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Effect of Gas-to-Liquid Diesel Fuels on Combustion Characteristics, Engine Emissions, and Exhaust Gas Fuel Reforming. Comparative Study

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New diesel-type fuels such as biodiesels and gas-to-liquid (GTL) fuel have been developed in order to aid vehicle manufacturers in achieving forthcoming emission regulations, by improving engine out emissions and exhaust gas after-treatment performance. Furthermore, synthetic fuels are virtually free of sulfur and aromatic hydrocarbons and can improve the performance and durability of the catalytic fuel reformers that are designed to provide H₂ to fuel cells, internal combustion (IC) engines, and after-treatments. Combustion and exhaust-gas reforming experiments with GTL and ultralow sulfur diesel (ULSD) were run under several engine and reformer operating regimes. Using a single cylinder bench engine, the combustion of GTL fuel (and blends with conventional diesel fuel) was found to reduce NO_x emissions substantially and improve engine thermal efficiency but led to an increase in smoke for the default injection timing in the experiment. However, by optimizing the injection timing in a GTL-fueled engine, the harmful emissions of NO_x and smoke were both reduced simultaneously while still giving improvements in engine thermal efficiency. In general, it was found that the NO_x/particulates tradeoff curve shifted to lower emissions for GTL fuel and GTL fuel blends. During exhaust-gas reforming, the use of GTL fuel was found to increase fuel conversion, while producing more hydrogen and less methane.

Introduction

The growing demand for diesel vehicles and the emergence of premixed compression ignition engines (e.g., homogeneous charge compression ignition—HCCI) reflect society's response to the environmental changes caused by combustion-powered transportation. Clearly, the general trend is toward higher efficiency engines and improved fuel economy, something that puts current technology spark ignition (SI) engines in a relatively weak position compared to compression ignition (CI) engines. With the focus on emission of greenhouse gases, and given the contribution of transportation sources to this problem, a greater penetration of CI engines can help to reduce vehicle CO₂ emissions. With ongoing improvements aimed at enhancing performance and reducing noise and emissions, the diesel engine has become an increasingly attractive option for passenger car applications.^{1–4}

Although, the diesel engine is an attractive solution for CO₂ reduction, there remains a challenge to control simultaneously NO_x and particulate matter (PM) emissions to a level required by prevailing regulations. Among other solutions to reduce both NO_x and PM—such as reformed EGR,^{3–5} SCR catalysts,^{6–9} and particulate filters (DPF)^{10,11}—alternative fuels like biofuels and 'designer' fuels such as GTL fuel can also help.^{11–15}

Synthetic ultra-clean diesel fuels can be manufactured from the Fischer–Tropsch process. The starting material can either be natural gas (gas to liquids) or biomass (biomass to liquids).¹⁵ They are extremely clean fuels, virtually free of sulfur and aromatic hydrocarbons, can facilitate further reduction of engine

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(1) Wallington, T.; Kaiserb, E.; Farrelle, J. *Chem. Soc. Rev.* **2006**, *35*, 335–347.

(2) Farrauto, R.; Heck R. *Catal. Today* **2000**, *55*, 179–187.

(3) Tsolakis, A.; Megaritis, A.; Yap, D.; Abu-Jrai, A. *SAE Pap.* **2005**, No. 2005-01-2087.

(4) Tsolakis, A.; Megaritis, A. *Int. J. Hydrogen Energy* **2005**, *30*, 731–745.

(5) Tsolakis, A.; Golunski, S. *Chem. Eng. J.* **2006**, *117*, 131–136.

(6) Houel, V.; Millington, P.; Pollington, S.; Poulston, S.; Rajaram, R.; Tsolakis, A. *Catal. Today* **2006**, *114*, 334–339.

(7) Houel, V.; David, J.; Millington, P.; Pollington, S.; Poulston, S.; Rajaram, R.; Torbati, R. *J. Catal.* **2005**, *230*, 150–157.

(8) Burch, R.; Ottery, D. *App. Catal.* **1996**, *9*, L19–L24.

(9) Burch, R.; Millington, P. *Catal. Today* **1995**, *26*, 185–260.

(10) Allansson, R.; Blakeman, P. G.; Cooper, B. J.; Hess, H.; Silcock, P. J.; Walker, A. P. *SAE Pap.* **2002**, No. 2002-01-0428.

(11) Boehman, A. L.; Song, J.; Alam, M. *Energy Fuels* **2005**, *19*, 1857–1864.

(12) Szybist, J. P.; Kirby, S. R.; Boehman, A. L. *Energy Fuels* **2005**, *19*, 1484–1492.

(13) Schaberg, P.; Botha, J.; Schnell, M.; Herrmann, H. O.; Pelz, N.; Maly, R. *SAE Pap.* **2005**, No. 2005-01-2187.

(14) Maly, R.; Schnell, M.; Botha, J.; Schaberg, M. In *Effects of GTL diesel fuels on emissions and engine performance*. Proceedings of the 2004 DEER Conference, Coronado, CA, Aug 29–Sep 2, 2004.

(15) Vosloo, A. *Fuel Process. Tech.* **2001**, *71*, 149–155.

out emissions, and improve the performance of the catalytic after-treatments and fuel reformers.

Hydrogen has been long believed to be one of the most promising alternative fuels for internal combustion engines from the point of emission control and engine performance. The use of pure hydrogen or as an addition to the main hydrocarbon fuel has been reported to be beneficial in terms of emissions (NO_x , HC, CO, particulate matter) and engine performance.^{3,4,16–21} A solution to problems related to H_2 storage and distribution can be the on-board H_2 production from diesel-type fuels, using fuel reforming techniques such as autothermal reforming and partial oxidation. Among the most promising technologies is a combination of reforming and exhaust-gas recirculation (referred to as REGR), which allows the fuel/air feed to the engine to be enriched with reformat.^{5,16,22–25}

The aim of this work was to perform a comparative study of conventional ULSD and GTL diesel fuels in terms of combustion characteristics, exhaust gas emissions (mainly NO_x and smoke), and reformer performance (e.g., H_2 production and process efficiency). As the diesel engine used in this study was equipped with a pump-line-nozzle-type fuel injection system, all the observed effects may not apply to common rail or unit injection equipped engines.

2. Experimental

2.1. Combustion. The experiments were carried out in a Lister Petter TR1 engine. The full engine test rig has been described in detail in previous publications.¹⁶ The engine is an air-cooled, single-cylinder, direct injection diesel engine. The main engine specifications are as follows: bore 98.4 mm, stroke 101.6 mm, conrod length 165.0 mm, displacement volume 773 cm^3 , compression ratio 15.5, maximum power 8.6 kW at 2500 rpm and maximum torque 39.2 Nm at 1800 rpm. The standard injection timing is 22° CA (degrees crank angle) before top dead centre (BTDC) as set by the manufacturer. Advancing the injection timing was achieved by placing standard shims provided by the engine's manufacturer under the fuel pump. The exhaust gas was recycled from the engine exhaust to the inlet (external EGR) and the volumetric flow rate of the EGR was calculated according to the reduction in the air volumetric flow rate.

The fuels used were ultralow sulfur diesel (ULSD) and GTL fuel provided by Shell Global Solutions, UK. The fuel properties are given in Table 1.

The combustion of ULSD, GTL, a ULSD–GTL blend (50/50 by volume; shown as GD50), and GTL advancing the injection by 4° CA was examined at twelve engine operating conditions (speed-indicated mean effective pressure (IMEP)); the speeds used were 1200, 1500, and 1800 rpm with 2, 3, 4, and 5 bar IMEP at each speed. The results obtained from four different engine conditions shown in Table 2 with two different EGR percentages (10 and 20 vol %) are presented and discussed.

The inlet charge was kept as much as possible at the same temperature (in the range of 25–30 °C) when using EGR, so that

Table 1. Fuel Properties

fuel analysis	method	ultralow sulfur diesel (ULSD) US07	
		FT-GTL	
cetane number	ASTM D613	53.9	79
density at 15 °C (kg m^{-3})	ASTM D4052	827.1	784.6
viscosity at 40 °C (cSt)	ASTM D445	2.467	3.497
50% distillation (°C)	ASTM D86	264	295.2
90% distillation (°C)	ASTM D86	329	342.1
LCV (MJ kg^{-1})	ASTM D2622	42.7	43.9
sulfur (mg kg^{-1})		46	0.05
aromatics (wt %)		24.4	0.3
C (wt %)		86.5	85
H (wt %)		13.5	15
O (wt %)			
H/C ratio (molar)		1.88	2.10

Table 2. Engine Conditions and Fuels Tested.

engine condition	speed (rpm)	IMEP (bar)	fuel	injection timing
1	1500	2.0	ULSD	standard
			GD50	standard
			GTL	standard
			GTL	advanced
2	1500	3.0	ULSD	standard
			GD50	standard
			GTL	standard
			GTL	advanced
3	1500	4.0	ULSD	standard
			GD50	standard
			GTL	standard
			GTL	advanced
4	1500	5.0	ULSD	standard
			GD50	standard
			GTL	standard
			GTL	advanced

the effects of the inlet charge temperature on the ignition delay and combustion process could be eliminated.

2.2. Exhaust-Gas Reforming. The proposed engine-reformer system with the minireformer installed at the EGR is shown in Figure 1.

A reforming catalyst with a nominal composition of 1%Rh/CeO₂–ZrO₂ (by weight) was prepared by impregnating 50 g of 50:50 (mole basis) ceria–zirconia powder with 30 cm^3 of an aqueous solution of rhodium nitrate (containing 0.5 g rhodium). The impregnated powder formed a slurry, which was dried at 120 °C for 8 h, before being calcined in static air at 500 °C for 2 h. The catalyst was made into an aqueous suspension, which was uniformly coated onto ceramic monolith substrates with a high cell density (900 cpsi). The monolith aspect ratio (A/R = length over diameter) of 2.3 was selected on the basis of earlier results, which showed that a low ratio reduces the contribution from the water–gas shift reaction and hence improves efficiency.⁵

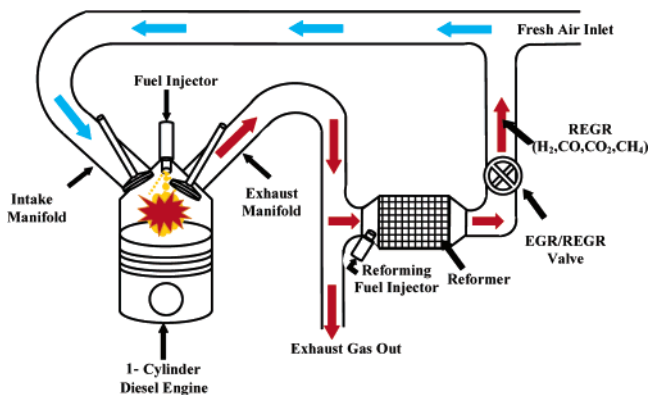


Figure 1. Major components of REGR system.

(16) Tsolakis, A.; Megaritis, A.; Wyszynski, M. L. *Energy Fuels* **2003**, 17, 1464–1473.

(17) Jamal, Y.; Wyszynski, M. *Int. J. Hydrogen Energy* **1994**, 19, 557–572.

(18) Kumar, M. S.; Ramesh, A.; Nagalingam, B. *Int. J. Hydrogen Energy* **2003**, 28, 1143–1154.

(19) Apostolescu, N.; Chiric, R. *SAE Pap.* **1996**, No. 960603.

(20) Andreatta, D.; Dibble, R. W. *SAE Paper* **1996**, No. 960852.

(21) White, C. M.; Steeper, R. R.; Lutz, A. E. *Int. J. Hydrogen Energy* **2006**, 31, 1292.

(22) Ahmed, S.; Krumpelt, M. *Int. J. Hydrogen Energy* **2001**, 26, 291.

(23) Trimm, D. L.; Onsan, Z. I. *Catal. Rev. Sci. Eng.* **2001**, 43, 31.

(24) Tsolakis, A.; Megaritis, A. *Int. J. Hydrogen Energy* **2004**, 29, 1409–1419.

(25) Tsolakis, A.; Megaritis, A.; Golunski, S. E. *Energy Fuels* **2005**, 19, 744–752.

Table 3. Fuel Flow Rates and Input Power for the Different O/C Ratios

O/C	ULSD (mL h ⁻¹)	ULSD power input (kW)	GTL (mL h ⁻¹)	GTL power input (kW)
1.4	26.1	0.255	28.0	0.268
1.6	23.4	0.229	24.9	0.238
1.8	20.8	0.204	21.9	0.210
1.9	19.1	0.187	20.4	0.195
2.1	16.8	0.164	17.9	0.171

The reformer was placed in a tubular furnace, the temperature of which was set by a thermocouple in the reformer inlet. Temperature profiles were obtained by slowly withdrawing a fine thermocouple, along the length of a central monolith channel. The effect of fuel at different O/C ratios on the reaction profiles was examined using one engine exhaust gas composition (Vol: 15.33% O₂, 3.42% H₂O, 3.23% CO₂, 0.02% CO in N₂). We did this by injecting fuel into exhaust gas at 290 °C, which mimicked the output from a diesel engine operating at partial load. The fuel flow-rates (mL h⁻¹) for the different O/C ratios are shown in Table 3. The fuel injector was positioned 10 cm upstream of the catalyst, allowing the fuel to vaporize and mix with the synthetic exhaust gas before reaching the front face of the monolith.

The theoretical reactor product gas concentrations for each operating condition were calculated using the STANJAN equilibrium model (v 3.89, Stanford University). The calculations were performed at constant pressure and temperature. The temperature used was equal to the maximum reaction temperature measured along the monolith for each test during steady-state reforming.

The process efficiency η was defined as the chemical power (kW) of the product stream divided by the chemical power of the diesel fuel in the feed:

$$\eta(\%) = \frac{\text{LCV}_{\text{fuelprod}} \dot{m}_{\text{fuelprod}}}{\text{LCV}_{\text{fuelin}} \dot{m}_{\text{fuelin}}} \times 100 \quad (1)$$

where $\text{LCV}_{\text{fuelprod}}$ and $\text{LCV}_{\text{fuelin}}$ are the lower calorific values of the combustible products (i.e., H₂, CO, CH₄) and the diesel fuel, respectively, and $\dot{m}_{\text{fuelprod}}$ and \dot{m}_{fuelin} are the corresponding mass-flow rates. The predicted efficiency was calculated from the equilibrium product composition expected at the maximum temperature reached in the catalyst bed for each set of inlet conditions.

Gas analysis included measurement of carbon dioxide, carbon monoxide (ndir—nondispersive infrared), hydrocarbons (fid—flame ionization detector), oxygen (electrochemical method), and NO_x (chemiluminescence) emissions. The hydrogen concentrations were measured by gas chromatography. The apparatus was calibrated using certified gases (10% H₂ in N₂ and 30% H₂ in N₂). Smoke was measured using a Bosch smoke meter, giving smoke emissions in terms of Bosch smoke numbers (BSN).

3. Results and Discussion

3.1. Combustion. Although the use of GD50 and pure GTL did not affect significantly the start of combustion compared to diesel fuel, it reduced significantly the fuel burnt in the premixed combustion phase, as can be seen in Figure 2. This resulted in the reduced in-cylinder pressure and hence lower temperature. The reduction of the premixed combustion phase was more noticeable for the three engine operating conditions with 3, 4, and 5 bar IMEP. The main reason for this reduced premixed combustion phase and unaffected start of combustion is mainly the lower GTL density and higher cetane number (CN) compared to diesel fuel as discussed below.

The use of pure or blended GTL fuel affected differently the pump-line-nozzle-type fuel injection system timing compared to diesel, because of the different densities and bulk modulus of compressibility of the fuels.¹² GTL has lower density and is more compressible than diesel fuel, so the pressure in the fuel

injection system can develop slower; pressure waves can propagate later for the same nominal pump timing. As a result, the injection of GTL fuel starts later with lower pressure and rate, and at the same degree crank angle, the mass of GTL or GD50 injected is lower than the corresponding mass of diesel. On the other hand, the significantly higher GTL cetane number (CN = 79) compared to conventional diesel (CN = 54) leads to shorter ignition delay (defined as the time between start of injection and start of combustion).

For the majority of engine loads used (2, 4, and 5 bar IMEP), the total combustion duration of GD50 and GTL was increased compared to diesel fuel, and the end of the combustion was shifted to a later stage. Furthermore, the controlled diffusion combustion duration was longer for GTL and GD50, and as the engine load was increasing, the difference in the diffusion combustion duration between GTL and diesel was expanding.

Shorter premixed combustion with more pronounced diffusion combustion in parallel with the lower peak cylinder pressures (Figure 2) and temperatures explains the lower NO_x formation rates and higher smoke associated with the use of GTL and GD50 compared to diesel as shown in Figure 3.

The physical and chemical properties of the fuel are the most important factors that dictate the optimum fuel injection timing for the pump-line-nozzle injection system, so the pump timing has to be optimized to fit the properties of the new fuel. In the case of the GTL-fueled engine, the reduced premixed combustion, lower NO_x, lower fuel consumption, and increased smoke allow injection timing to be advanced. With advanced injection timing by 4° crank angle, the combustion of GTL was shifted to earlier stages and it seemed to increase the rate of the fuel burn in the premixed combustion phase (Figure 4); this resulted in the increase of NO_x emissions compared to standard injection timing. Shifting the combustion to earlier stages gives more time and higher temperatures during the expansion stroke in which oxidation of the soot is more effective.

Overall, the combustion of GTL with optimized injection timing indicated that the NO_x—smoke tradeoff curve is shifted to lower values while improving the engine thermal efficiency compared to the combustion of the diesel fuel (Figure 3).

There is an improvement in brake specific fuel consumption, measured in g/(kW h), for GTL and GTL blends as compared to ULSD. This is expected since GTL fuel has a higher calorific value on a gravimetric basis than ULSD (Table 1). GTL fuel gives a higher thermal efficiency in the specific engine than ULSD. The reduction of the premixed combustion phase in the case of GTL fuel allows injection timing to be advanced, which results in improved engine efficiency while still maintaining NO_x and combustion noise at low levels. In the case of ULSD, advancing the injection timing can lead to improved engine thermal efficiency but this will result in the considerable increase of NO_x emissions and engine combustion noise. At the lowest load condition (2 bar IMEP), the results suggest that the same engine power could be generated by 10% less fuel energy when GTL is employed. This benefit of GTL has been overlooked in a recent influential well-to-wheels study.²⁶

Further tests were then performed with GTL to evaluate the potential benefit associated with the use of exhaust gas recirculation (EGR) for the four engine operating loads (Figures 5 and 6).

In comparison with the results that were obtained with GTL with advanced injection timing, EGR provided additional NO_x reduction (Figure 5) without a extensive penalty in smoke as

(26) CONCAW/JRC/EUCAR, Well to Wheels study 2005 update. <http://ies.jrc.cec.eu.int/wwt.html>.

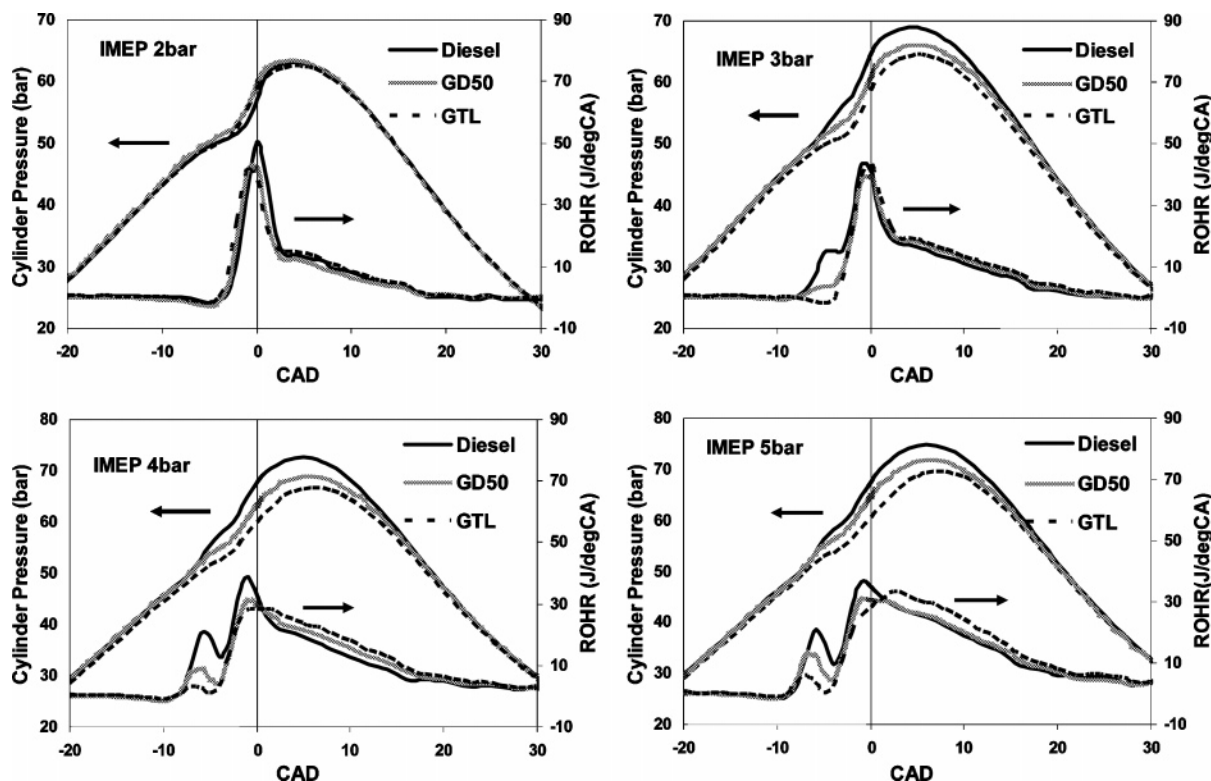


Figure 2. Cylinder pressure and rate of heat release (ROHR) from the combustion of diesel, GD50, and GTL.

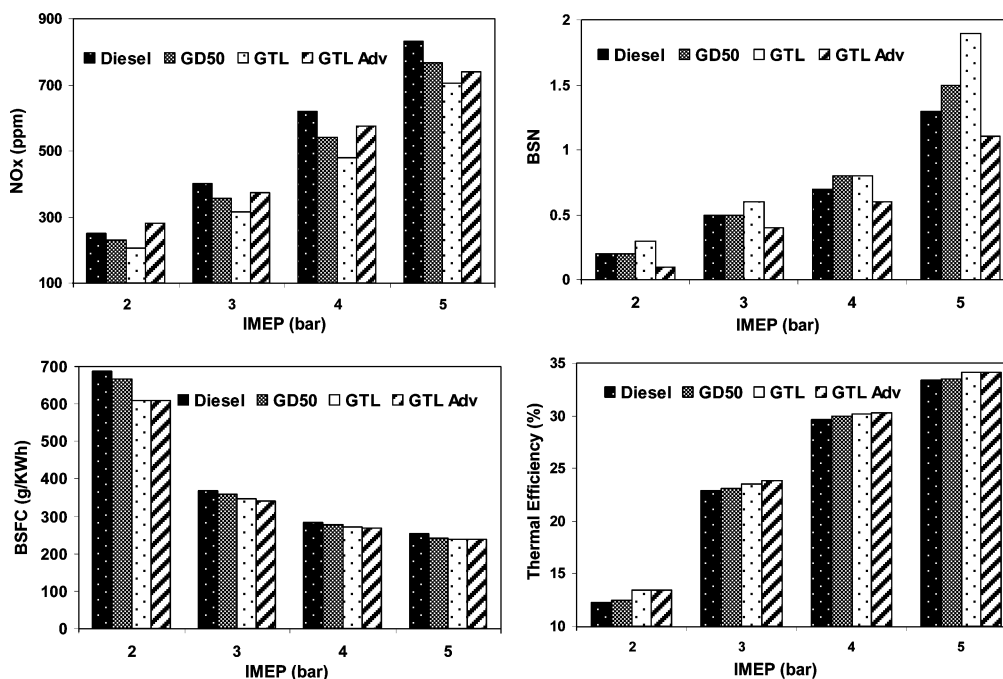


Figure 3. NO_x , BSN, brake specific fuel consumption (BSFC), and thermal efficiency for diesel, GTL, GD50, and GTL with advanced injection timing.

in the case of standard injection timing, engine thermal efficiency (Figure 6), and fuel economy.

From the combustion and emissions trends, it is clear that in an up-to-date highway diesel engine equipped with a modern injection system (e.g., common rail) and the flexibility of the injection timing and pressure, combined with the use of EGR for the different diesel–GTL fuel blends, can improve significantly the engine fuel economy and emissions. Furthermore, most compression ignition (CI) engines are not able to operate at maximum efficiency due to emissions limitations. Because of the emissions benefits associated with combustion of GTL

fuel, it is possible to operate under a more efficient control strategy with the use of this fuel.

3.2. Exhaust-Gas Reforming. In an ongoing study, we have already shown the potential for reducing adverse effects on smoke, particulates, and fuel economy, by incorporating an exhaust gas fuel reformer in the EGR loop to provide the engine with H_2 rich gas.^{3,4} Some of the primary fuel is injected into the reformer, where it reacts with steam and oxygen on the surface of a catalyst to produce a hydrogen-rich gas, which is fed back to the engine. In this way, the reforming process utilizes several of the waste products (O_2 , H_2O , CO , HC , heat) emitted

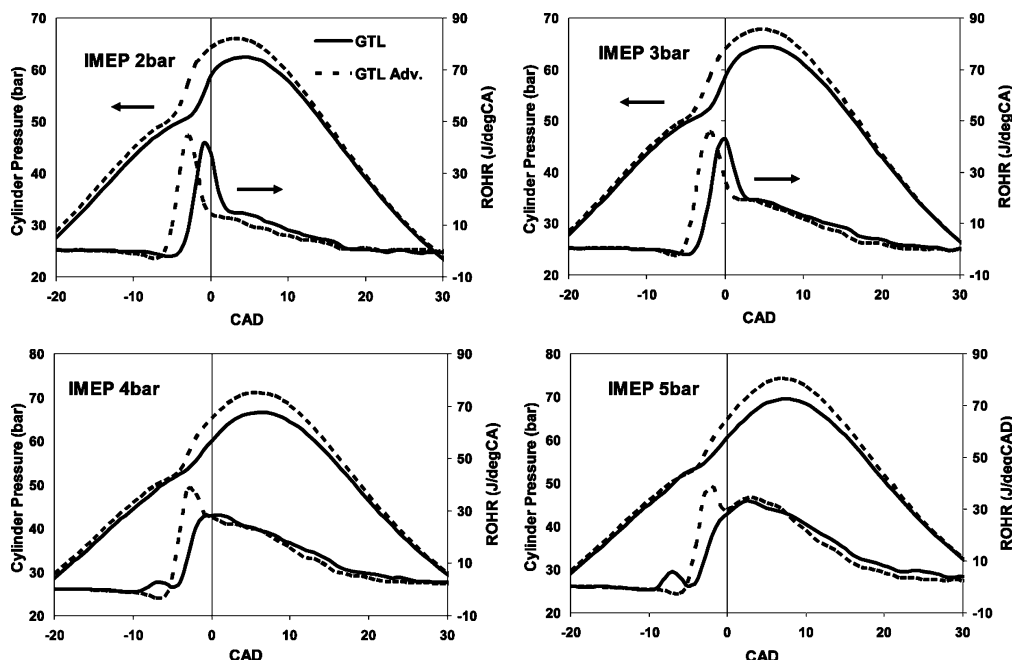


Figure 4. Cylinder pressure and rate of heat release (ROHR) for the GTL-fueled engine with standard and advanced injection timing.

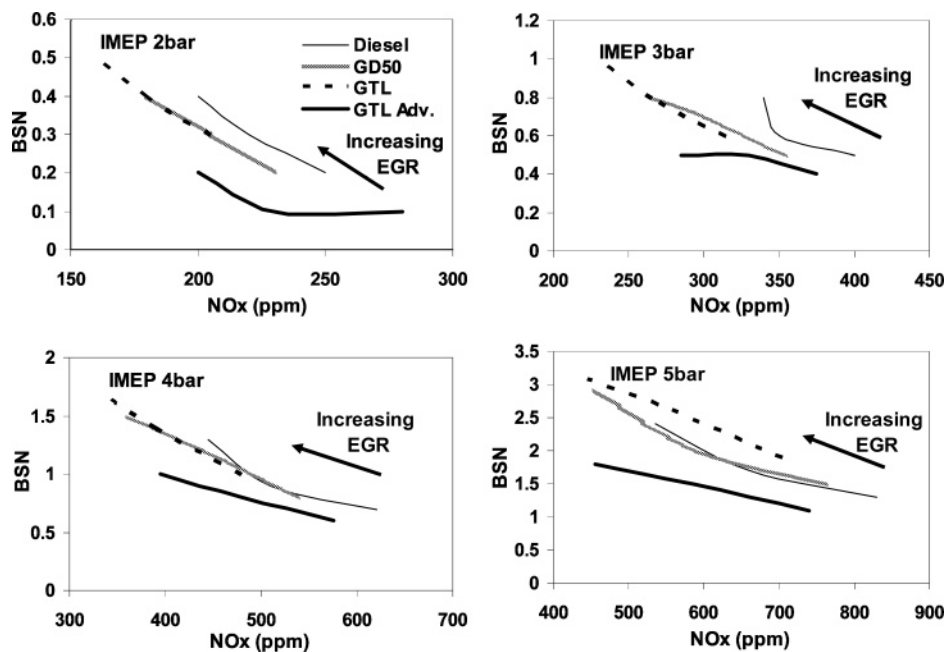


Figure 5. Effect of EGR (0%, 10%, and 20% volume) on the NO_x –smoke tradeoff.

during internal combustion. Unlike the large-scale manufacture of syngas ($\text{CO} + \text{H}_2$), where the inlet conditions are kept constant and the reformer is usually operated isothermally, an exhaust-gas reformer is a largely passive, adiabatic reactor. In practice, this means that the catalyst in an exhaust-gas reformer has to be capable of functioning effectively under variable feed rates and inlet temperatures with minimal external control.^{5,16,17,24,25}

During exhaust-gas reforming, the temperature profiles were nonuniform along the length of the catalyst bed, with the temperature rising steeply to a peak (close to the inlet face of the bed) before declining much more gradually. The onset of this peak was associated with a rapid decline in gas-phase oxygen, indicating that the diesel fuel was being oxidized as soon as it came into contact with the catalyst. Some of the heat was back-radiated, so that the gas temperature in the 1.5 cm

preceding the catalyst bed was around 200 °C higher than the gas-feed temperature (290 °C in our tests). For the fixed space velocity of around 70 kh^{-1} used in this study, lowering the O/C ratio caused a reduction in the peak height and width as well as the outlet temperature, but it did not have an effect on the peak position (Figure 7). For the different O/C ratios, the peak temperature was recorded at 0.5 cm downstream of the monolith inlet. The temperature profiles for ULSD and GTL under the same O/C ratio are similar, and the small differences are possibly due to small changes in the engine exhaust gas composition during the day of testing. The slightly higher peak temperature recorded in the case of ULSD reforming compared to GTL can be due to the higher content of aromatic hydrocarbons in the ULSD. This can lead to the reduction of the endothermic reaction rates and hence poorer use of the heat produced from the oxidation reaction.²⁷

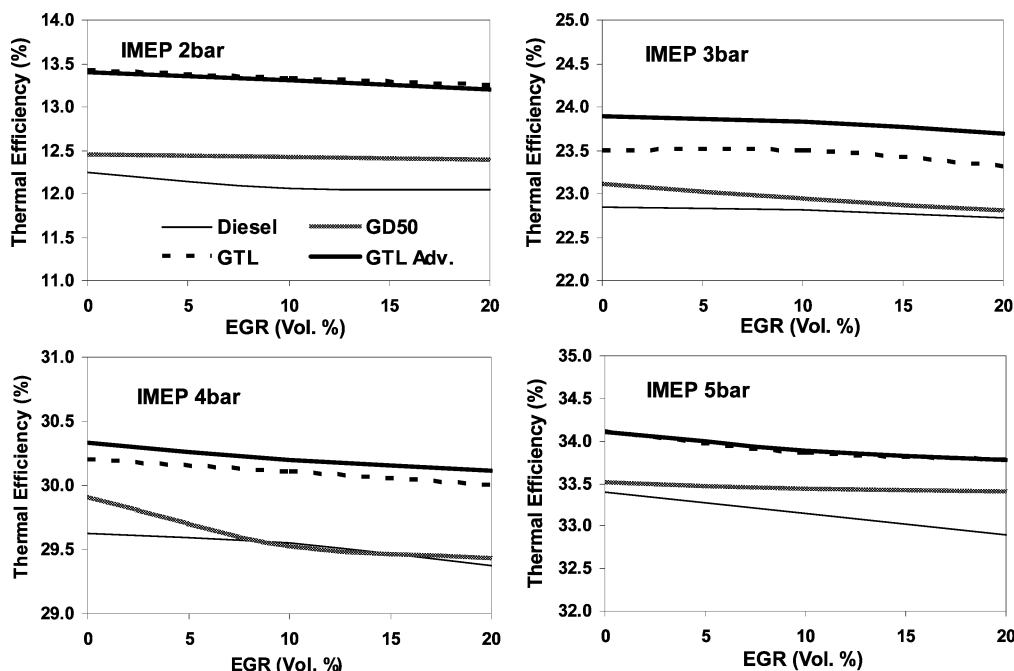


Figure 6. Effect of EGR (0%, 10% and 20% volume) on the engine thermal efficiency.

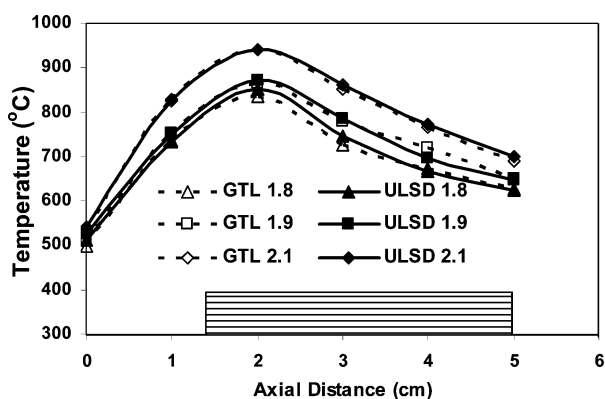


Figure 7. Reactor temperature profiles for various fuels. The numbers refer to the O/C ratio

The main aim of these experiments was to assess the ease with which these two fuels can be reformed at a constant engine exhaust gas flow and composition. The reduction of O/C due to increased fuel flow improves the H_2 and CO content in the product gas and reduces the CO_2 content. The results showed that the O_2 content at the reactor output is always $\sim 0\%$ regardless of the O/C ratio. The oxygen was completely consumed at the inlet of the monolith by always using the same fuel quantity in the exothermic complete oxidation reaction independently of the O/C ratio. As the fuel flow added to the reactor was increased (i.e., O/C was reduced), there was more available fuel for the endothermic ($\Delta H > 0$) H_2 -generating reaction (e.g., dry and steam reforming reactions—DRR and SRR, respectively). This resulted in the increased H_2 and CO production and in the improved process efficiency (Figures 8 and 9). The reduction of CO_2 in the reactor outlet arose from the increased product gas volume and possibly from a contribution from dry reforming where CO_2 reacts with fuel to produce CO and H_2 at temperatures higher than $800^\circ C$.

Furthermore, the reduction of the peak temperature as a consequence of the increased fuel flow rate (O/C ratio reduction)

resulted in the promotion of the methanation reaction. The methane formation was more significant in the ULSD reforming compared to GTL fuel. The formation of methane under similar conditions has been reported by other researchers, and this can be a significant effect, particularly at low temperatures (where it is thermodynamically favored) and when the catalyst contains precious metals.^{28,29} For an O/C ratio of 1.4, the peak temperature (not shown here) was around $750^\circ C$, while the temperature at the outlet of the monolith was around $580^\circ C$.

For the GTL reforming tests, due to the lower energy density (energy per unit volume) of the fuel compared to ULSD, the volumetric fuel flow was increased (Table 3) in order to achieve similar O/C ratios for both fuels. The reforming of GTL increased the hydrogen content in the reformer product gas by 4% compared to ULSD fuel reforming. The higher H/C ratio of the GTL fuel and the reduced methane production are the main reasons for the increased H_2 concentration in the product gas compared to ULSD reforming. Both CO and CO_2 contents were about the same for both fuels.

The reactor product gas composition from the reforming of the two fuels was similar to that predicted using equilibrium calculations. The slightly below-equilibrium CO and above-equilibrium H_2 and CO_2 concentrations for the majority of the O/C ratios (Figure 8) indicate that there is a contribution from the water–gas shift reaction, which takes place in the cooler zone ($< 700^\circ C$) of the catalyst monolith. In an earlier study, we estimated that the optimum water–gas shift range for our catalyst was $550\text{--}700^\circ C$.⁵ From the temperature profiles, it is clear that, as the O/C was reduced, more of the catalyst monolith was below $700^\circ C$ (Figure 7).

All the tests presented in this study were carried out at constant space velocities. In the case of transient conditions (i.e., on-road), the increased or reduced space velocity will affect significantly the reaction profiles. With increasing space velocity, the maximum temperature rises, the peak shifts further along

(27) Kopasz, J. P.; Applegate, D.; Miller, L.; Liao, H. K.; Ahmed, S. *Int. J. Hydrogen Energy* **2005**, *30*, 1243–1250.

(28) Breen, J. P.; Burch, R.; Coleman, H. M. *Appl. Catal., B* **2002**, *39* (1), 65–74.

(29) Comas, J.; Marino, F.; Laborde, M.; Amadeo, N. *Chem. Eng. J.* **2003**, *98* (1–2), 61–68.

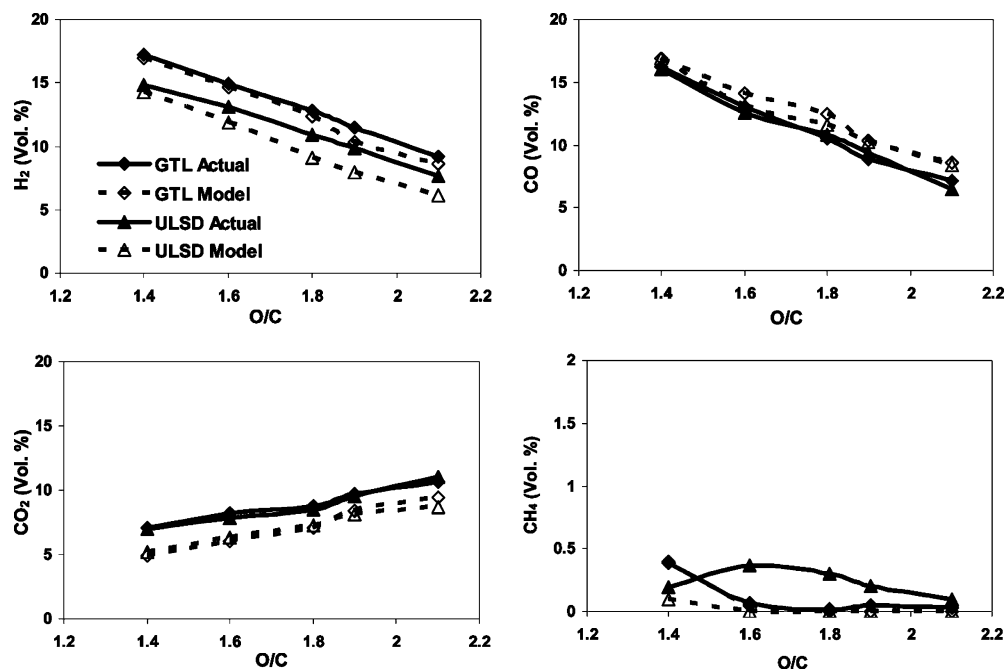


Figure 8. Measured and predicted product distribution.

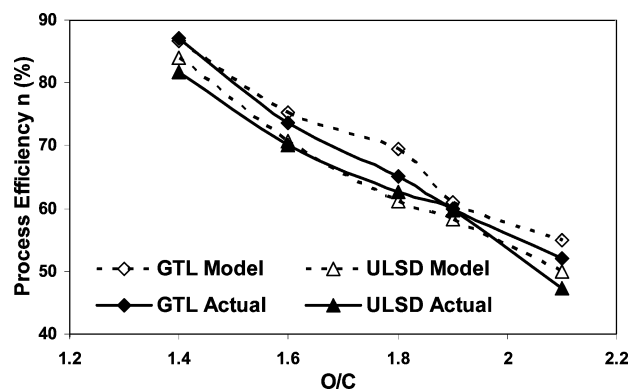


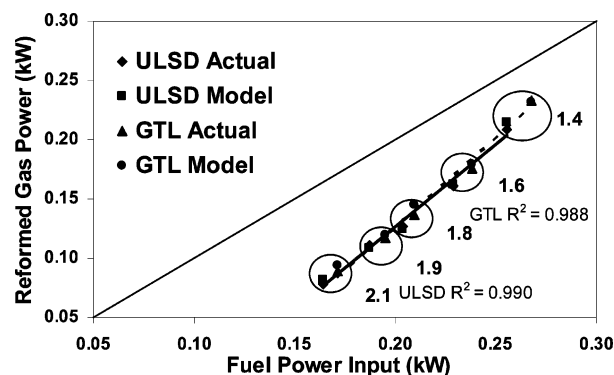
Figure 9. Measured and predicted efficiency.

the catalyst bed, and the temperature of the gases leaving the reactor is higher.⁵

The best process efficiency (calculated using eq 1) was achieved for O/C = 1.4, and the actual values are identical with the predicted equilibrium values (Figure 9). As reported in the experimental section, the catalyst aspect ratio (AR) was selected to minimize the contribution of the water–gas shift reaction. From the results presented in Figure 8, it seems that this has been appreciably achieved. In principle, the greatest benefit to the process efficiency would come from dry reforming.⁵ The measured CO_2 concentrations, which were higher than the equilibrium values, provide evidence that the rhodium catalyst used in this study was surprisingly inactive for this reaction.

Under the same O/C conditions (alike mass flow rates), both actual and predicted efficiency values in general are higher for GTL fuel compared to ULSD, something that is expected since, for a given value of O/C, the GTL in the feed gas will be richer than the ULSD because of the higher H/C ratio in the fuel.

The power of the gaseous fuel produced in the reactor (eq 1 numerator) versus the input chemical power of the GTL and ULSD fed into the minireactor (eq 1 denominator) for the different O/C ratios tested is shown in Figure 10. The diagonal line represents the case of 100% reforming process efficiency. For values above the diagonal line, the reactor product gas will have a higher calorific value than the input feed GTL or ULSD,

Figure 10. Chemical power of actual and calculated reformed gas produced by reforming of GTL (dashed line, $R^2 = 0.988$) and ULSD (complete line, $R^2 = 0.990$).

and hence, the efficiency calculated using eq 1 will be higher than 100%. This is the case where the exhaust gas temperature is high enough to drive the endothermic reactions such as steam reforming and dry reforming. For the same fuel mass flow rate, the fuel power added to the reactor was higher in the case of the GTL reforming as can be seen from Table 1 and Figure 10. This was due to the higher calorific value of GTL (43.9 MJ kg^{-1}) compared to ULSD (42.7 MJ kg^{-1}). From Figure 10, it is clear that the power of the fuel produced for both fuels was proportional to the power of the fuel used. The vertical distance of each point from the diagonal line represents the power losses in the reforming process. As the O/C ratio decreased, the distance of the points from the diagonal line was reduced. Also, all the points, independently of the fuel, are moving in the same line (ULSD $R^2 = 0.99$ and GTL $R^2 = 0.988$) for the different O/C ratios, and if the tests had been carried out under the same input fuel power, then the process efficiency shown in Figure 9 would not have been notably different for the two fuels.

Diesel-type fuels like ULSD/GTL and biodiesel offer high energy storage and have high hydrogen density on both a volumetric and gravimetric basis. The reduced aromatic content of these fuels can lead to lower required reforming temperatures, while at the same time avoiding coke formation.²⁷ However, the low reforming temperatures of fuels that contain sulfur can

accelerate the catalyst deactivation due to sulfur poisoning. As reported in an earlier study, during exhaust-gas reforming over the same Rh-based catalyst, the presence of SO₂ in the gas mixture results in the permanent selective poisoning of the catalytically active sites for steam reforming.³⁰ The GTL fuel, being free of sulfur and aromatic hydrocarbons, can therefore significantly increase the long term performance and durability of the reforming catalyst.^{22,31}

The fuel properties (e.g., density, viscosity, CN, aromatic HC) and hence combustion of the new fuels such as GTL and biofuels are different from conventional fuels, and this will affect the engine performance and emissions. Similarly, the catalyst and reformer design have to be optimized according to the specifications of the new fuels in order to value the beneficial effects. For this reason, and those related to the production of small volumes, these fuels will be likely to be used as blends with conventional fuels. Although, modern diesel engine injection systems such as common rail (CR) are less sensitive to fuel properties (e.g., CN) compared to pump-line-nozzle injection systems, engine tuning will be required in order to accomplish the highest improvements in engine performance.

Conclusions

A comparative combustion and fuel-reforming study between conventional ULSD and GTL diesel fuels has been conducted. The engine-reformer system operation with synthetic fuels such as GTL can improve significantly system performance and emissions.

(30) Peucheret, S.; Feaviour, M.; Golunski, S. *Appl. Catal., B* **2006**, 65, 201–206.

(31) Tsolakis, A.; Megaritis, A. *Biomass Bioenergy* **2004**, 27, 493–505.

The main other findings can be summarized as follows:

- The combustion of GTL in an unmodified diesel engine (nonoptimized injection timing) resulted in a significant reduction in the NO_x emissions but with an increase in the smoke emissions due to shorter premixed combustion and longer diffusion combustion especially at high loads. However, using a diesel–GTL (50% by volume) mixture, the smoke was reduced without significant changes in the NO_x values compared with GTL fuel. Besides, both GTL and its mixture with diesel show enhanced fuel economy (gravimetric basis) and better engine thermal efficiency.
- In the case of GTL by optimizing the injection, emissions of NO_x and smoke were both reduced simultaneously while still giving improvements in engine thermal efficiency.
- As expected, EGR reduced the NO_x emissions and increased the smoke emissions for all tested fuels and conditions and fuels. However, the lower smoke emissions in the case of GTL fuel with advanced injection timing facilitate NO_x reductions by exploiting the higher EGR tolerance of GTL fuels. Thus, a more favorable NO_x–smoke tradeoff may be selected to reduce both NO_x and smoke.
- The experimental and calculated results revealed that both GTL and ULSD fuels can be reformed into hydrogen rich gas in the exhaust-gas reforming. The use of synthetic fuels such as GTL, free of sulfur and aromatic hydrocarbons, improves the reforming process compared to ULSD in terms of hydrogen production and fuel conversion (reduced CH₄).

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