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# Influence of Blending n-Butanol Alcoholysis Derived Advanced Biofuels with Diesel on the Regulated Emissions from a Diesel Hybrid Vehicle

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# Abstract

Globally, transport is one of the largest greenhouse gas emitting sectors. Decarbonization of the transport sector whilst reducing pollutant emissions, and thus improving air quality, will likely involve the utilization of multiple strategies, including hybridization and alternative fuels. The EU mandates the use of advanced biofuels within liquid fuels. Alcoholysis of lignocellulosic feedstocks, using n-butanol as the solvent, can produce such potential advanced biofuel blends. Butyl blends, consisting of n-butyl levulinate (nBL), di-n-butyl ether (DNBE), and nbutanol (nBuOH) were selected for this study. They were chosen, so that when blended with a standard B7 EN 590 summer grade diesel, the density, kinematic viscosity, and flash point limits of existing fuel standards were met. Three butyl blends with diesel, two at 10 vol% biofuel and one at 25 vol% biofuel, were tested in a Euro 6 emission standard compliant diesel hybrid vehicle to determine the influence of the butyl blends on emissions, fuel economy, and exhaust after-treatment system performance. No modifications to the vehicle were made. Real Driving Emissions (RDE) were measured using a Portable Emissions Measurement System (PEMS) for the regulated emissions of CO, particle number (PN), and nitrogen oxides (NOx=NO+NO2). The same driver conducted three sets of RDE tests for each blend, in order to eliminate the variations caused by different drivers. The RDE testing and data analysis was conducted in accordance with RDE package 4 legislation. When using the butyl blends, there was no noticeable change in the drivability of the vehicle, and only a small fuel economy penalty of up to 5% with both the 10 vol% and 25 vol% biofuel blends relative to diesel. CO, NOx, and PN emissions were below or within one standard deviation of the Euro 6 not-to-exceed limits for all fuels tested. The CO and PN emissions reduced relative to diesel by up to 72% and 57%, respectively. NO<sub>x</sub> emissions increased relative to diesel by up to 25%, and increased as the *n*BL fraction increased within the blend, and as the biofuel fraction increased to 25 vol%. The increase in NO<sub>x</sub> emissions when using the biofuel blends was likely due to a reduced efficiency of the selective catalytic reduction (SCR) system, as less NO<sub>X</sub> was removed following injection of the reductant, AdBlue. Overall, the fuel blends show good potential to contribute towards the decarbonization of the transport sector, although optimization of the after-treatment and emissions control systems, particularly related to NOx control, may be necessary in order to ensure emissions limits can be met.

Keywords: Diesel; Hybrid; Advanced Biofuels; Real Driving Emissions,

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#### 1. Introduction

Diesel vehicles have been used for decades in many applications in the transport, agriculture, and construction sectors. Whilst the number of light-duty diesel vehicles has fallen, in the heavy-duty vehicle sector the numbers have increased due to the increased need to transport goods on the road [1-3]. Per-vehicle pollutant emissions have reduced with each generation of vehicle manufacture, as emissions limits have reduced with each version of the emissions standards [4]. However, increases in vehicle numbers have countered this trend, and are one of the main causes of greenhouse gas emissions from the transport sector remaining relatively stagnant over the last 20 years [1-3].

One technology used to improve fuel efficiency and to reduce pollutant emissions is hybridization. Parallel hybrid vehicles are the most common type, where the internal combustion engine (ICE) powers the wheels and can also charge batteries used to power the electric motor that also drives the wheels. There have been few investigations into Real Driving Emissions (RDE) from diesel hybrids. Also, the reality is that hybrid vehicles still have an ICE fueled by predominantly fossil fuels, although low percentages of biodiesel are now used within standard diesel fuel blends [5]. To further decarbonize the transport sector, low-carbon alternative fuels are needed, and at increasing volumes within available blends. The use of advanced biofuels in the transport sector is mandated in the European Renewable Energy Directive (RED II) [6]. Displacing fossil fuels with advanced biofuels could contribute to reducing the carbon intensity of the fuels, with additional potential to improve tailpipe emissions of regulated air pollutants.

RED II mandates the use of advanced biofuels produced from lignocellulosic materials and non-food materials listed in Annex 9 of the directive, where the net CO2 should be less than 50% of the fossil fuel they are displacing [6]. One process that uses Annex 9 materials and produces a potential advanced biofuel blend is acid catalysed alcoholysis [7]. The alcohol used in the alcoholysis dictates the products formed. The use of n-butanol produces blends containing nbutyl levulinate (nBL), n-butanol (nBuOH), and di-nbutyl ether (DNBE), referred to here as butyl blends. Depending on the component fractions, such blends have been shown to remain compliant with fuel standards [7, 8]. These three advanced biofuel components have been tested in several small engine studies with differing results, showing both increases and reductions in legislated emissions. There is an additional need to investigate how such fuel blends will perform during transient operation and in real world applications in vehicles. This study used tailored three-component butyl blends, further blended with diesel, that have been shown to meet selected physical property standard limits, in a Euro 6 diesel hybrid vehicle. The aim was to investigate the

influence of the blend composition on vehicle performance and regulated pollutant emissions.

In previous work, Antonetti et al. [7] studied the utilization of a butyl-based blend representative of the product composition from alcoholysis blended with a EN 590 diesel. The biofuel blend consisted of 70 wt% nBuOH, 20 wt% DNBE, 10 wt% nBL, and this was blended at 10 to 30 vol% with diesel. When these blends were tested in a two-cylinder engine at engine speeds between 1500 - 2500 rpm, the fuel smoke number and carbon monoxide (CO) emissions reduced relative to diesel as the biofuel fraction increased, and the NO<sub>X</sub> (NO+NO<sub>2</sub>) and hydrocarbon (HC) emissions remained similar to those of diesel. However, a blend with this high fraction of *n*BuOH is unlikely to meet the flash point limit of EN 590 [8]. In contrast, Wiseman et al. [9] tested a range of butylblends with diesel, at 10 and 25 vol% biofuel which met the flash point, density, and viscosity limits of BS 2869 and EN 590 [5, 10]. When tested in a singlecylinder generator set (genset) engine at 3000 rpm, the CO and total hydrocarbon emissions increased with increasing nBL and biofuel fractions, whereas the particle number (PN) and fine particulate matter (PM<sub>2.5</sub>) reduced. NO<sub>x</sub> emissions remained similar to those of diesel, primarily due to the longer ignition delays of the biofuel blends increasing the duration of the premixed combustion phase. The work showed that the use of high *n*BL fractions would require more effective emissions control to prevent increases in CO and hydrocarbon emissions relative to diesel. In a vehicle this could be achieved using exhaust aftertreatment systems, or by adjusting injection parameters such as timing, duration, and pressure. The injection pressure in a vehicle will be approximately 10 times that of the injection pressure used in the genset tested, hence improving fuel atomization. This may favor more complete combustion, and thus prevent the increases in engine-out CO and hydrocarbon emissions that were observed in the genset testing [11].

With vehicle emissions limits becoming more stringent with each version of the emissions standards. the after-treatment systems in diesel vehicles have become increasingly complex. The light duty Euro 6 standard set strict limits on NOx, PN, and CO emissions [12, 13]. The control of these required the introduction of catalysts and devices such as selective catalytic reduction (SCR), diesel particulate filters (DPFs), and diesel oxidation catalysts (DOCs) [4, 14]. In addition to the after-treatment systems, exhaust gas recirculation (EGR) is also used to control NOx emissions. The compatibility of existing aftertreatment and emission control systems with the use of advanced biofuel blends needs to be established if such blends are to be used as drop-in low-carbon alternatives to diesel.

There has been a limited number of studies investigating the real-world emissions from diesel hybrid vehicles. Franco et al. [15] conducted realworld testing for three diesel hybrid vehicles, two Euro 5 vehicles and one Euro 6 vehicle, equipped with gas Portable Emissions Measurement System (PEMS) units. The real-world testing and analysis did not follow the RDE methodology, as Franco et al. [15] conducted the testing before the RDE legislation was implemented. The three vehicles tested had a DOC, DPF and EGR installed as standard. The Euro 6 vehicle also had an SCR system. The vehicles used were type approved before the implementation of the RDE. Franco et al. [15] conducted both New European Drive Cycle (NEDC) and Worldwide Harmonized Light Vehicle Test Procedure (WLTP) testing on two of the vehicles, a Euro 5 plug-in hybrid and the Euro 6 vehicle. They found that the on-road emissions NO<sub>X</sub> factors were higher than the emissions limits for the applicable standard for all three vehicles. The NO<sub>x</sub> emissions from the Euro 6 vehicle were 0.52 g/km, 6.5 times the limit of 0.08 g/km. This indicates that the SCR system was not operating efficiently enough to reduce tailpipe NOx emissions on the road, even though the NO<sub>X</sub> emissions were under the limits in the NEDC test for type approval [15]. The CO emissions were all below the 0.5 g/km limit for all vehicles. For the Euro 6 vehicle they reported that the periods of low emissions were those with high electrical motor usage, and the times of high NO<sub>X</sub> emissions occurred during periods of high velocity×acceleration, where the engine load and temperature are highest, producing high concentrations of thermal NOx and thus higher tailpipe NO<sub>X</sub> emissions [15]. With high numbers of Euro 6 vehicles on the road being pre-RDE, there is a high possibility that many of these vehicles have realworld emissions much higher than the emissions limits. Since it is likely that these vehicles will remain in use for many years, reducing emissions through other means such as fuel blending, could be important.

The aim of this study is to assess the influence of biofuel blend composition on the regulated emissions, fuel economy, and after-treatment system performance when tested in a Euro 6 compliant diesel hybrid vehicle.

#### 2. Methodology

Three repeats of the cold start RDE for each fuel blend were conducted. The same driver performed each test to minimize variability due to different driving styles. The vehicle, analyzers, test route, and fuel blends used are outlined in the following subsections. The fuel blends were tested in the vehicle without any changes to the fuel system or engine control parameters.

#### 2.1 Test Vehicle

The vehicle used in this study was a Euro 6b compliant, 2018 Mercedes C300h. It is a diesel hybrid vehicle with a twin turbocharged, common-rail direct injection compression ignition engine. The vehicle specification is summarized in Table 1.

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Fest vehicle specification and charact	eristics.
Description (units)	Value
Year of Registration	2018
Number of Cylinders	4 in-line
Displacement (cm <sup>3</sup> )	2143
Maximum Engine Power (kW)	150
Maximum Torque (Nm)	750
Transmission	7-speed automatic
Electric Motor Power (kW)	20
Hybrid Battery Capacity (kWh)	0.7
After-treatment Systems	DOC, DPF, SCR
Type Approval Test	NEDC
Mileage Pre-Testing (km, approx.)	150,000

Prior to conducting the RDE testing, the existing exhaust and after-treatment was replaced with a second complete exhaust system equipped with k-type thermocouples and sample probes before and after each after-treatment system. The second exhaust system was around 6 months old, and had been used for less than 16,000 km. The original Mercedes exhaust sensors were installed into the second exhaust system.

#### 2.2 Test Route

The RDE compliant route was developed for the city of Leeds, UK, as shown in Fig. 1. To ensure that the correct distances were used for each phase of the RDE, some test sections of the route were repeated. The urban, rural, and motorway sections are determined by vehicle speed and not by GPS location. Hence, the urban section can be achieved by repeating a loop within the appropriate speed limits. The speed ranges for the urban, rural, and motorway sections are 0–60 km/h, 60–90 km/h, and >90 km/h, respectively. The details of the route are summarized in Table 2.



Fig. 1. Map of the test route driven. It does not show sections repeated to achieve the total distance.

Table 2 RDE Test Route Characteristics.

Description (units)	Value
Total Trip Distance (km)	97.2
Urban Distance Share (%)	31.5 - 37.7
Rural Distance Share (%)	29 - 35.6
Motorway Distance Share (%)	29.6 - 35.2
Urban Speed Range (km/h)	0 - 60
Rural Speed Range (km/h)	60 - 90
Motorway Speed Range (km/h)	>90
Average Test Duration	1 hr 54 min
Altitude Range (m)	24 - 103
Cumulative Elevation Gain (m/100km)	563

Cold start RDE tests were conducted and started after rush hour to have free flow traffic, as this is a test requirement [16].

#### 2.3 On-Board Equipment and Analyzers

The vehicle was equipped with an OBS-ONE (Horiba, Japan) gas analyzer and PN unit connected to a C-tube exhaust flow tube. The C-tube had integrated sample probes for the two analyzers, a thermocouple, and high- and low-pressure pitot tubes to determine exhaust flow rate. The PN unit measured solid particles with aerodynamic diameters between 23 nm to 1000 nm, as required for Euro 6 [13]. The emissions, calibrated ranges, and the measurement techniques are summarized in Table 3. A weather station, to measure temperature and relative humidity, was mounted to the rear pillar to be in the flow of air during the RDE. The OBS-ONE logged data at 10 Hz.

Table 3

Measurements conducted using OBS-ONE System [17, 18].

Emission	Measurement	Calibrated	
	Technique	Range	
СО	Non-Dispersive	0 - 10	
	Infrared	vol%	
$CO_2$		0 - 20	
		vol%	
NO <sub>X</sub>	Chemiluminescence	0 - 3000	
		ppm	
PN (23 -	<b>Condensation Particle</b>	$0 - 5 \times 10^7$	
1000 nm)	Counter – Isopropanol	#/cm <sup>3</sup>	
	Working Fluid		
Exhaust	Pitot Flow Meter	0.3 - 10	
Flow Rate		m <sup>3</sup> /min	

Engine control unit (ECU) parameters were logged using a Rebel LT logger (Influx Technologies, UK) connected to the on-board diagnostics (OBD) port. These parameters included engine speed (rpm), engine coolant temperature, and pre- and post-SCR NO<sub>x</sub> concentrations from the two onboard NO<sub>x</sub> sensors. Most channels were logged at 1 Hz, with some logged at higher frequencies due to their rapid fluctuations such as fuel injection mass. A Personal Daq 56 logger (Omega, UK) was used to record the temperature data from the k-type thermocouples installed along the exhaust at 1 Hz.

The total equipment weight, including the batteries used to power the analyzers, was around 300 kg.

# 2.4 Fuel Blend Preparation

The fuel blends were prepared in 20 L batches, using splash blending methods. The required volumes of the fuel components were added to the fuel drums in order of the least to most volatile, sealing the drum between additions to ensure minimal losses of fuel components. The drums were shaken for one minute. The blends were prepared at least 48 hours in advance and were shaken again before use.

The fuel blends tested (Table 4) were selected as they had showed promising performance and emissions when tested in a single-cylinder engine and were found to be compatible with the materials used in the fuel delivery system [9]. This work aims to investigate the influence of the fuel blends on the emissions and performance of a Euro 6 compliant vehicle to determine if they can be used as drop-in fuels. Unlike the genset, the Mercedes incorporates an ECU and after-treatment systems. The diesel (D100) used, was a summer grade EN 590 compliant diesel with 7 vol% biodiesel (Tate Oil). Purities of the model biofuel components were: *n*BL (C<sub>9</sub>H<sub>16</sub>O<sub>3</sub>) (98%, Fisher), DNBE (C<sub>8</sub>H<sub>18</sub>O) (99+%, Fisher), and *n*BuOH (C<sub>4</sub>H<sub>9</sub>OH) (99% extra pure, Fisher).

Table	4
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Fuel Blends Tested with values from [9].

r del Diendis Tested with values from [7].				
Blend	Diesel : Biofuel	<i>n</i> BL: DNBE :	Calculated	
	Ratio (vol%)	nBuOH Ratio	Lower Heating	
		(vol%)	Value (MJ/kg)	
D100	100:0	0	42.5 - 42.9	
D90Bu10	$00 \cdot 10$	65 · 20 · 5	41.4	
-65:5:30	90.10	05.50.5	41.4	
D90Bu10	$00 \cdot 10$		41.1	
- 85:5:10 90.10		<b>85</b> · 10 · 5	41.1	
D75Bu25	75.25	65.10.5	20 0	
- 85:5:10	15:25		30.0	

When the fuel blends were changed, the previous fuel was drained from the vehicle by pumping the fuel out using the fuel hose that was connected to the inlet of the fuel filter. This portion of the fuel system was flushed twice, with 3 L of the new fuel blend being used. Then the fuel tank was filled with the test fuel blend and pumped until the fuel was drawn through. This line was then reconnected, and the vehicle was driven around 20 km to use the remainder of the previous fuel that was in the fuel lines between the fuel filter and the engine.

### 2.5 Data Processing

The 10 Hz OBS-ONE data was processed using the accompanying Horiba post-processing software

following the RDE Package 4 methodology [16]. As part of this analysis, 1 Hz data was generated using the average of the 10 Hz data. The processing gave the emissions factors for each RDE phase and the total RDE, along with the fuel economy determined using a carbon balance method. A CO<sub>2</sub> moving average window (MAW) method was used to ensure test conformity and compliance. The CO<sub>2</sub> window is created using half the CO<sub>2</sub> emitted for each phase of the WLTP. A WLTP test was conducted by Horiba MIRA to acquire the required CO<sub>2</sub> emissions data.

The 1 Hz data from all data loggers was time aligned using the correlation method in the pem.utils R package [19, 20]. The OBS data was used as the base data set with each other logger then aligned to it using the channels summarized in Table 5.

Table 5

Data used for time alignment.

Logger	Data Channel used for Time Alignment
Rebel LT	Exhaust pressure with exhaust mass flow
Daq 56	Pre-SCR thermocouple data

### 3. Results and Discussion

The error bars shown on each plot represent one standard deviation across the three tests conducted.

### 3.1 Drivability and Fuel Economy

When using the biofuel blends there were no discernible differences in drivability during the RDE tests. The engine and ECU were able to cope with the additional oxygen content in the fuel, as well as changes in density, and cetane number due to the presence of the biofuel components.

Fuel economy was defined as the number of liters of fuel required to complete 100 km. The average fuel economy values for the cold RDE tests and the relative changes are displayed in Fig. 2.



Fig. 2. Comparison of C300h fuel economy for each fuel blend tested.

The fuel economy of each fuel tested showed a maximum of 5% increase compared to diesel in the

vehicle tests. When the same fuels were tested in a genset, the brake specific fuel consumption increased by up to 11% compared to diesel when the genset engine was under load [9]. There are likely to be several contributing factors for these differences. For example, the high fuel injection pressures in the C300h (1988 bar) compared to the genset (196 bar) would improve fuel atomization and thus combustion. In fact, the reduction in the fuel's energy content has not had a significant impact on the fuel economy. D75Bu25 - 85/10/5 has a lower heating value which is 9% lower than that of diesel (Table 4), but only showed a 3% increase in fuel consumption. Therefore, these oxygenated biofuels can be blended to a significant fraction with diesel without a significant reduction in fuel economy.

# 3.2 Influence of Biofuel Blends on CO Emissions

Addition of the biofuel blends caused the CO emissions to reduce in each of the RDE sections and overall, as shown in Fig. 3. The emissions were all below the Euro 6 limit of 500 mg/km.



Fig. 3. Comparison of CO emissions from C300h for each RDE section with each fuel blend tested and comparisons to the Euro 6 limit.

The total CO emissions were reduced by 51%, 70%, and 72% relative to diesel, for D90Bu10 -65/30/5, D90Bu10 - 85/10/5, and D75Bu25 -85/10/5, respectively. The reduction for the CO emissions in each section were similar to the total reduction when using D75Bu25 - 85/10/5, showing it had a benefit at all engine loads and vehicle speeds. Although the changes in CO emissions were not statistically significant at a 95% confidence level (mostly due to the large variability in CO emissions during the diesel tests and a small sample size of three), the test data indicates reductions in the different RDE sections (Fig. 3). The reduction in CO correlated with the biofuel fraction, as D75Bu25 -85/10/5 had a greater reduction in tailpipe CO compared to the other blends. Since all emissions were measured at the tailpipe, the emissions control from the DOC would require further testing to

determine if it had operated at a constant efficiency with each fuel blend. It is likely that the addition of the biofuel blends had a direct influence on the CO formation during combustion, as Antonetti et al. [7] observed reductions in CO emissions when testing similar biofuel blends in a small engine. The reduction in CO emissions from the vehicle was likely due to the increased oxygen content in the fuel, combined with the high fuel injection pressure used in common rail diesel engines [11]. This is evident when comparing the changes in CO emissions from a single cylinder engine, where the fuel injection pressure is around ten times lower than in the Mercedes, and CO emissions more than doubled for the high *n*BL blends compared to diesel [9]. The increased atomization of the oxygenated biofuel blends will favor complete combustion, hence reducing the CO emissions relative to diesel. Reductions in CO emissions would be beneficial for air quality and for public health, as exposure to CO would be reduced [4, 21].

# 3.3 Influence of Biofuel Blends on PN Emissions

The PN emissions from the C300h were below the Euro 6 limit of  $6 \times 10^{11}$  #/km for all fuel blends tested [12]. In an analogous manner to the CO emissions, the total PN emissions were reduced upon addition of the biofuel blends, as shown in Fig. 4. For the two Bu10 blends, there were slight increases in the average PN emissions during the rural and motorway phases relative to diesel. However, when accounting for the standard deviations, there are no discernible differences between the Bu10 blends and diesel, which could be due to the DPF effectiveness with all the fuels. During the urban phase of the RDE the DPF is less effective. Therefore, the reductions are likely due to lower engine out PN due to the addition of the biofuel blends.



Fig. 4. Comparison of PN emissions from C300h for each RDE section with each fuel blend tested. Error bars are one standard deviation from the three repeats.

The average total PN emissions were reduced by 13%, 14%, and 57% relative to diesel, for D90Bu10 –

65/30/5, D90Bu10 – 85/10/5, and D75Bu25 – 85/10/5, respectively. The largest reductions were in the urban phase, with a 69% reduction for D75Bu25 – 85/10/5. The reductions in the urban phase and total emission factor for D75Bu25 – 85/10/5 were statistically significant. Reductions in the PN emissions will be beneficial for air quality, particularly in an urban setting [4, 21].

The reduction in PN is likely due to a combination of factors, including the increased oxygen presence favoring complete combustion, and a reduced fuel net aromatic content, which would reduce the formation of particle precursors [7, 9]. The reductions in PN were expected, as when the three biofuel blends were tested in a genset engine, the total PN and PM2.5 were reduced by up to 85% and 58%, respectively, for D75Bu25 - 85/10/5 compared to diesel when the engine was under load [9]. The reductions in the RDE were not as high as observed in the genset testing, but this could be due to the OBS-ONE measuring solid particles, and not total PN. However, the studies by Wiseman et al. [9] and Antonetti et al. [7] demonstrated that total PN, PM2.5, and fuel smoke number reduced when using these fuel blends in gensets. Therefore, the reductions from a vehicle under transient operation conditions was expected.

# 3.4 Influence of Biofuel Blends on NO<sub>X</sub> Emissions

The RDE emissions for diesel and the biofuels are over the Euro 6 limit for NO<sub>X</sub> (Fig. 5). This is due to the limits being set for the WLTP laboratory-based test, which is not fully representative of real-world driving. Hence, another factor, the conformity factor (CF), was introduced. The applicable CF value for a pre-RDE vehicle is 2.1, resulting in a not-to-exceed (NTE) limit of 168 mg/km, as shown by the blue line in Fig. 5 [12]. The total NO<sub>X</sub> emissions when using D75Bu25 - 85/10/5 exceeded the 168 mg/km limit, but they are within one standard deviation of it. NO<sub>X</sub> emissions from the C300h increased relative to diesel upon the addition of the biofuel blends. The total NO<sub>X</sub> emissions increased by 13%, 12%, and 26% relative to diesel, for D90Bu10 - 65/30/5, D90Bu10 -85/10/5, and D75Bu25 - 85/10/5, respectively. The increases in NO<sub>X</sub> emissions were not statistically significant at a 95% confidence level, likely due to the small sample size. The results in Fig. 5 indicate that there needs to be better NOx control, especially for motorway driving where NO<sub>X</sub> emissions were highest for all fuel blends. Addition of the biofuel blends to diesel and their use in this vehicle could result in compliance to the emissions limits when accounting for the variability. However, the increases in NOx for the biofuel blends do indicate that more effective emissions control strategies may be needed for these blends since the emissions control strategy was likely to have been optimized around using diesel as a fuel.



Fig. 5. Comparison of  $NO_X$  emissions from C300h for each RDE section with each fuel blend tested and comparisons to the Euro 6 limit and the 2018 CF.

The increases in NO<sub>X</sub> align with reductions in PN and CO, indicating that there is a soot-NO<sub>X</sub> trade-off for the biofuel blends [22]. Fewer local rich zones within the engine, would lead to a reduction in particle formation. This may also lead to an increase in combustion temperatures, and thus increased thermal NO<sub>X</sub> production [22]. However, the exhaust gas temperatures did not significantly increase with the addition of the biofuel. A comparison between diesel and D75Bu25 – 85/10/5 is shown in Fig. 6. Therefore, this indicates that the SCR system was not as efficient at removing the NO<sub>X</sub> emissions when using the biofuel blends compared to when running with diesel.

To determine the influence of the biofuel blends on the engine out NO<sub>X</sub> emissions, the NO<sub>X</sub> emissions factor before AdBlue (the SCR reductant) was injected was compared to NO<sub>X</sub> emissions for the same duration following AdBlue injection during the urban phase of the RDE. Fig. 7 shows that D75Bu25 – 85/10/5 had lower average NO<sub>X</sub> emissions over all three RDE test than diesel before AdBlue was injected. The influence of the addition of AdBlue can be seen in Figs. 6a&b for an example single trip when using diesel and D75Bu25 – 85/10/5. The NO<sub>X</sub> concentration clearly reduces following the injection of AdBlue, as shown in Fig. 6 by the green lines, where the blue lines indicate the requested AdBlue amount.

The NO<sub>X</sub> emissions before the SCR system was activated were 11% and 7.4% of total NO<sub>X</sub> emissions for diesel and D75Bu25 – 85/10/5, respectively. Additionally, even though there was less NO<sub>X</sub> produced with the biofuel blend, the mass of NO<sub>X</sub> removed once AdBlue was injected was lower compared to that when using diesel: 65% removal for the D75Bu25 – 85/10/5 blend compared to 71% removal for diesel. This indicates that the SCR was not as efficient at removing NO<sub>X</sub> when using the biofuel blends compared to when running with diesel. There may, therefore, be a need to optimize the SCR system operation, which could include optimization of the catalyst and the AdBlue injection strategy when running with the biofuel blends used in this study.



Fig. 6. Influence of AdBlue on NO<sub>X</sub> emissions during the starts of a cold start RDE test for a - D100 and b - D75Bu25 - 85/10/5.



Fig. 7. Comparison of  $NO_x$  emissions with and without AdBlue when the duration of AdBlue was the same as having no AdBlue present for D100 and D75Bu25 – 85/10/5.

Since the NO<sub>X</sub> emissions before AdBlue injection are a significant fraction of the total NO<sub>X</sub> emitted during the test, there is an indication that the use of an SCR catalyst that is active at lower temperatures, would enable lower NO<sub>X</sub> emissions during this phase of driving [23]. Such a catalyst would need to have sufficient onboard ammonia storage capability to ensure a sufficient reductant concentration was present before AdBlue injection [11]. During cold start periods reducing NO<sub>X</sub> emissions would be beneficial for air quality, as most cold start driving starts in residential areas [4, 21].

#### 4. Conclusions

The study has shown the potential of advanced biofuel blends produced using alcoholysis processes as drop-in fuels for an existing vehicle. The butyl blends tested could be used without any engine modification with only a small fuel economy penalty of 3% for the 25 vol% biofuel, and 5% for D90Bu10 – 65/30/5 relative to D100. There were no noticeable differences to the vehicle drivability during the RDE when using the biofuel blends compared to diesel.

Whilst there were changes in tailpipe emissions, it is pertinent that this vehicle was developed to operate with diesel, with after-treatment strategies potentially optimized around that fuel. This may be the reason for increased NO<sub>x</sub>, but reduced CO and PN emissions, whilst maintaining fuel economy. The reduction in PN, even with the DPF, highlights that the additional oxygen content and the net reduction in the fuel aromatic content was likely to have contributed to the reduction of PN, as well as CO. However, the increased NO<sub>X</sub> relative to diesel would require increased control or optimization for the SCR reagent injection strategy. This may require more resilient SCR catalysts that can maintain performance whilst using the biofuel blends studied, since the fraction of NOx removed following AdBlue injection was lower with D75Bu25 - 85/10/5 than it was for diesel.

Ensuring that fuel blends were within the physical property limits for diesel and were compatible with fuel system materials ensured safe operation and reduced the likelihood of fuel system faults. This was evident by driving over 600 km on each fuel blend without any issues.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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