of the propane to syngas by a combined partial oxidation and steam reforming reactions. The product then is called reformat (Ref.: H_2 and CO).

Table 2
Fuel properties.

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

Table 3
Gas properties. Data given at 1 atm.

Property	Propane	Hydrogen	Carbon monoxide
Relative density (15.6 °C, 1 atm)	1.5	0.07	0.97
Boiling point (°C)	−42.1	−252.8	−191.5
Latent heat of vaporisation at 15.6 °C (kJ/kg)	358.2	454.3	214.85
Flammability range (%vol. in air)	2.2–9.5	4–75	12.5–63
Autoignition temperature (°C)	470	560	630
Sulphur (%wt)	0–0.02	–	–
LCV (MJ/kg)	46.3	120	10.9
Theoretical air requirement (kg/kg)	15.6	34.2	2.45

The other half of the propane is also fed to the engine with the reformat (LPG + Ref.).

3. Results and discussion

3.1. Effect of reformat and hydrogen

3.1.1. Combustion and engine performance characteristics

The combustion studies with 1% LPG only are shown as the effects of both, reformat and H_2 are more significant than in the rest of the ratios. At low load the LPG addition retarded the start of the combustion (SOC) with respect to the baseline diesel only combustion, and the combustion duration was significantly reduced (Fig. 2). At high load the relatively high in-cylinder temperature conditions facilitated the injected diesel fuel vaporisation and atomisation, creating good ignition centre area for the improvement in combustion and fuel oxidation [13]. In addition, the reformat and H_2 addition reduced the ignition delay, promoted faster combustion of the mixture and increased the in-cylinder pressure.

Combustion duration results were obtained from 10% to 90% mass fraction burnt and is depicted in Fig. 3. The reduction in the amount of the injected liquid fuel when gaseous fuels were inducted (Fig. 4) resulted in shorter liquid fuel injection duration and hence shorter combustion duration (e.g. reduced diffusion combustion phase). Furthermore, it became slightly shorter with the H_2 presence, although there was less liquid fuel replacement compared to LPG (Fig. 4). High flame speed of H_2 contributed to faster combustion leading to more gaseous fuels–air mixture ignited spontaneously [6,10].

At low load, up to 60% liquid fuel replacement in mass basis (Fig. 4) was reached at the maximum fraction of LPG addition with acceptable cycle-to-cycle combustion variability (i.e. COV of IMEP < 5%). The lower liquid fuel replacement obtained in the case of reformat and H_2 additions than in the case of LPG was due to the low H_2 and CO volume energy densities.

The brake thermal efficiency of LPG–diesel dual fuel combustion was improved for the two different engine loads with utilising the LPG-reformed gas (Fig. 5). The low cetane number (CN) and narrow flammability limit of propane (LPG) might cause unstable combustion of the premixed air–fuel mixture that was ignited by the pilot diesel fuel leading to incomplete combustion of LPG, thus decreasing engine thermal efficiency. However, with the presence of the LPG-reformed gas the mixture was easier to ignite, and intensified thermal diffusion extending combustion zone. It also contributed in consuming most of the in-cylinder charge because of increased flame stretch area and laminar flame thickness and hence improving thermal efficiency [9,14]. Shorter combustion duration also resulted in reduced time available for heat transfer to the cylinder wall thus could reduce heat loss which increased the thermal efficiency [6]. These improvements of the combustion reaction intensity mainly in the expansion stroke, allowed more of the chemical energy of the combustible mixture to be converted to useful work. Augmenting the inducted H_2 fraction, in the case of LPG + H_2 , slightly further enhanced the thermal efficiency.

Considering that the quantity of LPG in the intake for 0.5% LPG, 1% LPG + Ref. and 1% LPG + H_2 is the same, it can be stated that the use of LPG-reformed gas resulted in higher liquid fuel replacement and thermal efficiency with the same concentration of LPG (Figs. 4 and 5). Therefore, reformat and H_2 can compensate for the thermal efficiency penalty seen with LPG.

3.1.2. Regulated engine-out gaseous emissions

The total HC and CO emissions with LPG increased compared with the baseline condition for all tested engine conditions (Fig. 6). This could be resulted from non-homogeneity in the

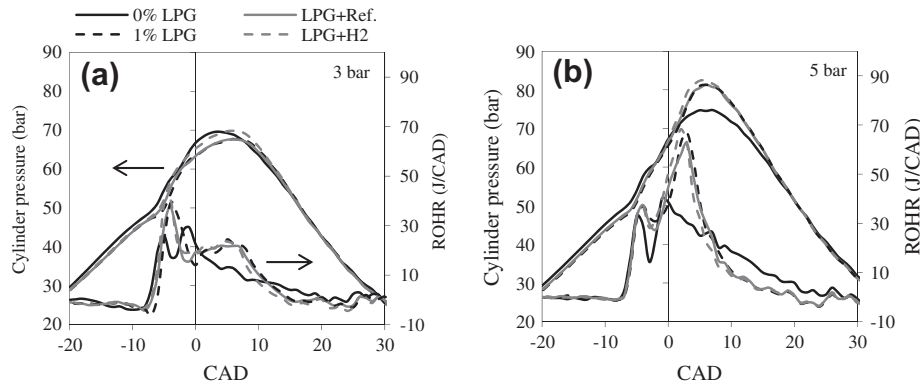


Fig. 2. In-cylinder pressure and rate of heat release.

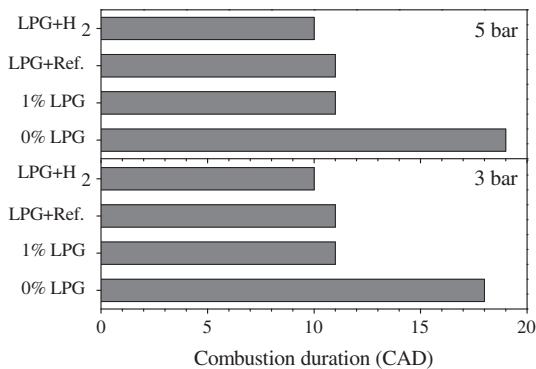


Fig. 3. Combustion duration according to 10–90% mass fraction burnt.

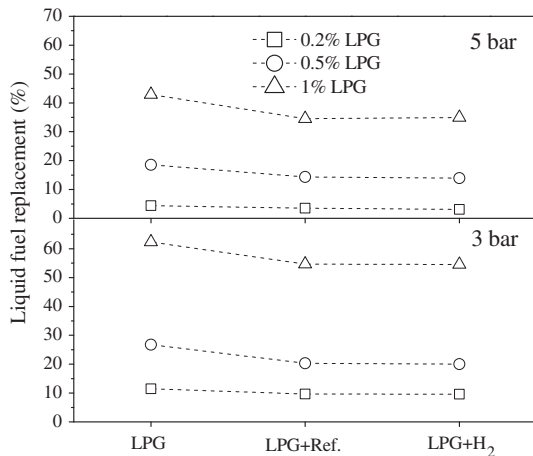


Fig. 4. Liquid fuel replacement.

in-cylinder mixture, the delay in the combustion, low temperature combustion and insufficient oxygen which can lead to unburned propane and other gaseous emissions formation [5,15].

However, the application of reformat and H₂ as additional fuels to LPG–diesel improved these emissions. With the H₂ addition the H/C ratio of the mixture increased and also enhanced the homogeneity of the mixture due to the high mass diffusivity of H₂ leading to reduced HC and CO emissions [10]. The improved combustion characteristics seen with the H₂ presence as a result of it created in-cylinder conditions (i.e. higher temperature) that enhanced the LPG combustion efficiency [9]. However, the increase of CO emissions seen in the case of reformat addition is due to the un-combusted CO part of the added reformat.

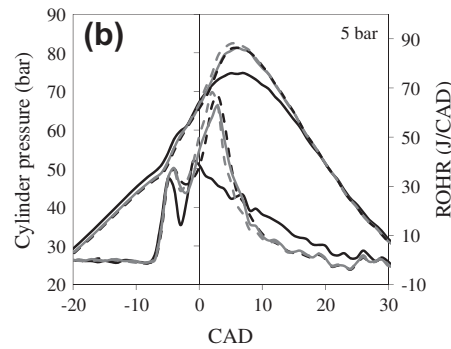


Fig. 5. Engine thermal efficiency.

With the LPG-reformed gas addition the increase in the in-cylinder pressure was evident as a result of both high premixed combustion and H₂ combustion characteristics thus increasing the flame temperature and hence increasing NO_x emissions as can be seen in Fig. 6c [10]. However, CO dilution could reduce the flame temperature in the entire mixture [16] thus NO_x in this case is lower compared with H₂ addition.

3.1.3. Unregulated engine-out hydrocarbon species

The HC species produced during dual fuelling are derived from incomplete combustion or thermal cracking of propane and they will contain three or less carbon atoms in their molecule. Therefore, the studied species here are volatile hydrocarbons with three or less atoms of carbon and those which have extensively been studied in standard diesel operation such as olefin (ethylene, propylene), acetylene and other short-chain paraffin (methane and ethane) (Fig. 7) [17,18].

The concentration of all of these HC species increased with propane addition especially at low load. At high load the rates of propane oxidation were improved and the concentration of the different HC species in the engine exhaust was reduced. This clearly indicates that the emissions are heavily related to the in-cylinder temperature (thermal pyrolysis) [19].

Among these species propylene was studied because of its high tendency to generate ozone (MIR: 11.66). Also, it is one of the first and most abundant compound produced during the combustion of propane [20]. As it is shown in Fig. 7 the propylene increasing rate in LPG–diesel dual fuel combustion is higher than other hydrocarbons species with respect to the baseline condition. However, the concentration of these species was reduced with the addition of the LPG-reformed gas. The presence of H₂ in the combustion

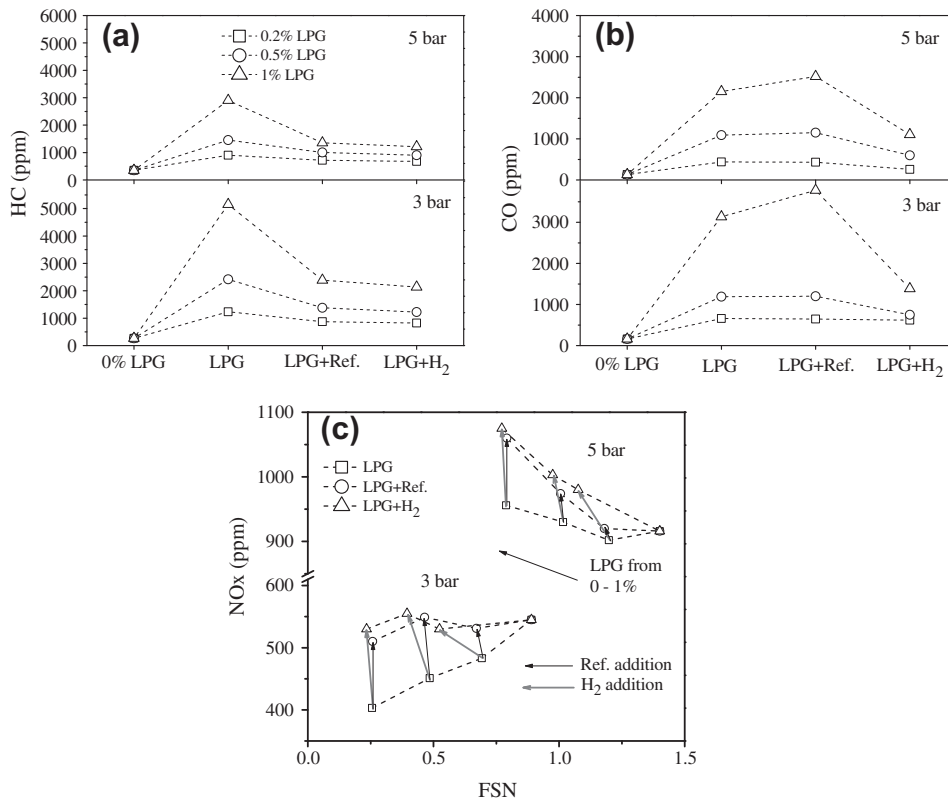


Fig. 6. Regulated engine-out gaseous emissions and FSN.

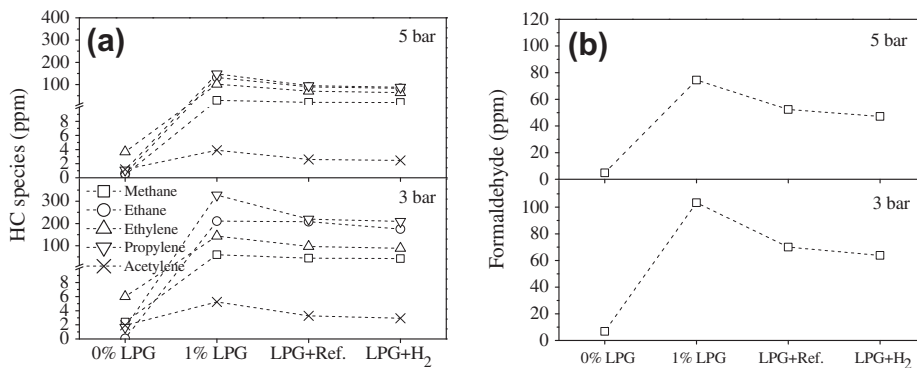


Fig. 7. Hydrocarbons species and formaldehyde emissions for 1% LPG addition.

chamber is associated with the improved oxidation rates of propane due to higher in-cylinder temperatures (e.g. increases cylinder pressure) compared with LPG addition only. However, the reduction of propylene, acetylene, ethylene, ethane, and methane species was not proportional to the reduction seen with the total HC. This could be attributed to the fact that with reformed and H₂ propane was involved in the combustion process leading to the increase of smaller HC species such as propylene.

Formaldehyde (CH₂O) (MIR: 9.46) as a member of carbonyl compound strongly pollutes the atmosphere as it acts as a source of free radical for tropospheric photochemistry. It may also affect the human health through eyes and lung irritation [21]. Formaldehyde concentration measured in the engine exhaust is higher under the LPG–diesel combustion compared to the baseline diesel combustion only (Fig. 7b). The addition of reformed and H₂ assisted the straight-chain aliphatic hydrocarbon oxidation, like propane, and reduced formaldehyde, as an intermediate product

of hydrocarbon fuel combustion, with respect to LPG–diesel combustion only.

3.1.4. Smoke and particulate emission

The addition of LPG clearly reduced smoke emissions (Fig. 6c). When half of the LPG is firstly reformed (reformate composed of H₂ and CO) the smoke level was relatively similar to only LPG (indicated with full black arrow), while soot was clearly reduced by complete H₂ production via the WGSR. This net effect of reformate and H₂ is the result of different factors which have been isolated.

- Dilution effect (overall lambda). The induction of gaseous fuels replaced liquid fuel and oxygen in the intake and modified the mixture oxygen stoichiometric requirements. These effects resulted in a different overall lambda. In all the conditions the overall lambda for reformate and H₂ additions are higher than in the case of LPG leading to lower soot emissions.

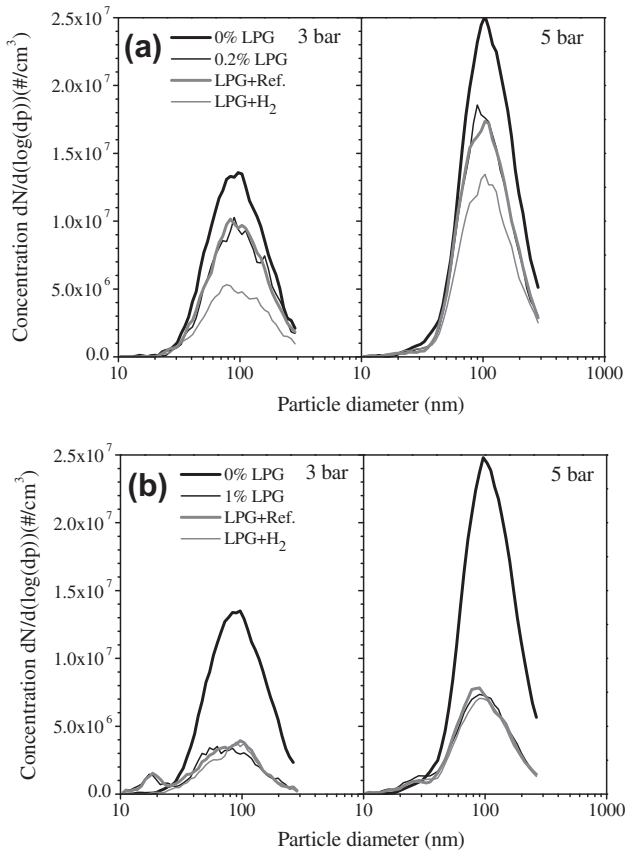


Fig. 8. Particulate size distributions.

- **Local rich regions effect.** It is suggested that the replacement of liquid fuel influences not only the overall lambda but also the local lambda. Gaseous fuels replaced part of the liquid fuel reducing the formation of locally liquid fuel rich regions in the combustion chamber where soot is mainly produced. The liquid fuel replacement with reformat and H₂ was lower than in the case of LPG (Fig. 4). Therefore, higher soot levels are expected in the case of reformat and H₂ and compared to LPG due to this effect.
- **Chemical effects.**

Inhibition of soot formation. According to Frenklach and Wang [22] it is suggested that soot formation increases with the increased H/H₂ ratio. Therefore, H₂ addition will decrease this ratio and as a result will decrease soot formation. In addition, it has been

suggested that after certain H₂ concentrations, further H₂ addition does not result in further soot reductions when the H/H₂ reaches the saturation value [23,24]. In contrast, the effect of CO is opposite to the H₂. CO is oxidised by OH forming atomic hydrogen through the reaction $\text{OH} + \text{CO} = \text{CO}_2 + \text{H}$. This results in an increase of the atomic hydrogen and as a consequence in an enhancement of soot growth.

Enhancement of soot oxidation. H₂ addition promotes the formation of OH, through the reactions $\text{O}_2 + \text{H} = \text{OH} + \text{O}$ and $\text{H}_2 + \text{O} = \text{OH} + \text{H}$ [25]. As the OH radical plays an important role in the soot precursors and soot oxidation processing, this could lead to a reduction in both the particle surface area and the number of soot nuclei [24]. However, when the H₂ concentration is higher than the saturation level, there is not further OH promotion [24]. Opposite with the addition of CO the concentration of oxygen and OH radical are reduced and this could result in a reduction in the soot precursors and soot oxidation rate.

- **Thermal effect.** The OH production heavily depends on in-cylinder temperature [26]. As it was shown in the combustion plots, H₂ increases in-cylinder temperature and as a result, this could lead to a higher OH concentration resulting in an enhancement in soot oxidation.

Therefore, it can be concluded that the soot benefit of the H₂ contained in the reformat was slowed down by the presence of CO. Coherently, when CO was substituted by H₂ a clear reduction in smoke was obtained as an overall result of the different factors previously discussed. Considering different H₂ additions, the soot benefits obtained with H₂ are lower in 1% LPG addition with respect to 0.2% and 0.5% approaching to the hydrogen saturation value limit.

Particulate size distribution results are focused on 0.2% and 1% LPG addition as 0.5% LPG gave an intermediate tendency in both engine loads (Fig. 8). The addition of LPG-reformed gas made the concentration for every diameter decreased gradually with the increase in the gaseous fuels concentration. Further H₂ addition reduces more the particle number concentration for each diameter. This trend is coincident to the obtained in smoke emissions and the reasons previously commented in the soot section can be applied here. As consequence, most of the carbon of the parent fuel (i.e. ULSD and LPG) is converted to gaseous products (i.e. HC, CO, CO₂) and there is no further conversion to soot.

A small nucleation mode was obtained in the case 1% LPG at both low and high engine load as depicted in Fig. 8b. These nucleation particles consist of droplets of hydrocarbons which underwent nucleation rather than adsorption or condensation onto soot particle surface. The nucleation of gaseous hydrocarbons depends on gaseous hydrocarbon concentration and volatility, soot

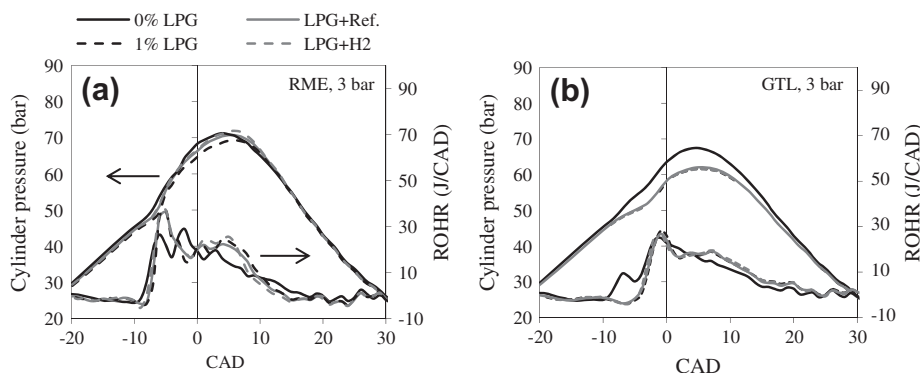


Fig. 9. In-cylinder pressure and rate of heat release for different liquid fuels.

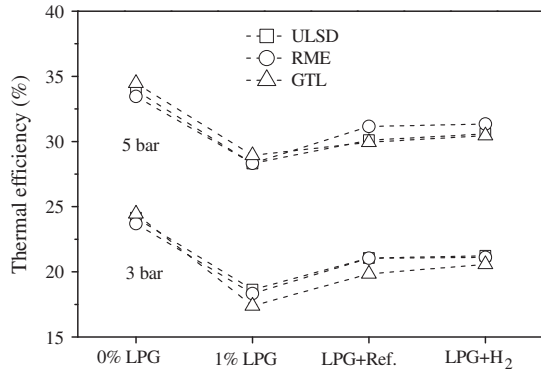


Fig. 10. Engine thermal efficiency for different liquid fuels.

concentration and exhaust temperature [27]. Nucleation appears when the engine output hydrocarbon emissions are higher while soot concentration is limited (low load and high LPG addition) (Fig. 6a and c). As a result, some of the gaseous HC cannot be adsorbed or condensed onto the soot particles (reduced soot surface availability) and hence they self nucleate forming new particles of small size.

3.2. Effects of liquid fuels

3.2.1. Combustion and engine performance

In LPG-RME dual fuelling the SOC was slightly advanced when H₂ was introduced but was not affected in the case of LPG-GTL fuelling (Fig. 9). The variations on the SOC are influenced by some parameters such as the quantity and quality of pilot fuel and pre-ignition reaction activity. In the case of RME fuelling, apart from oxygen availability the SOC was also affected by the higher amount

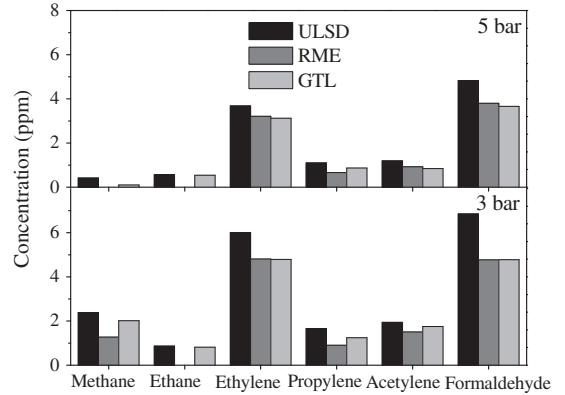


Fig. 12. HC species and formaldehyde at baseline condition for different liquid fuels.

of pilot fuel available in the combustion chamber. It was mainly due to the relatively lower calorific value of RME thus more in-cylinder injected fuel mass was needed per cycle to reach the required engine load. Higher pilot fuel quantity could lead to larger pilot fuel flame area and reaction zones which provided better hydrogen-containing charge mixture combustion and increased burned fraction. Therefore, they could contribute to the earlier SOC. For GTL fuelling case, the GTL's retarded injection and delayed SOC under dual fuelling (i.e. LPG-GTL) mode lowered the in-cylinder temperature. Although GTL has relatively high CN, its lower density and bulk modulus significantly influenced the start of injection and the SOC in dual fuelling. These combustion characteristics and low in-cylinder temperature condition affected the pre-ignition reaction activity of the hydrogen-contained mixture which affected the engine-out emissions (explained later).

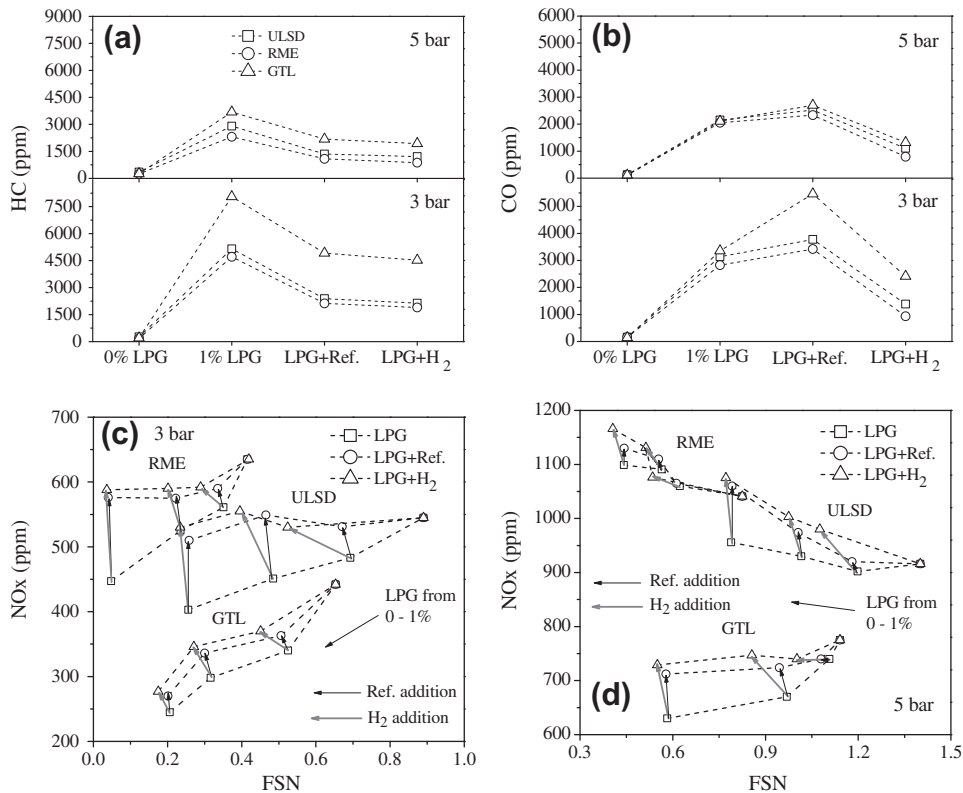


Fig. 11. Regulated gaseous engine-out emissions and FSN for different liquid fuels.

The thermal efficiency of RME and GTL was fairly comparable to that of the conventional diesel fuel in baseline condition (Fig. 10). However, in dual fuel operation GTL and 1% LPG and with reformat and H₂ addition exhibited the greatest decline compared to other fuels. Although the thermal efficiency increased in the case of reformat and H₂ addition (compared with LPG addition only) but the LPG–GTL dual fuelling combustion characteristics (i.e. low in-cylinder temperature) were likely to be the significant factor for the thermal efficiency deterioration. The low in-cylinder pressure because of retarded combustion initiation was an influential effect which could lead to low adiabatic flame temperature, low effective combustion and heat loss to the cylinder wall. On the other hand, a positive effect in thermal efficiency through the combination of RME fuelling with hydrogen at high load was observed. The improved ignition ability seen in the dual fuelling with RME as a result from the high in-cylinder temperature and lower stoichiometric air requirement (high oxygen content in RME), supported by faster H₂ combustion improved combustion efficiency.

3.2.2. Regulated engine-out gaseous emission

RME exhibited the lowest total HC and CO emission over all the engine operating conditions (Fig. 11). With the use of oxygenated fuels like RME, the availability of oxygen in the fuel spray improved the mixture oxidation. This can compensate the reduced oxygen concentration in dual fuelling system and improve H₂ combustion. In addition, the higher density of RME also contributed in better in-cylinder charge mixing through better fuel penetration associated in a non-common rail fuel system and hence released greater energy in the premixed combustion stage, leading to reduced HC and CO emissions [12,28]. It has also been suggested that a fuel with high density has larger cone-shape spray [29]. Therefore, with these better fuel spray characteristics of RME and diffusivity of H₂ could improve mixture homogeneity, flame propagation and lead to increased oxidation rates. The low in-cylinder pressure as a result of the late SOC seen with LPG–GTL fuelling directly impacted the HC and CO emission (Fig. 9b). It has been shown that GTL has advantages in reducing the regulated emissions as a result of its physical and chemical characteristics. Its high H/C ratio and

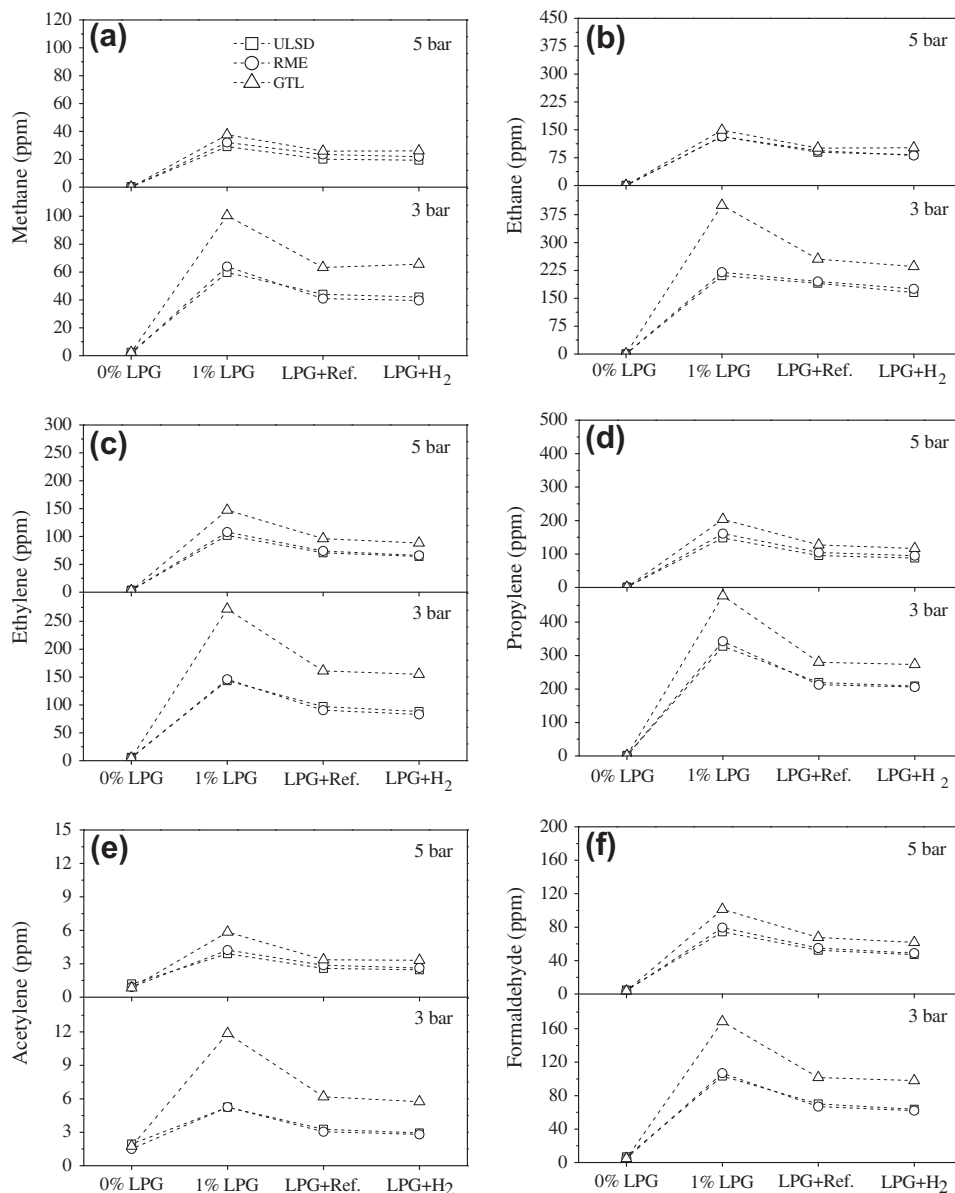


Fig. 13. Hydrocarbon species and formaldehyde emissions for 1% LPG addition.

more volatile combined with H₂ addition were likely to enhance the mixture homogeneity which can result in the reduction in carbon-contained emissions. In addition, it was thought that the emissions reduction also supported by its high ignitability due to GTL's high CN. However, low in-cylinder temperature as seen in the LPG–GTL dual fuel combustion characteristics significantly inhibited the HC and CO oxidation rates. Under low in-cylinder temperature the charge mixture cannot be completely burned. Therefore, there was a possibility that part of H₂ was not involved in the combustion as a result of its high autoignition temperature.

NO_x emissions were higher with RME and lower with GTL fuelling. It has been suggested that in mechanical injection system, the high bulk modulus and speed of sound of biodiesel advanced the start of injection (SOI) leading to advanced combustion pronounced premixed combustion phase [30]. As a result, an increase in the in-cylinder pressure and temperature elevated the thermal NO_x formation. Additionally, another theory concludes that the low soot produced (explained later) with RME resulted in low soot radiative heat transfer from flames hence increasing NO_x [30].

Meanwhile, the low bulk modulus of compressibility and high CN of GTL reduced the peak of the premixed combustion rate thus hampered the NO_x formation rate [31]. In addition, the relatively lower C/H ratio of GTL than those of other fuels tended to reduce the adiabatic flame temperature and hence the propensity to produce NO_x [32]. Under dual fuel mode the trend of the NO_x emissions was kept similar obtaining the lowest NO_x emissions for GTL. In all cases, NO_x decreased with LPG addition but slightly increased with the reformat and H₂ addition as it was explained in the previous section. However, GTL shows better trend where the increasing rate is lower compared to other fuels and the emission levels are below to those in baseline condition even at high load.

3.2.3. Unregulated engine-out hydrocarbon species

Hydrocarbon species emissions were lower in the case of RME and GTL combustion compared to that of ULSD at baseline condition. The reduction of the total HC and some of the species examined here including formaldehyde (Fig. 12) was mainly due to oxygen content for the RME and the high CN and H/C ratio for GTL [18].

However in dual fuel operation, HC species emissions level with RME was relatively similar to that of ULSD (Fig. 13). It has been shown that the oxygen content in RME and high in-cylinder temperature which seen in the combustion characteristics were associated to the reduction in HC species in RME dual fuelling. However, its slightly high equivalence ratio (results of liquid fuel replacement are not shown) was likely to increase the emission as has been shown by Zhu et al. [33]. Therefore, these parameters contributed to the relatively similar results in RME and ULSD. In dual fuel mode GTL showed the highest HC species emissions. This mainly was attributed to low in-cylinder temperature results in a reduction in the fuel oxidation capability.

It is observed at baseline condition that formaldehyde level is lower in the case of RME and GTL compared with ULSD. It is thought that the carboxyl group from biodiesel has been removed under high temperature, decarboxylation, reducing the propensity to form oxygenated compounds [34]. The decrease of formaldehyde also can be linked to the increased H/C ratio hence we would expect a decrease of the emission with GTL fuelling [35]. As in the case of the rest HC species the formaldehyde emissions tend to increase in dual fuel operation. It indicates that formaldehyde emissions not always associated to initial pilot fuel composition but from multiple sources (like unburned propane) and species in the combustion chamber [35]. However, the LPG-reformed gas addition reduced the studied hydrocarbon species. The hydrogen combustion facilitated the thermal cracking process of propane as a saturated hydrocarbon by removing the hydrogen and carbon

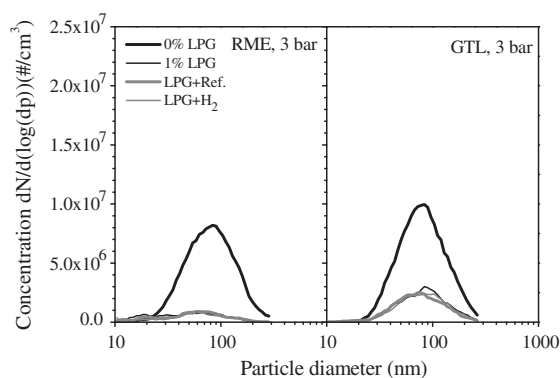


Fig. 14. Particulate size distributions for RME and GTL.

atoms from molecular structure became short-chain hydrocarbon molecules.

3.2.4. Smoke and particulate emissions

The amount of smoke was lower in the case of the oxygenated (i.e. RME) and non-aromatic fuel (GTL) compared to the conventional fuel (ULSD) without LPG addition (Fig. 11c and d).

On the dual fuel operation where the air supply was limited, the RME ability to reduce soot was maintained or even more effective than in the case of only liquid fuel combustion. As a fuel-borne oxygen, the oxygen in RME has better accessibility to the flame [34] improving mixture oxidation even in the locally fuel-rich regions resulting in a reduction in the smoke concentration. Apart from the oxygen content in RME, it is also suggested that the higher in-cylinder temperature in RME combustion could enhance OH formation than in the case of ULSD and GTL assisting further the soot oxidation process. Additionally, the higher oxygen availability in the combustion chamber with RME could react with hydrogen either from fuel or the syngas to produce more OH promoting soot precursors and soot oxidation. In addition, advanced SOI due to high bulk modulus of compressibility of RME led to better air–fuel mixture before SOC and advanced combustion hence provided longer residence time at high temperature for soot oxidation taking place. As GTL is a non-aromatic fuel the propensity to produce soot precursors through pyrolysis might be inhibited. It occurred through the oxidation by the OH radical in the presence of high temperature due to the reformat and H₂ combustion and limited soot precursors produced (specifically PAH) due to virtually no aromatic in GTL. Another reason for this soot reduction with RME and GTL is the C/H ratio which influences soot and particulate matter formation [36]. A large number of carbon atoms in the fuel (thus increasing C/H ratio) tend to form more particulates. Therefore, ULSD which has higher C/H ratio than that of RME and GTL produced more particulate matter whereas GTL which has low C/H ratio decreases the tendency to produce soot and particulate matter. Additionally, retarded SOC in the GTL dual fuelling might increase soot but it can be balanced by the no aromatic content in GTL.

It is clearly shown that the particulate number concentration (Fig. 14) was reduced in every diameter size with the application of dual fuel mode, and the level concentration trend was kept similar to the baseline condition, and followed the general trend ULSD > GTL > RME. Apart from the reduced fuelling levels and the reasons explained in the smoke section another argument for low PM can be the lower sulphate in RME and GTL compared with ULSD (Table 2) which results in low contribution to the sulphate fraction.

4. Conclusions

Reformat and H₂ combustion has shown to have the capability to increase the thermal efficiency and reduce gaseous (both

regulated and unregulated) and particulate emission with respect to LPG–diesel dual fuel combustion. These benefits are heavily attributed to the physical and chemical H₂ characteristics contained in the LPG-reformed gas.

The formation and oxidation of soot through LPG-reformed gas was associated to thermal, dilution and chemistry effects. Smoke and PM emissions under H₂ addition was lower than those of reformat addition. It was also obtained that smoke and PM was improved especially in the case of 0.2% and 0.5%, while there were not significant further reductions in 1% LPG addition. Therefore, the amount of the inducted H₂ can be optimised in order to get the best compromise between NO_x and soot.

RME as a pilot fuel in LPG-reformed diesel dual fuelling mode produced a synergistic effect with H₂ addition through better improvement in thermal efficiency and regulated emissions excluding NO_x than the rest of liquid fuels. These were achieved by high bulk modulus and oxygen content. However, in the case of GTL dual fuelling deterioration in both regulated (HC and CO) and unregulated emissions and also thermal efficiency were obtained as a result of its properties which affected the combustion characteristics and hence engine performance and emissions. The use of GTL in LPG-reformed dual fuel however, improved the soot–NO_x trade-off. It also showed a great potential where the increase of NO_x under reformat and H₂ addition could be minimised with the use of GTL.

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References

- [1] Sahoo BB, Sahoo N, Saha UK. Effect of engine parameters and type of gaseous fuel on the performance of dual-fuel gas diesel engines—a critical review. *Renew Sustain Energy Rev* 2009;13(6–7):1151–84.
- [2] Tsolakis A, Megaritis A, Yap D, Abu-Jrai A. Combustion characteristics and exhaust gas emissions of a diesel engine supplied with reformed EGR. *SAE Paper*. 2005; 2005-01-2087.
- [3] Korakianitis T, Namasivayam AM, Crookes RJ. Hydrogen dual-fuelling of compression ignition engines with emulsified biodiesel as pilot fuel. *Int J Hydrogen Energy* 2010;35(24):13329–44.
- [4] Saleh HE. Effect of variation in LPG composition on emissions and performance in a dual fuel diesel engine. *Fuel* 2008;87(13–14):3031–9.
- [5] Jian D, Xiaohong G, Gesheng L, Xintang Z. Study on diesel–LPG dual fuel engines. *SAE Paper* 2001 [2001-01-3679].
- [6] Lata DB, Misra A. Theoretical and experimental investigations on the performance of dual fuel diesel engine with hydrogen and LPG as secondary fuels. *Int J Hydrogen Energy* 2010;35(21):11918–31.
- [7] Karim GA, Liu Z. A predictive model for knock in dual fuel engines. *SAE Paper* 1992 [921550].
- [8] Tsolakis A, Hernandez JJ, Megaritis A, Crampton M. Dual fuel diesel engine operation using H₂. effect on particulate emissions. *Energy Fuels* 2005;19(2):418–25.
- [9] Szwaja S, Grab-Rogalinski K. Hydrogen combustion in a compression ignition diesel engine. *Int J Hydrogen Energy* 2009;34(10):4413–21.
- [10] Verhelst S, Wallner T. Hydrogen-fueled internal combustion engines. *Progr Energy Combust Sci* 2009;35(6):490–527.
- [11] Tsolakis A, Torbati R, Megaritis A, Abu-Jrai A. Low-load dual-fuel Compression Ignition (CI) engine operation with an on-board reformer and a diesel oxidation catalyst: effects on engine performance and emissions. *Energy Fuels* 2009;24(1):302–8.
- [12] Rounce P, Tsolakis A, Leung P, York APE. A comparison of diesel and biodiesel emissions using dimethyl carbonate as an oxygenated additive. *Energy Fuels* 2010;24(9):4812–9.
- [13] Karim GA. Combustion in gas fueled compression: ignition engines of the dual fuel type. *J Eng Gas Turbines Power* 2003;125(3):827–36.
- [14] Tang C, He J, Huang Z, Jin C, Wang J, Wang X, et al. Measurements of laminar burning velocities and Markstein lengths of propane–hydrogen–air mixtures at elevated pressures and temperatures. *Int J Hydrogen Energy* 2008;33(23):7274–85.
- [15] Goto S, Lee D, Shakal J, Harayama N, Honjyo F, Ueno H. Performance and emissions of an LPG lean-burn engine for heavy duty vehicles. *SAE Paper* 1999 [1999-01-1513].
- [16] Karim GA, Wierzbka I, Boon S. Some considerations of the lean flammability limits of mixtures involving hydrogen. *Int J Hydrogen Energy* 1985;10(2):117–23.
- [17] Payri F, Bermúdez VR, Tormos B, Linares WG. Hydrocarbon emissions speciation in diesel and biodiesel exhausts. *Atmos Environ* 2009;43(6):1273–9.
- [18] Efthimios Z. Regulated and non-regulated pollutants emitted from two aliphatic and a commercial diesel fuel. *Fuel* 2008;87(7):1141–7.
- [19] Flynn PF, Durrett RP, Hunter GL, zur Loye AO, Akinoyemi OC, Dec JE, et al. Diesel combustion: an integrated view combining laser diagnostics, chemical kinetics, and empirical validation. *SAE Paper* 1999 [1999-01-0509].
- [20] Lindgren M, Arrhenius K, Larsson G, Bäfver L, Arvidsson H, Wetterberg C, et al. Analysis of unregulated emissions from an off-road diesel engine during realistic work operations. *Atmos Environ* 2011;45(30):5394–8.
- [21] Carlier P, Hannachi H, Mouvier G. The chemistry of carbonyl compounds in the atmosphere – a review. *Atmos. Environ.* (1967). 1986; 20(11): p. 2079–99.
- [22] Frenklach M, Wang H. Detailed modeling of soot particle nucleation and growth. *Symp (Int.) Combust* 1991;23(1):1559–66.
- [23] Schefer RW. Combustion of hydrogen-enriched methane in a lean premixed swirl burner. In: *Proceedings of the 2001 DOE Hydrogen Program, Review NREL/CP-570-30535*; 2001.
- [24] Pandey P, Pundir BP, Panigrahi PK. Hydrogen addition to acetylene–air laminar diffusion flames: studies on soot formation under different flow arrangements. *Combust Flame* 2007;148(4):249–62.
- [25] Saxena P, Williams FA. Testing a small detailed chemical-kinetic mechanism for the combustion of hydrogen and carbon monoxide. *Combust Flame* 2006;145(1–2):316–23.
- [26] Dec JE, Coy EB. OH radical imaging in a DI diesel engine and the structure of the early diffusion flame. *SAE Paper* 1996 [960831].
- [27] Kittelson D, Arnold M, Watts W. Review of diesel particulate matter sampling methods, final report. Univ Minnesota Center Diesel Res 1999.
- [28] Sun J, Caton JA, Jacobs TJ. Oxides of nitrogen emissions from biodiesel-fuelled diesel engines. *Progr Energy Combust Sci* 2010;36(6):677–95.
- [29] Yamane K, Ueta A, Shimamoto Y. Influence of physical and chemical properties of biodiesel fuels on injection, combustion and exhaust emission characteristics in a direct injection compression ignition engine. *Int J Eng Res* 2001;2(4):249–61.
- [30] Schönborn A, Ladommatos N, Williams J, Allan R, Rogerson J. The influence of molecular structure of fatty acid monoalkyl esters on diesel combustion. *Combust Flame* 2009;156(7):1396–412.
- [31] Song J, Cheenkachorn K, Wang J, Perez J, Boehman AL, Young PJ, et al. Effect of oxygenated fuel on combustion and emissions in a light-duty turbo diesel engine. *Energy Fuels* 2002;16(2):294–301.
- [32] Miyamoto N, Ogawa H, Nurun NM, Obata K, Arima T. Smokeless, low NO_x, high thermal efficiency, and low noise diesel combustion with oxygenated agents as main fuel. *SAE Paper* 1998 [980506].
- [33] Zhu R, Cheung CS, Huang Z, Wang X. Regulated and unregulated emissions from a diesel engine fueled with diesel fuel blended with diethyl adipate. *Atmos Environ* 2011;45(13):2174–81.
- [34] Lapuerta M, Armas O, Rodríguez-Fernández J. Effect of biodiesel fuels on diesel engine emissions. *Progr Energy Combust Sci* 2008;34(2):198–223.
- [35] Zervas E, Montagne X, Lahaye J. Emission of alcohols and carbonyl compounds from a spark ignition engine. Influence of fuel and air/fuel equivalence ratio. *Environ Sci Technol* 2002;36(11):2414–21.
- [36] Tree DR, Svensson KI. Soot processes in compression ignition engines. *Progr Energy Combust Sci* 2007;33(3):272–309.