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Influence of Blending Advanced Biofuel Mixtures with Diesel on Emissions from a Compression Ignition Engine

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Abstract

Compression ignition engines are likely to be reliant on liquid fuels in the short term. Reducing their carbon footprint could benefit from blending fossil fuels with lower carbon alternatives such as advanced biofuels. Blends of alkyl levulinate, dialkyl ether, and alcohol can be produced from lignocellulosic biomass using acid catalysed alcoholysis. Ethyl and butyl-based blends, derived from ethanol and n-butanol, respectively, were investigated in this study using a single-cylinder generating set engine. Particulate emissions reduced significantly upon addition of the biofuel, but CO and total hydrocarbon specific emissions increased relative to diesel for all blends, resulting in non-compliance with the Euro Stage V emissions standard. Optimisation of the engine or utilisation of after-treatment systems would be beneficial to meeting standards with such advanced biofuel blends.

Introduction

Heavy-duty vehicles (HDVs), heavy machinery, and off-grid electricity are likely to rely on compression ignition (CI) engines for the short to medium-term. CI engines are typically fuelled with diesel and are likely to be dependent on liquid fuels in the short-term. The main sectors using CI engines include agricultural, transport, and construction sectors, and small scale power generation where diesel generator sets (gensets) are commonplace. Decarbonisation targets of many countries aim to reach net zero greenhouse gas emissions by 2050. As part of this strategy, the revised EU Renewable Energy Directive (REDII) mandates that advanced biofuels should be 3.5% of the total energy contribution in the transport sector by 2032 [1]. To achieve this target, low-carbon liquid alternatives to diesel are required.

For fuels to be sold commercially, and to maintain vehicle warranties, the fuel must comply with a specific standard. In Europe and the UK, grade I diesel used in road vehicles must comply with EN 590. In the UK, grade II diesel used in non-road mobile machinery (NRMM) must comply with BS 2869, and in the US the diesel standard is ASTM D975 [2-4]. Fuel standards set limits for a range of physical and combustion properties, such as flash point, density, kinematic viscosity at 40 °C (KV40), and cetane number (CN) or derived cetane number (DCN) [2, 3]. In addition, properties such as ignition delay time (IDT) and adiabatic flame temperature change with different fuel formulations and these can impact the emissions [5].

One potential method of obtaining low-carbon alternative fuels is the alcoholysis of lignocellulosic biomass. This process could potentially produce tailorable advanced biofuel blends of three main products: an alkyl levulinate, a dialkyl ether, and the solvent alcohol [6]. Ethyl-based blends are produced using ethanol (EtOH), and consist of ethyl levulinate (EL), diethyl ether (DEE), and ethanol. Butyl-based blends are produced using n-butanol (BuOH), and consist of n-butyl levulinate (BL), di-n-butyl ether (DNBE), and BuOH.

Table 1. Fuel components properties. ULSD is ultra-low sulphur diesel.

Fuel Component	DCN[a]	KV40[b] (mm^2/s)	Density at 15 °C[b] (g/cm^3)	Adiabatic Flame Temperature[c] (K)
ULSD	>51	2.00 – 4.00	0.820 – 0.845	2200 -2250
EL	6	1.553	1.017	2875
BL	14	2.017	0.973	2860
EtOH	8	1.099	0.895	2242
BuOH	12	2.261	0.811	2450
DEE	140-160	-	0.720	2300
DNBE	115	0.736	0.768	2865

[a]from [7]. [b]measured by an Anton Paar SVM3000. [c]from [5, 8].

Fuel blends can be formulated to ensure physical and combustion properties meet the limits set in the relevant fuel standard. Meeting the standards for property limits could help to minimise the impact of blending on existing infrastructure and engine performance. For example, Howard et al. [9] determined a blending law to calculate the DCN of ethyl-based blends of the type discussed here, where the DCN could be tailored to any value up to 130.

Antonetti et al. [10] and Frigo et al. [11] studied a range of butyl-based blends that were non-compliant with the physical property limits in existing fuel standards [2, 3], and tested these blends in small diesel engines. They showed that the addition of butyl-based blends reduced the fuel smoke number (FSN) relative to diesel. However, they found increased CO and total hydrocarbon (THC) emissions relative to diesel. This was likely due to the reduced DCN of the blends causing longer IDTs relative to diesel [10, 11]. Longer IDTs would have increased the premixed combustion but reduced the time available for complete

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combustion, leading to increased CO and THC emissions [10, 11].

In addition to decarbonisation targets, engine applications must comply with relevant tailpipe emissions standards. For HDVs the current emissions standard is Euro VI and for NRMM, such as gensets, the relevant standard is Euro Stage V. For HDVs, the new Euro VII emissions standard will come into force in 2025 [12, 13]. The Euro VII emissions limits for HDVs are stricter than those of Euro VI. For example, the particle number (PN) limit will reduce from 6×10^{11} to 1×10^{11} #/kWh, with a reduction in the diameter of solid particles that contribute towards the PN from 23 nm to 10 nm [12, 14]. The reduction in emissions limits could lead to an increased requirement for exhaust after-treatment systems. However, the use of low-carbon alternative fuels that inherently improve the emissions could also be potentially useful technologies. The emissions standard applicable in this work is the Euro Stage V emissions standard with the limits displayed in table 2 [13].

Table 2. Euro Stage V CI genset emissions limits [13]. PM is particulate matter.

Engine Power (kW)	**CO (g/kWh)**	**NO_X+THC (g/kWh)**	**PM (g/kWh)**	**PN (#/kWh)**
0<P<8	8.0	7.5	0.6	-

Methodology

Butyl-based fuel blends were formulated to meet the BS 2869 limits for grade II diesel, specifically to comply with the flash point, density, and KV40 limits [3]. Ethyl-based fuel blends were initially formulated to have a DCN >40, determined using the equation developed by Howard et al. [9]. The fuel components used are summarised in table 3.

Table 3. Fuel components used.

Fuel Component	**Purity**	**Supplier**
ULSD	EN590 compliant with 7 vol% biodiesel	Crown Oils
EL	98%	Sigma
BL	98%	Fisher Scientific
EtOH	99.97%	VWR
BuOH	99%	Sigma
DEE	≥99.8% with 8 ppm Butylated Hydroxytoluene	Sigma
DNBE	99+%	Sigma

The fuel blends were tested in a Euro Stage V compliant Yanmar L100V genset engine, with its specification summarised in table 4. The engine was operated under steady-state conditions for 20 minutes at each set load. There were no modifications made to the engine or to the fuel injection to compensate for the changes in the fuel composition. The emissions analysed and the appropriate sampling methods are summarised in table 5. Here we analysed $PM_{2.5}$, defined as the mass of PM per unit volume of air passing a size-selective inlet with a 50% cut point efficiency at 2.5µm aerodynamic diameter. The specific emissions for each fuel were calculated using ISO 8178 weighting factors and were compared to the Euro Stage V limits [13, 15].

Table 4. Yanmar L100V engine specification.

Property	**Value**
Number of Cylinders	1
Cycle	Four-Stroke
Compression Ratio	21.2
Cooling	Air Cooled
Injection	Direct
Injection Timing (° before TDC)	13.5
Engine Speed (revolutions per minute (RPM))	3000 ± 100
Maximum Displacement (cm^3)	435
Engine Power (kW)	0.26 – 5.7

Table 5. Emissions analyses.

Emission	**Analyser**
CO	Non-Dispersive Infrared MEX7100D
THC	Flame Ionisation Detection MEXA7100D
NO_X	Chemiluminescence MEXA 7100D
$PM_{2.5}$	Particulate separating cyclone and filter papers
PN	DMS500

Results and Discussion

Impact of Engine Stability on Emissions

It is vital for gensets to have stable operation, not only to maintain consistent power delivery and power generation, but also to ensure combustion can be controlled. Unstable operation resulted in fluctuations in emissions and RPM (figure 1), which could be more difficult to manage using after-treatment systems due to inconsistent emissions with transient spikes.

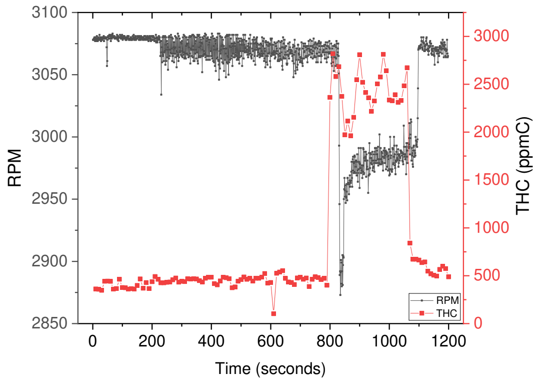

Figure 1. THC emissions during an engine test with unstable operation. Fuel blend: 75% ULSD 25% Biofuel (75 vol% EL/5 vol% EtOH/20 vol% DEE).

For the ethyl-based blends studied, DEE had to be no more than 3 vol% of the total blend to have stable operation and achieve the maximum 92% load. The high DEE fraction should give a high blend DCN due to its high DCN. However, DEE's high volatility and low viscosity were detrimental to the performance of the fuel delivery system. The high volatility may have caused vapour locking, i.e. where the fuel pump could not pump fuel through the fuel lines due to pockets of DEE vapour causing blockages. All of the butyl-based blends studied had stable engine operation. This highlighted that the physical properties of the blends need to be carefully considered and optimised, along with the combustion properties. The fuel blends with stable operation are summarised in table 6.

Table 6. Blends with stable engine operation at all loads.

Blend	Diesel (vol%)	Biofuel (vol%)	Levulinate:Alcohol:Ether (vol%)
Ethyl-1	85	15	75:5:20
Ethyl-2	85	15	95:5:0
Butyl-1	90	10	65:5:30
Butyl-2	90	10	75:5:20
Butyl-3	90	10	85:5:10
Butyl-4	90	10	85:10:5
Butyl-5	90	10	90:5:5
Butyl-6	75	25	85:5:10
Butyl-7	75	25	90:5:5

Changes in the Gaseous Emissions

As the engine was not modified, the changes in the emission were due to the addition of the biofuel blends. Any increases in CO and THC emissions (ΔCO and ΔTHC) were indications of less complete combustion. For the ethyl-based blends, the DEE in the blend caused a greater increase in THC emissions relative to the ULSD baseline. As the engine load increased, the ΔTHC emissions increased for ethyl-1, whereas ethyl-2 had less of an increase at higher loads than lower loads, as shown in figure 2.

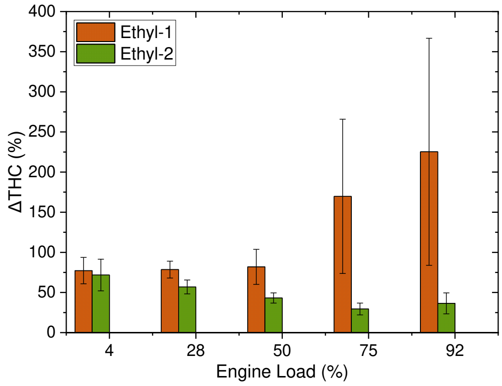

Figure 2. Change in THC emissions relative to ULSD baseline for the ethyl-based blends.

For the butyl-based blends, the ΔTHC decreased as engine load increased, with reductions at 92% load, as shown in figure 3. At <50% load there was a correlation between the increase in THC emissions and the increasing BL fraction. The reduction in THC emissions at the higher loads is a positive outcome for the butyl-based blends as they would have a lower DCN than ULSD due to BL's low DCN [7]. Additionally, gensets typically operate at >50% load, and a reduction in THC emissions could improve local air quality in regions where gensets are used for power generation.

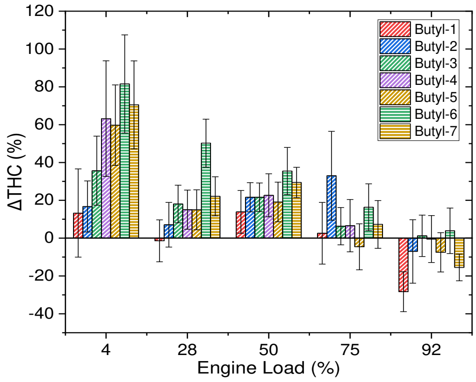

Figure 3. Change in THC emissions relative to ULSD baseline for the butyl-based blends.

The changes in CO emissions when using the ethyl-based blends had the same behaviour as the THC emissions (figure 4). At higher loads, the blend with DEE had a greater increase in CO, highlighting that DEE did not, in practice, act as a DCN enhancer due to fuel delivery issues. The increased CO and THC emissions at the higher loads were further indications there was some instability at these loads.

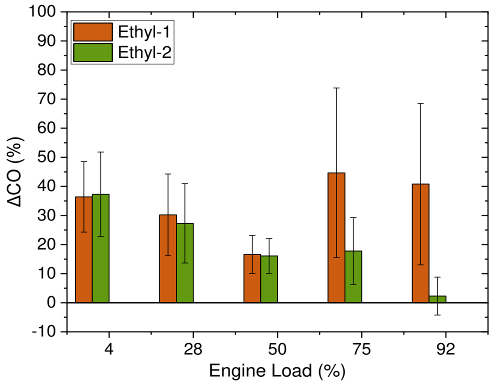

Figure 4. Change in CO emissions relative to ULSD baseline for the ethyl-based blends.

Figure 5 shows the CO emissions from the butyl-based blends. They had the same trend as the THC emissions, where the increase in CO emissions reduced as the engine load increased. There was a correlation between both the total biofuel fraction, and the BL fraction in the blend, and the increase in CO emissions.

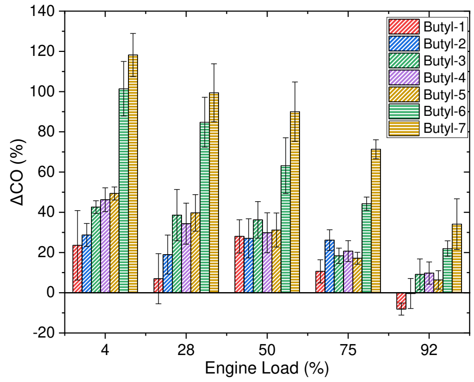

Figure 5. Change in CO emissions relative to ULSD baseline for the butyl-based blends.

Changes in Particulate Emissions using the Advanced Biofuel Blends

For the ethyl-based blends, it was not possible to measure the PN due to the potential condensation of unburnt fuel in the DMS500. However, the $PM_{2.5}$ mass could be measured. The $PM_{2.5}$ emissions using the ethyl-based blends increased with the blend containing DEE (figure 6), whereas, at higher loads, the $PM_{2.5}$ emissions decreased with the blend without DEE. The increase may have been due to condensation of unburnt fuel onto the filter papers.

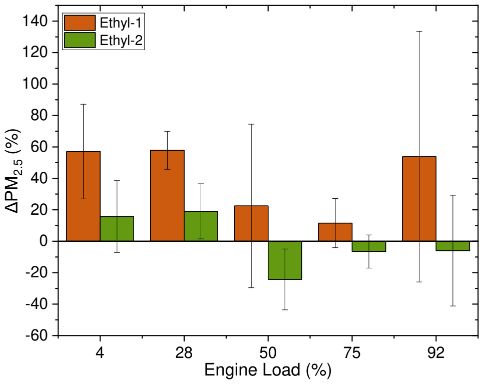

Figure 6. Change in $PM_{2.5}$ emissions relative to ULSD baseline for the ethyl-based blends.

The reduction in $PM_{2.5}$ with the ethyl-based blends was less than it was with the butyl-based blends. The reduction in $PM_{2.5}$ when using the butyl-based blends was correlated to the BL fraction in the biofuel blend (figure 7). The reduction in $PM_{2.5}$ relative to diesel follows the trends commonly observed with the utilisation of oxygenated biofuel blends, such as the reduction in FSN, observed by Antonetti et al. [10] and Frigo et al. [11] when testing butyl-based blends. The reduction in $PM_{2.5}$ was expected, and there was a visible difference in the colour of the filter papers used to collect the $PM_{2.5}$ samples upon addition of the biofuel blends (figure 8). At higher loads, more total $PM_{2.5}$ was generated throughout the test compared to lower loads due to more fuel being consumed, hence the darker colours.

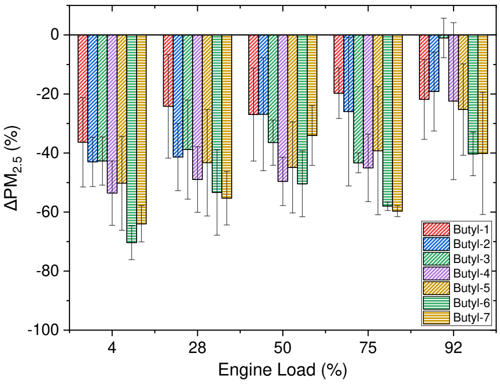

Figure 7. Change in $PM_{2.5}$ emissions relative to ULSD baseline for the butyl-based blends.

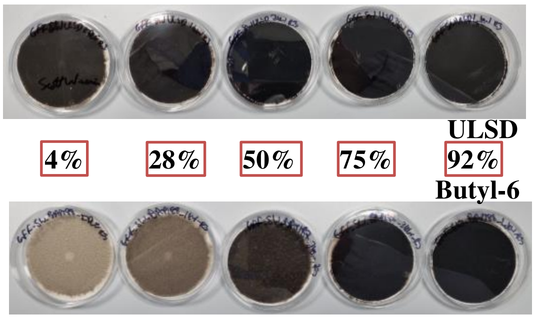

Figure 8. Examples of $PM_{2.5}$ collected on filter papers at each engine load.

Scanning electron microscope (SEM) images of the captured $PM_{2.5}$ (figure 9) show a change in the particles' morphology, from spherical to cylindrical, upon addition of the butyl-based blends. This is possibly indicative of additional particle agglomeration or condensation of higher molecular weight organic compounds for the biofuel blends. The SEM images are of total $PM_{2.5}$ captured, where there is likely to have been additional agglomeration of the collected $PM_{2.5}$ relative to the exhaust composition. Hence, the exhaust particle number size distributions (PNSDs) were also analysed using the DMS500.

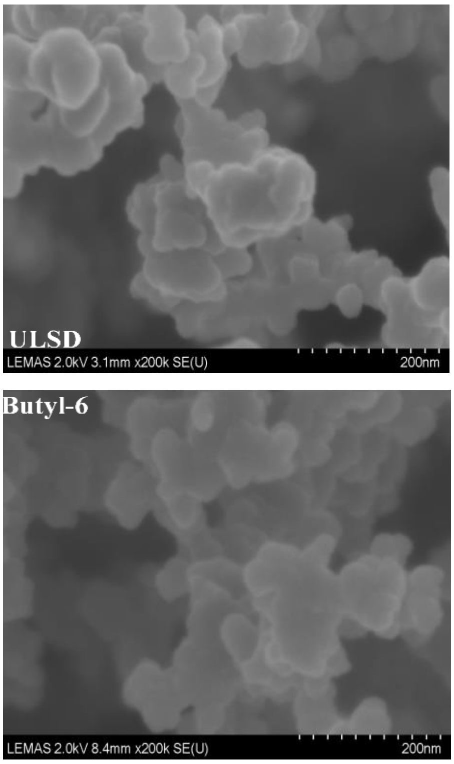

Figure 9. SEM images of captured $PM_{2.5}$ on the filter papers.

The addition of the butyl-based blends resulted in a consistent reduction in PN for most blends at all powers (figure 10). The PN reduction at 92% load, with butyl-7 was less than for the other blends. Since the PN measured was the total PN, there is the potential that with high BL fractions there were droplets of condensed unburnt fuel and semi-volatile particles being measured, as the boiling point of BL is 232 °C and the DMS500 was held at 55 °C.

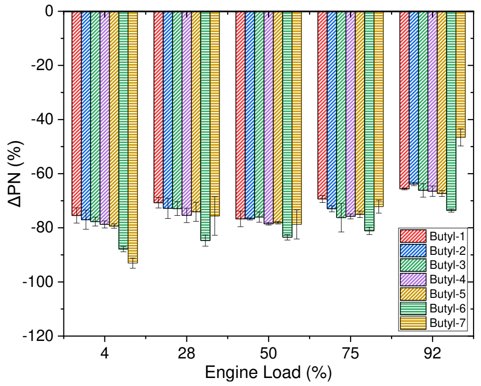

Figure 10. Change in PN emissions relative to ULSD baseline for the butyl-based blends.

Along with reductions in PN emissions, the size distributions of the particles changed (figure 11). The area under the PNSD curve represents the total PN and clearly reduces on the addition of the biofuel blends. The shape of the curve also changes showing an increase in the peak particle size for the biofuel blends. For ULSD, the peak was around 60 nm, whereas with the butyl-based blends at 92% load, the peak diameter increased to around 100 nm. This indicates there may have been fewer nucleation particles, and an increase in either agglomerated particles, or the condensation of organics as indicated in the SEM images. Larger particles may be more readily removed using diesel particulate filters (DPFs), and with a lower PN, the DPF regeneration may need to be less frequent for the biofuel blends [16].

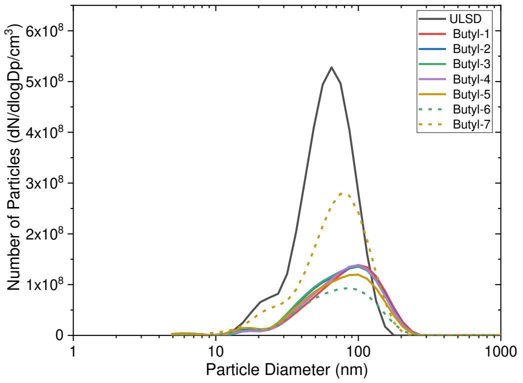

Figure 11. PNSD for the butyl-based blends at 92% load.

Causes for the Changes in the Emissions

The addition of the ethyl and butyl-based blends leads to longer IDTs due to reductions in their DCNs relative to ULSD [7]. As a result, the ignition was further away from top dead centre, reducing the maximum in-cylinder temperature and pressure and thus the amount of complete combustion. The longer IDTs also promote incomplete combustion due to there being less time available for combustion to occur in the cylinder, leading to increased CO and THC emissions. It was expected that there would be an increase in particulate emissions due to less complete combustion. However, there was more premixed combustion due to the longer IDTs since the fuel injection timing is fixed in the Yanmar L100V engine. The increased premixed combustion potentially reduced the number of rich zones in the cylinder, where particles are typically produced [11].

In addition to increased premixed combustion, the oxygen fraction in the fuel blend increases upon the addition of the biofuel blends. For the butyl-based blends, the O/C ratios for the 10 vol% biofuel blends were consistent with each other, regardless of the biofuel blend composition. The addition of the biofuel blends also reduced the aromatic content of the blend relative to ULSD. Therefore, the production of soot precursors should reduce.

Specific Emissions

The calculated specific emissions for the ethyl and butyl-based blends are shown in table 7, where the PM emissions are for $PM_{2.5}$. ULSD-FB and ULSD-FJ are used as comparisons for the ethyl and butyl blends, respectively. These represent ULSD baselines taken with different corresponding fuel injectors.

Table 7. Specific emissions for blends with stable operation.

Blend	CO (g/kWh)	NO_X +THC (g/kWh)	PM (g/kWh)	PN (#/kWh)
Stage V limits	8.0	7.5	0.6	-
ULSD-FB	9.4 ± 1.0	11.0 ± 1.0	0.13 ± 0.03	$(1.1 \pm 0.2) \times 10^7$
Ethyl-1	12.1 ± 0.9	12.1 ± 2.9	0.20 ± 0.05	-
Ethyl-2	11.8 ± 1.0	11.1 ± 0.6	0.15 ± 0.02	-
ULSD-FJ	8.2 ± 0.5	11.6 ± 0.8	0.49 ± 0.09	$(2.5 \pm 0.4) \times 10^8$
Butyl-1	9.4 ± 1.0	11.1 ± 1.5	0.34 ± 0.08	$(6.9 \pm 1.0) \times 10^7$
Butyl-2	10.1 ± 0.6	11.7 ± 1.0	0.29 ± 0.06	$(6.5 \pm 1.3) \times 10^7$
Butyl-3	11.3 ± 0.8	12.7 ± 1.1	0.30 ± 0.07	$(6.4 \pm 1.1) \times 10^7$
Butyl-4	10.9 ± 0.7	12.4 ± 1.1	0.23 ± 0.06	$(5.9 \pm 0.9) \times 10^7$
Butyl-5	11.1 ± 0.7	12.9 ± 1.0	0.25 ± 0.08	$(6.0 \pm 0.8) \times 10^7$
Butyl-6	14.7 ± 1.3	13.5 ± 1.0	0.18 ± 0.05	$(3.8 \pm 1.5) \times 10^7$
Butyl-7	15.6 ± 1.7	13.0 ± 1.3	0.19 ± 0.07	$(1.1 \pm 0.2) \times 10^8$

Due to the weighting factors used in ISO 8178, all of the biofuel fuel blends tested resulted in non-compliant CO and NO_X+THC emissions even though there were reductions in THC and CO emissions for some blends at higher loads [15]. The main contributor to the increases in the NO_X+THC specific emissions were the increases in THC emissions. To control the increases in CO and THC several strategies are possible such as i) the optimisation of the engine operation, through for example, advanced injection timing, ii) the addition of an additive to enhance the DCN of the blend, iii) installation of a diesel oxidation catalyst to control the emissions [17].

Conclusions

Maintaining low emissions from the Yanmar L100V engine depended upon achieving stable operation. It was found that fuel delivery issues that occurred for all but very low fractions of DEE, led to unstable operation and a lack of ability to achieve maximum load. Where stable operation was achieved, there were significant reductions in $PM_{2.5}$/PN emissions for all biofuel blends relative to ULSD.

Changes in the size and morphology of the sampled PM were also seen, corresponding to an increase in larger diameter agglomerates. The increases in CO and THC emissions were expected for the biofuel blends, due to their longer IDTs.

Blends with physical properties that were compliant with the relevant fuel standards showed stable operation and demonstrated the potential for minimal changes in emissions if the fuel blend was tailored. The butyl based blends all had a similar reduction in PN and caused a significant reduction in $PM_{2.5}$ relative to ULSD. The blends with higher DNBE fractions had lower increases in CO and THC across all load settings, with some reductions at the highest load. Reductions in PN could facilitate meeting the lower Euro VII limits, without reliance on exhaust after-treatment systems.

Overall, the butyl-based blends showed better promise as low-carbon alternatives to diesel compared to the ethyl-based ones, and could have the potential to contribute to the REDII target. However, optimisation of engine operation for blend formulations, or exhaust after-treatment systems, would need to be retrofitted to ensure all existing emissions limits are met for the particular engine type studied here.

Acknowledgements

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References

[1] The European Parliament and Council of the European Union, Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources. https://eur-lex.europa.eu (accessed 29/10/2019 2019).

[2] British Standards Institution. BS EN 590:2022. Automotive fuels - Diesel - Requirements and test methods. Milton Keynes: BSI, 2022.

[3] British Standards Institution. BS 2869:2017. Fuel oils for agricultural, domestic and industrial engines and boilers Milton Keynes: BSI, 2017.

[4] E. Christensen, A. Williams, S. Paul, S. Burton, R.L. McCormick, Properties and Performance of Levulinate Esters as Diesel Blend Components, Energy & Fuels 25 (2011) 5422-5428.

[5] E. Koivisto, N. Ladommatos, M. Gold, Compression Ignition and Exhaust Gas Emissions of Fuel Molecules Which Can Be Produced from Lignocellulosic Biomass: Levulinates, Valeric Esters, and Ketones, Energy & Fuels 29 (2015) 5875-5884.

[6] T. Flannelly, S. Dooley, J.J. Leahy, Reaction Pathway Analysis of Ethyl Levulinate and 5-Ethoxymethylfurfural from d-Fructose Acid Hydrolysis in Ethanol, Energy & Fuels 29 (2015) 7554-7565.

[7] J. Yanowitz, M.A. Ratcliff, R.L. McCormick, J.D. Taylor, M.J. Murphy, Compendium of Experimental Cetane Numbers, 2017.

[8] P.-A. Glaude, R. Fournet, R. Bounaceur, M. Molière, Adiabatic flame temperature from biofuels and fossil fuels and derived effect on NOx emissions, Fuel Processing Technology 91 (2010) 229-235.

[9] M.S. Howard, G. Issayev, N. Naser, S.M. Sarathy, A. Farooq, S. Dooley, Ethanolic gasoline, a lignocellulosic advanced biofuel, Sustainable Energy & Fuels 3 (2019) 409-421.

[10] C. Antonetti, S. Gori, D. Licursi, G. Pasini, S. Frigo, M. Lopez, J.C. Parajo, A.M.R. Galletti, One-Pot Alcoholysis of the Lignocellulosic Eucalyptus nitens Biomass to n-Butyl Levulinate, a Valuable Additive for Diesel Motor Fuel, Catalysts 10 (2020) 509.

[11] S. Frigo, G. Pasini, G. Caposciutti, M. Antonelli, A.M. Raspolli Galletti, S. Gori, R. Costi, L. Arnone, Utilisation of advanced biofuel in CI internal combustion engine, Fuel 297 (2021) 120742.

[12] European Commission, Proposal for a regulation of the European Parliament and of the Council on type-approval of motor vehicles and engines and of systems, components and separate technical units intended for such vehicles, with respect to their emissions and battery durability (Euro 7) and repealing Regulations (EC) No 715/2007 and (EC) No 595/2009. https://single-market-economy.ec.europa.eu/ (accessed 29/11/2022 2022).

[13] European Parliament, Regulation (EU) 2016/1628 of the European Parliament And Of The Council of 14 September 2016 on requirements relating to gaseous and particulate pollutant emission limits and type-approval for internal combustion engines for non-road mobile machinery, amending Regulations (EU) No 1024/2012 and (EU) No 167/2013, and amending and repealing Directive 97/68/EC. http://eur-lex.europa.eu/ (accessed 17/01/2022 2022).

[14] European Parliament, Regulation (EC) No 595/2009 of the European Parliament and of the Council of 18 June 2009 on type-approval of motor vehicles and engines with respect to emissions from heavy duty vehicles (Euro VI) and on access to vehicle repair and maintenance information and amending Regulation (EC) No 715/2007 and Directive 2007/46/EC and repealing Directives 80/1269/EEC, 2005/55/EC and 2005/78/EC. http://eur-lex.europa.eu/ (accessed 15/07/2020 2020).

[15] British Standards Institution. BS ISO 8178-4:2020. Reciprocating internal combustion engines. Exhaust emission measurement. Steady-state and transient test cycles for different engine applications. Milton Keynes: BSI, 2020.

[16] J. Rodríguez-Fernández, J.J. Hernández, J. Sánchez-Valdepeñas, Effect of oxygenated and paraffinic alternative diesel fuels on soot reactivity and implications on DPF regeneration, Fuel 185 (2016) 460-467.

[17] C.T. Lao, J. Akroyd, N. Eaves, A. Smith, N. Morgan, D. Nurkowski, A. Bhave, M. Kraft, Investigation of the impact of the configuration of exhaust after-treatment system for diesel engines, Applied Energy 267 (2020) 114844.