

# Evaluation of the NO<sub>x</sub> emissions from heavy-duty diesel engines with the addition of cetane improvers

J Nuskowski\*, R R Tincher, and G J Thompson

Center for Alternative Fuels, Engines, and Emissions, Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, West Virginia, USA

*The manuscript was received on 5 January 2009 and was accepted after revision for publication on 29 April 2009.*

DOI: 10.1243/09544070JAUTO1114

**Abstract:** The exhaust emissions from heavy-duty diesel engines (HDDEs) contribute to the degradation of ambient air quality; therefore, environmental agencies have created stringent emissions standards. Since the implementation of these standards, overall engine and fuel technology improvements have created a significant reduction in emissions. This study was completed in order to evaluate oxides of nitrogen (NO<sub>x</sub>) emissions from fuels with and without cetane-improving additives in recent and early production electronically controlled HDDEs. Five engines spanning the model years from 1991 to 2004 were tested using the Federal Test Procedure (FTP) dynamometer cycle with both petroleum-based diesel and B20 as the neat fuel. It was found that the additives had the most impact on reducing emissions at low engine powers, but the engine power range with an NO<sub>x</sub> benefit varied between engines. The cetane improvers were found only to reduce NO<sub>x</sub> below a cylinder gas density of 35 kg/m<sup>3</sup> at top dead centre. The lower compression ratio of the 1992 DDC S60 engines reduced the cylinder gas density and provided a larger optimal operating range for the cetane improvers. The cetane improvers reduced NO<sub>x</sub> at low engine powers and cylinder gas density for the B20 fuel but were less effective than for the neat petroleum fuels.

**Keywords:** diesel fuel, additives, cetane improver, nitrogen oxides (NO<sub>x</sub>), emissions, heavy-duty diesel engine

## 1 INTRODUCTION

With ever-increasing concerns about the contribution of heavy-duty diesel engine exhaust constituents, the Environmental Protection Agency (EPA) has created a strict set of emissions regulations from these engines. The regulated diesel emissions include hydrocarbons (HCs), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), particulate matter (PM), and non-methane hydrocarbons (NMHCs). EPA heavy-duty diesel engine emission standards for model years 1988 to 2010 are listed in Table 1 for engines being tested over the transient Federal Test Procedure (FTP) engine dynamometer cycle [1]. The

years from 2007 to 2010 are a phase-in period for NO<sub>x</sub>. In October 1998, a court settlement between the EPA, California Air Resources Board, Department of Justice, and the major diesel engine manufacturers was reached on the issue of high NO<sub>x</sub> emissions during certain driving modes [2]. As a result, the 2004 emissions standards were moved to October 2002.

Through combined technology improvements in both engine design and fuel processing, a significant reduction in exhaust emissions has been possible. In order for future engines to reach the near-zero emissions mark, external engine technologies will need more development. These external technologies include after-treatment systems, turbocharger design, exhaust gas recirculation (EGR), and diesel particulate traps. Although engine technologies have a greater effect on emissions levels than fuel quality and properties do, the fuel does have an influence on the emissions level generated by the engine.

\*Corresponding author: Center for Alternative Fuels, Engines, and Emissions, Department of Mechanical and Aerospace Engineering, West Virginia University, Engineering Science Building, Morgantown, WV 26506-6106, USA.  
email: john.nuskowski@mail.wvu.edu

**Table 1** EPA heavy-duty diesel engine emissions standards [1]

Year	Emissions (g/kWh)					
	HCS	CO	NO <sub>x</sub>	PM	NMHCs + NO <sub>x</sub>	NMHCs
1988	1.74	20.79	14.35	0.80	N/A*	N/A*
1990	1.74	20.79	8.05	0.80	N/A*	N/A*
1991	1.74	20.79	6.71	0.34	N/A*	N/A*
1994	1.74	20.79	6.71	0.13	N/A*	N/A*
1998	1.74	20.79	5.36	0.13	N/A*	N/A*
2004 <sup>†</sup> (option 1)	1.74	20.79	N/A*	0.13	3.22	N/A*
2004 <sup>†</sup> (option 2)	1.74	20.79	N/A*	0.13	3.35	0.67
2007–2010	1.74	20.79	0.27	0.01	N/A*	0.19

\*N/A, not applicable.

<sup>†</sup>2004 was moved to October 2002.

Despite having a multitude of experimental data, the influence of the fuel properties on regulated emissions is still not clear [3]. The properties of diesel fuels that influence emissions are usually intercorrelated, which means care must be taken to separate the fuel property changes in the test fuel. If multiple fuel properties are changed simultaneously, then it is difficult to pinpoint an exact fuel property to an emission change. Techniques such as non-linear regression and neural network modelling can be used to help to find the effect of changing fuel properties on engine emissions.

The main objective of this study was to evaluate engine emissions with and without cetane-improving additives on recent and early electronically controlled heavy-duty diesel engines (HDDEs). These engines are of interest since their lifetime can be 10–20 years and are the high polluters that are the major contributors to the atmospheric loading of PM and NO<sub>x</sub>. The chosen engines were tested using the heavy-duty engine FTP dynamometer cycle. The study examined how the changes in fuel properties due to different fuel additives made an impact on the emissions from older and newer electronically controlled engines. One base fuel was a biodiesel B20 blend, which consisted of 20 vol% soy-derived biodiesel fuel and 80 vol% petroleum diesel fuel. The two other base fuels were petroleum diesel fuels.

## 2 REVIEW OF THE LITERATURE

Environmental considerations and emissions legislation have both highly influenced current formulation and properties of fuels. In order to have a low-emission diesel engine, the interaction between engine technologies, fuel quality, and emissions needs to be well understood [3]. It is fairly evident that improvements in engine technology have a greater impact on reducing emissions than fuel modification does [4].

Standards specify the requirements placed on diesel fuels, such as the ASTM D975 in USA, EN 590 in the European Union, and JIS K2204 in Japan [5]. The most important parameters specified within these standards that also influence emissions include density or specific gravity, cetane number, distillation temperatures, sulphur content, and aromatics. Research has shown that NO<sub>x</sub> and PM both respond to changes in cetane number and aromatic content [6]. A reduction in aromatic content leads to a reduction in NO<sub>x</sub> and PM, while an increase in cetane number tends to decrease NO<sub>x</sub> emissions. When varying the fuel properties, some studies have found that engine calibration changes in EGR rate and injection timing occur and have significant effects on emissions [7, 8]. Therefore, when studying the emission effects of changing fuel properties, the EGR rate and injection timing should be held constant between fuels. With a denser fuel, the start of injection occurs earlier because of the compressibility (bulk modulus) of the fuel [9] and this earlier start of injection (advanced engine timing) may increase the NO<sub>x</sub> emissions [9]. This effect is more pronounced with pump-line-nozzle fuel injection and the five engines tested utilized unit injectors, which minimize any bulk modulus effects.

Diesel fuels require certain properties to be sold for on-road heavy-duty diesel engines. As the requirements for fuel properties change, fuel suppliers can use fuel additives to obtain these properties without refinery modification. Some types of fuel additive are ignition, oxygenate, lubricity, combustion, flow, wax anti-settling, anti-foam, detergents, and anti-corrosion. During a study conducted by Shih [10], several fuel additives were investigated: ethylhexyl nitrate, di-tertiary butyl peroxide (DTBP), methyl *tert*-butyl ether, dichloromethane, diglyme, monoglyme, and ethanol. It was shown that these additives can have a large impact on the spray penetration of the fuel, air-fuel mixing process, ignition delay, chemical reaction rates, and heat release. Some of the additives had a positive effect on the reduction of regulated

emissions, but not necessarily all the constituents. It is known that there is an optimized dosage for each of these additives in order to reduce emissions. Two common ignition improver (or cetane improver) additives are a nitrate-based 2-ethylhexyl nitrate (2-EHN) and peroxide-based additive (DTBP). Previous diesel emission studies have shown mixed results of NO<sub>x</sub> reduction using 2-EHN or DTBP with some having up to 8 per cent reduction in NO<sub>x</sub> [11, 12] and with others showing no benefit [13] or an increase in NO<sub>x</sub> [14]. McCormick *et al.* [15] effectively blended biodiesel with DTBP and 2-EHN to reduce NO<sub>x</sub> and to maintain the PM emissions reduction from the use of biodiesel over its neat petroleum diesel on a 1991 Detroit Diesel Corporation (DDC) series 60 engine, while a 2002 Cummins ISB and 2003 DDC series 60 [16] had no effect on NO<sub>x</sub> when adding 2-EHN to B20.

There have been many suggestions for diesel fuel alternatives, such as vegetable oils and animal fats. The common sources of oil include soybean, rape, sunflower, coconut, palm, and used frying oil, but methods have also been developed to make biodiesel from such exotic materials as oils produced by certain species of algae [17]. Since biodiesel is renewable and a potential greenhouse gas-emissions-reducing fuel, it is one of the most attractive alternative fuels available. High prices present a barrier for a widespread use of biodiesel [3]. Since pure biodiesel can be up to twice the price of petroleum diesel, it can be blended with petroleum diesel. The most common blend in the USA is 20 vol % biodiesel and 80 vol % petroleum diesel, which is usually referred to as B20 [5].

Some of the characteristics of biodiesel, such as high cetane numbers and low sulphur levels, are advantageous; low heating value and operability problems at low ambient temperatures, especially from saturated feedstocks such as beef tallow and palm oil, are some of the drawbacks [5]. An almost sulphur-free biodiesel is attainable through vegetable oils, whereas animal-based biodiesel can contain small amounts of sulphur. Biodiesel is also biodegradable, which is advantageous from an environmental standpoint (fuel spills), but can be a drawback for engine use. A high concentration of biodiesel means the fuel is more susceptible to degradation and water absorption [3].

There is wide agreement in the literature that both biodiesel and blends of biodiesel have a decreased amount of CO and HCs [3]. This is mostly due to the high oxygen content, which allows for more complete oxidation in the combustion chamber. NO<sub>x</sub>

emissions have been attributed to the higher oxygen content with a biodiesel [18, 19]. Szybist and Boehman [20] observed a crank angle shift of 1° in the injection timing between pure diesel and pure biodiesel with an advance in ignition of up to 4° crank angle, which will influence emissions. The higher bulk modulus of compressibility for biodiesel, which affects the speed of sound, has been shown to create the advanced injection timing [21]. Cheng *et al.* [22] suggested that a higher flame temperature, which will increase NO<sub>x</sub> emissions, is created by a reduction in the radiation heat transfer due to the reduced particulate emissions for biodiesel fuel. A study by Ban-Weiss *et al.* [23] attributed the slight NO<sub>x</sub> increase for biodiesel to the higher degree of unsaturated HCs in biodiesel. Unsaturated HCs, which have more double bonds, were shown to have a higher adiabatic flame temperature than similar saturated HCs. Typically, owing to the lower energy content of biodiesel, the engine power output is reduced. The power output decreases as the percentage of biodiesel in the fuel increases.

### 3 EXPERIMENTAL SET-UP

The experimental procedures used in performing this study were conducted at the Center for Alternative Fuels, Engines, and Emissions (CAFEE) at West Virginia University which operates in compliance with Title 40 CFR Part 86, Subpart N and the standards set by ISO 8178 [1]. Five engines, namely 1991 DDC S60, 1992 DDC S60, 1992 rebuilt DDC S60, 1999 Cummins ISM 370, and 2004 Cummins ISM 370, were chosen for this study in order to represent a wide spectrum of engine technologies from the CAFEE inventory. In addition, all these engines were rated at approximately 275 kW, allowing a comparison between the engine technologies to be made while holding at least one variable constant. The specifications for these engines can be found in Table 2. The 1991 DDC series 60 engine was turbocharged and had direct injection. This engine was rebuilt to original DDC specifications to meet the EPA emissions standards for 1991. Two 1992 DDC series 60 engines were used for this study. One of the 1992 DDC series 60 engines was rebuilt to manufacturer specifications. This engine will be identified as the 1992 rebuilt DDC series 60 in this study. Two (1999 and 2004) Cummins ISM 370 engines were used to analyse more modern engine technology. The 1999 Cummins ISM 370 engine was turbocharged and had direct injection. The 2004 Cummins ISM 370 engine was similar to the 1999

Table 2 Engine specifications

Engine manufacturer	Engine model	Year	Configuration	Displacement (l)	Power rating (kW)	Torque rating (N m)	Compression ratio	Bore (mm)	Stroke (mm)	Air handling	EGR
DDC	Series 60	1991	Inline six cylinder	11.1	257 at 1800 r/min	1810 at 1200 r/min	16:1	130	139	Turbocharged, after-cooled	N/A
DDC	Series 60	1992	Inline six cylinder	12.7	272 at 1800 r/min	1966 at 1200 r/min	15:1	130	160	Turbocharged, after-cooled	N/A
DDC	Series 60 (rebuild)	1992	Inline six cylinder	12.7	265 at 1800 r/min	1912 at 1200 r/min	15:1	130	160	Turbocharged, after-cooled	N/A
Cummins	ISM 370 ESP	1999	Inline six cylinder	10.8	276 at 2100 r/min	1830 at 1200 r/min	16.3:1	125	147	Turbocharged, after-cooled	N/A
Cummins	ISM 370	2004	Inline six cylinder	10.8	276 at 2100 r/min	1966 at 1200 r/min	16.1:1	125	147	Turbocharged, after-cooled, VGT	Cooled EGR

Cummins ISM 370 with the exception of a variable-geometry turbocharger (VGT) and cooled EGR.

A full-scale dilution tunnel was used in order to measure the effects of exhaust emissions on a simulated real-world environment. A critical flow venturi was used as the method of measuring the diluted exhaust. The dilute exhaust analysers consisted of a Rosemount analytical model 402 heated flame ionization detector, Rosemount model 955 chemiluminescence detector, Horiba model AIA-210LE non-dispersive infrared (NDIR) analyser, and Horiba model AIA-210 NDIR analyser to measure total hydrocarbons, NO<sub>x</sub>, CO, and carbon dioxide (CO<sub>2</sub>), respectively. An Eco Physics CLD 844 CM h was used as a secondary NO<sub>x</sub> analyser for quality assurance purposes. The PM was gravimetrically measured in accordance with Title 40 CFR Part 86 Subpart N requirements using proportional sampling of the diluted exhaust through a pair of Pallflex 70 mm diameter model T60A20 fluorocarbon-coated glass microfibre filters in series. For fuel measurement, a carbon balance, fuel meter, and gravimetric methods were used to determine the amount of fuel consumed for quality assurance purposes.

Three base fuels were used over the duration of this project, which included two No. 2 diesel fuels and one biodiesel blend (B20). The No. 2 diesel fuels included were fuel A and fuel B (Table 3). The biodiesel blend (fuel C) was prepared by blending 80 vol% of fuel B and 20 vol% of a soy-derived biodiesel. The full fuel analysis for each of the test fuels is located in Table 3 with the ASTM methods used to analyse each property. Although the petroleum fuels, fuels A and B, were similar with cetane numbers of 51.7 and 49.2 respectively, fuel B had a higher sulphur content (340.7 wtppm) and higher aromatic content (34.2 per cent) compared with fuel A (3.7 wtppm and 27.1 per cent).

Two different diesel additives were used throughout the duration of the study in order to create different additive blend ratios of the base fuel. Each of the additives was known as a cetane improver, which reduced the ignition delay time to provide proper starting, smooth operation, and efficient combustion [5]. The additive fuel blends were mixed prior to the start of testing. The two additives were 2-EHN and DTBP.

#### 4 RESULTS AND DISCUSSION

The primary petroleum fuel was fuel A, which was tested on all three DDC engines and the 1999 Cummins engine. Fuel B was the base petroleum

**Table 3** Neat fuel analysis

Test method	Fuel property	Units	Value for the following		
			Fuel A	Fuel B	Fuel C (B20)
D613	Cetane number	—	51.7	49.2	51.1
D4052s	Density at 15 °C	kg/m <sup>3</sup>	833.5	848.1	855.6
D445 40c	Viscosity	mm <sup>2</sup> /s	2.47	2.69	2.96
D5186	Total aromatics	wt %	27.1	34.2	27.4
	Monoaromatics	wt %	21.2	24.8	19.8
	Polyaromatics	wt %	5.9	9.4	7.5
D5291	Carbon	wt %	85.9	86.8	84.8
	Hydrogen	wt %	13.2	13.0	12.9
	Oxygen	wt %	0.00	0.00	1.96
	Hydrogen-to-carbon ratio	—	1.84	1.79	1.81
	Oxygen-to-carbon ratio	—	0.000	0.000	0.017
D4629	Nitrogen	wtppm	6.4	70.6	39.9
D5453	Sulphur	wtppm	3.7	340.7	254.1
D86	Initial boiling point	°C	176.1	179.4	195.7
	5%	°C	190.5	198.0	214.5
	10%	°C	203.7	212.6	229.5
	15%	°C	210.9	222.2	237.9
	20%	°C	219.1	230.8	244.2
	30%	°C	233.6	245.1	256.3
	40%	°C	246.5	256.4	267.0
	50%	°C	256.8	265.9	277.7
	60%	°C	266.7	275.4	290.5
	70%	°C	276.4	286.7	304.5
	80%	°C	288.2	300.9	318.8
	90%	°C	305.4	320.0	331.3
	95%	°C	320.8	333.7	338.4
	Final boiling point	°C	338.1	346.8	347.9
	Recovered	ml	98.3	98.6	98.3
	Residue	ml	0.1	0.5	0.5
	Loss	ml	1.6	0.9	1.2
D93	Flash point	°C	67.8	70.6	82.8
West Virginia University	Lower heating value	MJ/kg	42.49	42.54	41.50

fuel for the 2004 Cummins engine tests and the base component for the B20 fuel (fuel C). The B20 biodiesel blend (fuel C) was tested on only the two Cummins engines and the rebuilt 1992 DDC S60 since there was a limited supply available. The test matrix for the tested fuels and engines is seen in Table 4. The table shows which fuels and additive concentrations were completed for each. It is noted that not every fuel–additive combination was tested on each engine. There were two reasons why this occurred. First, there were limited quantities of fuel and test cell time. Second, additional additives or additive concentrations were added as the testing progressed on the basis of knowledge gained throughout the campaign. As a result of these two reasons, the test matrix was filled in to provide the widest range of fuels and additives possible.

The transient FTP test was chosen for analysis since heavy-duty diesel engines used in on-road vehicles are tested and certified in the USA using the FTP and supplemental emissions test engine test cycles. It is noted that engine manufacturers are now required to perform in-use emissions testing. The FTP is the transient test cycle used to certify HDDEs and to analyse the emissions formed to simulate

on-road driving conditions in the USA. The test cycle includes four main segments: New York non-free-way, Los Angeles non-freeway, Los Angeles freeway, and a repeat of the New York non-freeway. The first and fourth segments represented light urban traffic with frequent stops and starts. The second segment represented crowded urban traffic with very few stops, and the third segment represented crowded freeway traffic [1, 3]. For each fuel evaluation, three repeat hot-start FTP tests were conducted to obtain an average value and some indication of run-to-run variation.

#### 4.1 NO<sub>x</sub> emissions

With the use of cetane improvers, the brake specific NO<sub>x</sub> emissions over the FTP tests showed significant reductions of 1.0 per cent, 3.5 per cent, 3.2 per cent, and 1.9 per cent for the 1991 DDC engine, 1992 DDC engine, rebuilt 1992 DDC engine, and 1999 Cummins engine respectively (Table 5). The 2004 Cummins engine had a significant increase in the brake specific NO<sub>x</sub> emissions of 1.3 per cent with the addition of 0.32 vol % 2-EHN and had no significant difference from 0.16 vol % 2-EHN and 0.26 vol %

**Table 4** Fuels examined for each test engine

Base fuel	Additive	Fuels examined*				
		1991 DDC S60	1992 DDC S60	1992 rebuilt DDC S60	1999 Cummins ISM 370	2004 Cummins ISM 370
Fuel A	None	X	X	X	X	—
	0.16 vol % 2-EHN	—	—	—	X	—
	0.21 vol % 2-EHN	X	—	X	—	—
Fuel B	0.26 vol % DTBP	X	X	X	X	—
	None	—	—	X	X	X
	0.16 vol % 2-EHN	—	—	—	—	X
	0.32 vol % 2-EHN	—	—	—	—	X
	0.40 vol % DTBP	—	—	—	—	X
Fuel C (B20)	None	—	—	X	X	X
	0.16 vol % 2-EHN	—	—	—	X	—
	0.26 vol % DTBP	—	—	—	X	X

\*X, tested fuels; —, non-tested fuels.

DTBP. Significant differences were determined with a Student *t* test at a *p* value of 0.95. The concentration levels of 2-EHN and DTBP added were determined on the basis of experience with these additives to obtain similar brake specific NO<sub>x</sub> emissions between the two cetane improvers.

Typically, when a transient test cycle is studied, only the integrated brake specific emissions are reported. For this study an additional approach was taken to give a more complete indication of the emission effects throughout the whole test cycle. The

effectiveness of each fuel additive was studied by creating an NO<sub>x</sub> percentage difference with respect to their neat fuel comparison as a function of engine power. To create the NO<sub>x</sub> percentage difference, the continuous NO<sub>x</sub> mass emission rate from each FTP test was averaged and time shifted to match the power curve, since the analysers measure the emissions with a time delay. Then, a sixth-order polynomial was fitted between engine power and the NO<sub>x</sub> emissions rate to obtain an empirical relation (Fig. 1). The engine power was normalized by the

**Table 5** Integrated brake specific NO<sub>x</sub> over the FTP cycle

Base fuel	Additive	Parameter	Value for the following*					
			1991 DDC S60	1992 DDC S60	1992 rebuilt DDC S60	1999 Cummins ISM 370	2004 Cummins ISM 370	
Fuel A	None	NO <sub>x</sub> (g/kWh)	5.98	6.81	6.77	5.24	—	
		0.16 vol %	NO <sub>x</sub> (g/kWh)	—	—	—	5.14	—
		2-EHN	Difference (%)	—	—	—	−1.9	—
	0.21 vol %	<i>p</i>	—	—	—	0.0000	—	
		2-EHN	NO <sub>x</sub> (g/kWh)	5.93	—	6.55	—	—
		Difference (%)	−0.9	—	−3.2	—	—	
	0.26 vol %	<i>p</i>	0.0125	—	0.0006	—	—	
		DTBP	NO <sub>x</sub> (g/kWh)	5.92	6.57	6.56	5.15	—
		Difference (%)	−1.0	−3.5	−3.2	−1.8	—	
	Fuel B	None	<i>p</i>	0.0077	0.0003	0.0009	0.0010	—
0.16 vol %			NO <sub>x</sub> (g/kWh)	—	—	6.88	5.41	3.15
2-EHN			NO <sub>x</sub> (g/kWh)	—	—	—	—	3.17
0.32 vol %		Difference (%)	—	—	—	—	0.5	
		2-EHN	<i>p</i>	—	—	—	—	0.2170 <sup>†</sup>
		Difference (%)	—	—	—	—	3.20	
0.40 vol %		Difference (%)	—	—	—	—	1.3	
		DTBP	<i>p</i>	—	—	—	—	0.0238
		Difference (%)	—	—	—	—	3.17	
Fuel C (B20)		None	Difference (%)	—	—	—	—	0.4
	0.16 vol %		<i>p</i>	—	—	—	—	0.3759 <sup>†</sup>
	2-EHN		NO <sub>x</sub> (g/kWh)	—	—	6.90	5.53	3.32
	0.26 vol %	NO <sub>x</sub> (g/kWh)	—	—	—	5.50	—	
		DTBP	Difference (%)	—	—	—	−0.6	—
		p-value	—	—	—	0.0259	—	
	0.26 vol %	NO <sub>x</sub> (g/kWh)	—	—	—	5.47	3.24	
		DTBP	Difference (%)	—	—	—	−1.0	−2.5
		p-value	—	—	—	0.0113	0.0302	

\*—, non-tested fuels.

<sup>†</sup>No significant difference at a 95 per cent confidence level.

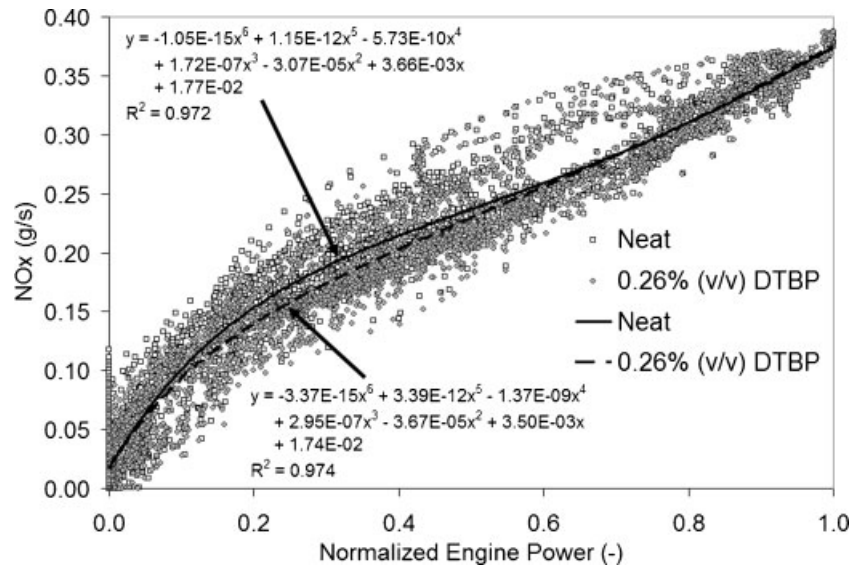


Fig. 1 NO<sub>x</sub> trend lines for 1992 rebuilt DDC S60

maximum power achieved during the FTP test. The sixth-order polynomials from the tested fuel with and without cetane improver were then used to find the NO<sub>x</sub> percentage difference as a function of the normalized engine power (Fig. 2). A negative percentage difference is an NO<sub>x</sub> reduction and a positive percentage difference is an NO<sub>x</sub> increase based on the neat fuel emissions levels. The bars shown in Figs 2 to 7 are the 95 per cent confidence interval, which is from the three repeat FTP tests for each fuel. The  $R^2$  value between NO<sub>x</sub> mass emissions and engine power was typically greater than 0.9 for the DDC engines and the 1999 Cummins engine. The 2004 Cummins engine had an  $R^2$  range of 0.81–0.84, which was lower than the other engines owing to the influence of the changing EGR rate at different engine powers over an FTP test.

DTBP and 2-EHN behaved similarly in the same engine. Figures 2 and 3 display the effect of adding DTBP and 2-EHN respectively to their respective petroleum neat fuel for all five engines. The bars represent the 95 per cent confidence interval of the curve fitted from the three FTP tests. For all five engines, the NO<sub>x</sub> reduced on the addition of DTBP and 2-EHN at low engine powers and had an NO<sub>x</sub> increase or no change at high engine powers. The engine power at which the NO<sub>x</sub> changed from a reduction to an increase or no change varied between the five engines. The 1992 DDC engines changed at a normalized engine power of 0.74–0.76. The NO<sub>x</sub> change occurred at a lower normalized engine power of 0.51–0.58 for the 1991 DDC engine. The increased engine power range where an NO<sub>x</sub> reduction occurs with the 1992 DDC engines res-

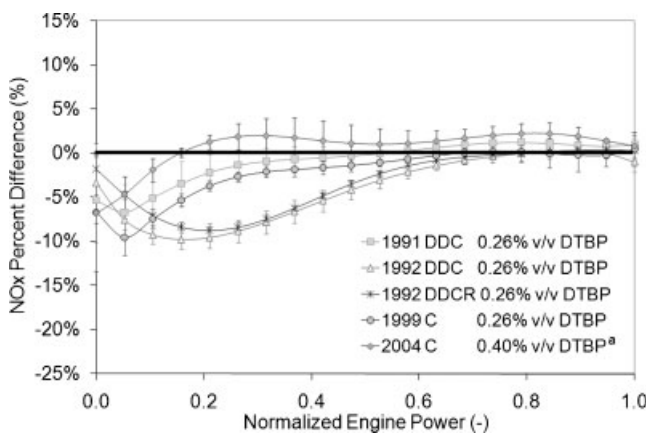


Fig. 2 NO<sub>x</sub> percentage difference when adding DTBP to fuel A for the five engines. The superscript a indicates that the neat fuel was fuel B

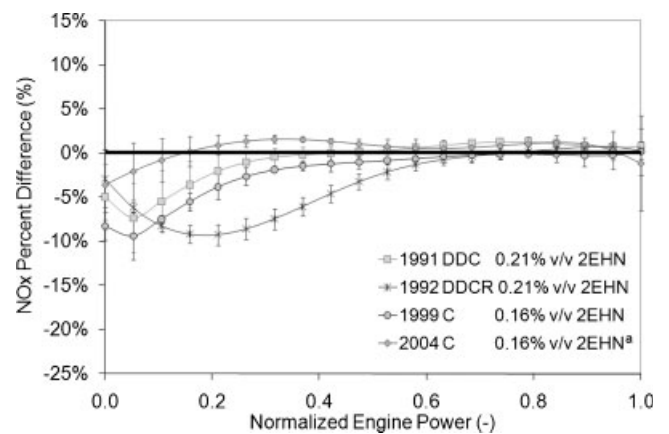
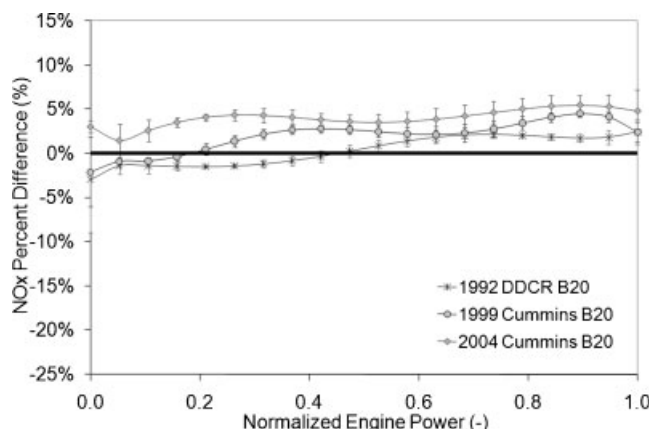


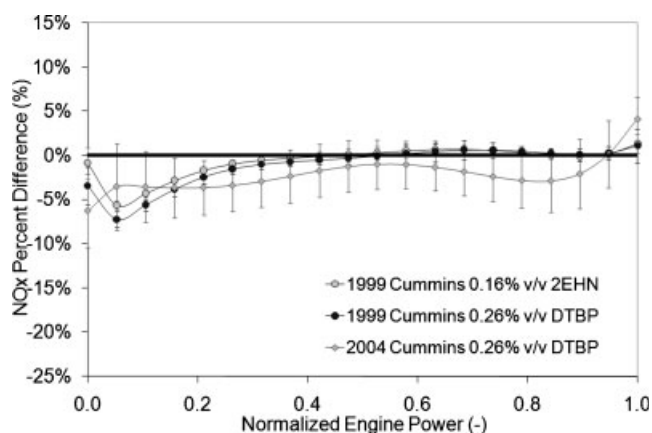
Fig. 3 NO<sub>x</sub> percentage difference when adding 2-EHN to fuel A for the five engines. The superscript a indicates that the neat fuel was fuel B



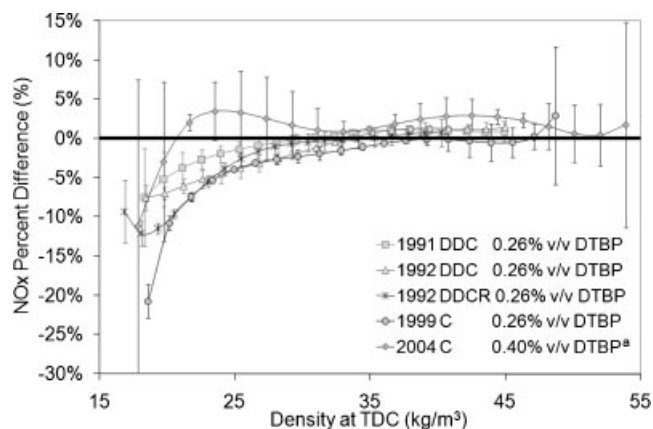
**Fig. 4** NO<sub>x</sub> percentage difference when adding 20 vol% biodiesel to fuel B (fuel C) for three engines

ulted in a greater NO<sub>x</sub> reduction for the integrated brake specific NO<sub>x</sub> than with the 1991 DDC engine. The 1999 Cummins engine went from an NO<sub>x</sub> reduction to an increase at a normalized engine power of 0.68–0.72. The 2004 Cummins engine had the smallest range of normalized engine power for an NO<sub>x</sub> reduction at 0–0.15. An NO<sub>x</sub> increase of up to 2 per cent was noticed with the two Cummins engines. The 1992 rebuilt DDC engine showed approximately 1 per cent NO<sub>x</sub> increase at high engine powers, but this was within the 1 per cent test-to-test repeatability.

The 20 per cent biodiesel increased the cetane number of the neat fuel from 49.2 to 51.1. This increased cetane number provided a similar NO<sub>x</sub> percentage difference trend to that of 2-EHN and DTBP for the rebuilt 1992 DDC engine and 1999 Cummins engine with a reduction at low engine powers and increase at high engine powers (Fig. 4).

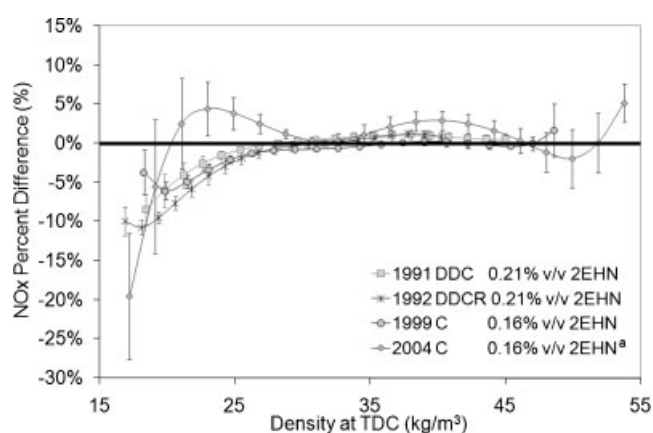


**Fig. 5** NO<sub>x</sub> percentage difference when adding DTBP or 2-EHN to fuel C (B20 blend) for the two engines



**Fig. 6** NO<sub>x</sub> percentage difference when adding DTBP to fuel A for the five engines. The superscript a indicates that the neat fuel was fuel B

Less NO<sub>x</sub> reduction occurred at low engine powers with the B20 fuel than with the cetane improvers and the location of the change from an NO<sub>x</sub> reduction to increase occurred at a lower engine power. In the rebuilt 1992 DDC engine and the 1999 Cummins ISM 370 engine, the B20 fuel (fuel C) reduced NO<sub>x</sub> below normalized engine powers of 0.42 and 0.18 respectively, compared with the base fuel (fuel B). The 2004 Cummins engine showed an NO<sub>x</sub> increase at all engine powers compared with the base fuel (Fig. 4). These results are similar to those in the study by Eckerle *et al.* [8], which showed no change or a reduction in NO<sub>x</sub> at low loads and an NO<sub>x</sub> increase at high loads with B20 in 2004 and 2006 5.81 Cummins ISB engines, which were equipped with EGR. Eckerle *et al.* [8] partially attributed the NO<sub>x</sub> changes from biodiesel to engine calibration changes with 5–8 per cent change in NO<sub>x</sub> due to different intake oxygen concentrations, which will be



**Fig. 7** NO<sub>x</sub> percentage difference when adding 2-EHN to fuel A for the five engines. The superscript a indicates that the neat fuel was fuel B



less of an issue with the non-EGR equipped engines used here (the 1992 DDC engines and the 1999 Cummins engine). In the 1998 and 2000 10.81 Cummins engines without EGR, an NO<sub>x</sub> reduction with B20 was shown for a low-load test cycle by Eckerle *et al.* [8], which correlates with the NO<sub>x</sub> reduction noticed at low engine power (Fig. 4).

The integrated brake specific NO<sub>x</sub> emissions over the FTP showed significant reductions of 0.6 per cent and 1.0 per cent when adding 0.16 vol % 2-EHN and 0.26 vol % DTBP respectively to the B20 (fuel C) fuel in the 1999 Cummins engine (Table 5). The 2004 Cummins engine showed a significant reduction of 2.5 per cent in NO<sub>x</sub> with 0.26 vol % DTBP added to the B20 fuel. At low engine powers, an NO<sub>x</sub> reduction was noticed for both Cummins engines (Fig. 5). The 1999 Cummins engine had no change in NO<sub>x</sub> above the normalized engine power of 0.48–0.62. The 2004 Cummins engine showed an increase in NO<sub>x</sub> only above 0.96. The dependence of engine year and power on NO<sub>x</sub> change when adding a cetane improver to a B20 fuel provides insight into the results reported in the literature [15, 16]. It should be noted that the cetane-improved B20 was compared with the B20 fuel (fuel C) and not the base petroleum fuel (fuel B).

The study by Higgins *et al.* [24] using a constant-volume combustion vessel showed that the reduction in ignition delay caused by 2-EHN was more significant under low-temperature and low-density conditions. Kobori *et al.* [25] found the same conclusions regarding 2-EHN in a rapid compression machine. In an effort to correlate these fundamental combustion studies with the production engines tested, the NO<sub>x</sub> percentage difference with additive was studied as a function of the density at top dead centre (TDC). The density at TDC was calculated from the ideal-gas law, intake pressure, intake temperature, and the compression ratio and is given by

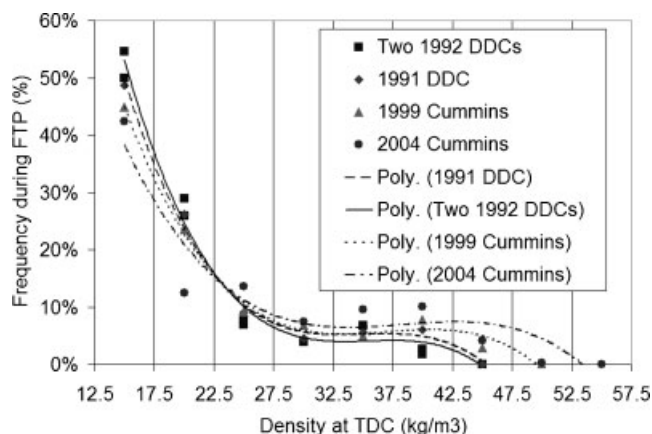
$$\rho_{\text{TDC}} = \rho_{\text{intake}} \text{CR} \quad (1)$$

where CR is the compression ratio. Equation (1) was derived from the ideal-gas law and assuming a polytropic process from intake conditions at bottom dead centre to TDC. The charge air was assumed to have no internal EGR. The density at TDC from equation (1) is the density that would occur at TDC during motoring conditions with the same intake pressure and temperature conditions.

Sixth-order polynomials were fitted between the  $\rho_{\text{TDC}}$  and the NO<sub>x</sub> emissions rate from the FTP tests

to determine the NO<sub>x</sub> percentage difference. The same methods were used as described above for the NO<sub>x</sub> percentage difference and engine power. The only change was that the engine operating points at idle were ignored because the measured intake conditions changed more rapidly than the measured emissions. At conditions when the engine goes from high load to idle, the analysers still reported NO<sub>x</sub> emissions owing to diffusion and dispersion in the sampling system, but the measured intake conditions (and therefore  $\rho_{\text{TDC}}$ ) have a much faster response. This caused a wide spread in the measured NO<sub>x</sub> emissions for  $\rho_{\text{TDC}}$  during idle.

The NO<sub>x</sub> percentage difference due to the addition of 2-EHN or DTBP correlated with the  $\rho_{\text{TDC}}$  for all the engines although the 2004 Cummins engine had large confidence intervals, suggesting that the correlation is not significant for this engine (Figs 6 and 7). Below a  $\rho_{\text{TDC}}$  of 35 kg/m<sup>3</sup>, the NO<sub>x</sub> was reduced owing to the cetane improver. The NO<sub>x</sub> percentage difference curves were not identical for all engines, but other variables besides the cetane improver affect the ignition delay, such as the injection timing, injection pressure [25], temperature at injection [25], and injector hole diameter [25]. The 2004 Cummins engine incorporates EGR, which affects the intake pressure, intake temperature, and concentration of intake oxygen. A lower concentration of intake oxygen will create a longer ignition delay and the varying EGR rate will minimize the correlation between  $\rho_{\text{TDC}}$  and the NO<sub>x</sub> percentage difference. With the engines having an NO<sub>x</sub> reduction at low cylinder densities with cetane improvers, the amount of time operated at these low densities will influence the resulting integrated brake specific NO<sub>x</sub> emissions. The frequency of time operated at each density from 12.5 to 57.5 kg/m<sup>3</sup>, with density bins of 5 kg/m<sup>3</sup>, showed that the 1992 DDC engines operated at low densities more frequently than the other engines (Fig. 8). A third-order polynomial was fitted between the frequency and the density bins to show the trend. The two 1992 DDC engines operated at 12.5–17.5 kg/m<sup>3</sup> for 52 per cent of the FTP, while the 2004 Cummins engine operated in that range only for 42 per cent of the FTP. The maximum density bin was 37.5–42.5 kg/m<sup>3</sup> for the 1992 DDC engines, while the two Cummins operated had a maximum at or above 47.5 kg/m<sup>3</sup>. The cetane improvers therefore worked more efficiently at lower densities and the more time operated at these low densities resulted in lower NO<sub>x</sub> emissions. The 1992 DDC engines had the lowest compression ratio and no EGR, which



**Fig. 8** Frequency distribution of the density at TDC for the five engines

resulted in the most  $\text{NO}_x$  benefit from cetane improvers. Engines such as refuse trucks or large-bore engines that operate primarily at relatively low engine powers and densities are optimal for cetane improvers.

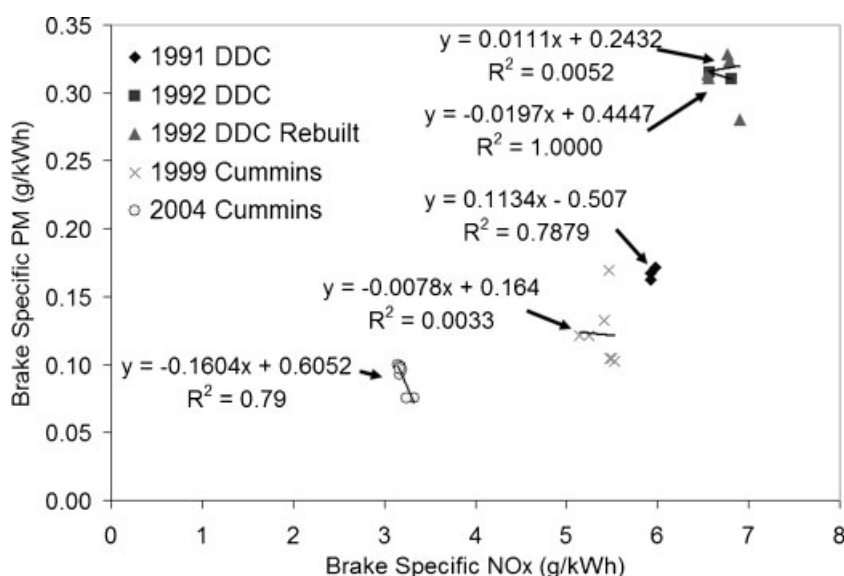
## 4.2 PM emissions

The PM reduced significantly for the B20 blends, which is consistent with the literature. One of the most difficult hurdles for engine manufacturers to overcome in reducing the overall  $\text{NO}_x$  and PM emissions to meet current and future standards is the  $\text{NO}_x$ -PM trade-off. This trade-off occurs because, when the combustion chamber is cooled, the overall production of  $\text{NO}_x$  is reduced. In return, owing to the cooler temperatures, the PM is not able to oxidize;

therefore, an increase in PM is seen. The two Cummins engines and the 1992 DDC showed this trend, as seen in Fig. 9. The figure includes all the fuels tested including the B20 for the two Cummins engines and the 1992 rebuilt DDC engine. The B20 will change the  $\text{NO}_x$ -PM trade-off linear fit. Figure 9 illustrates the effect of fuel properties on  $\text{NO}_x$  and PM, and it is shown that the fuel properties have a large impact on  $\text{NO}_x$  and PM emissions when keeping the engine control strategy consistent for each engine throughout the testing campaign, by using a production engine calibration. This was also shown by Gibble [26].

## 5 CONCLUSIONS

As the emissions standards continue to become increasingly stringent, engine manufacturers and fuel suppliers have to improve technologies in order to reduce engine-out emissions. The overall emission levels are lower for newer model years of the engines, and this is due to the improved engine technologies. The baseline fuels evaluated in this work showed a decreasing emissions trend with newer model years, with cetane improvers (2-EHN and DTBP) showing a greater impact on the older-technology engines. The additives reduced  $\text{NO}_x$  up to a normalized engine power of 0.51–0.58, 0.74–0.76, 0.68–0.72, and 0.15 for the 1991 DDC, 1992 DDCs, 1999 Cummins, and 2004 Cummins engines respectively but showed no  $\text{NO}_x$  change or increased  $\text{NO}_x$  production above this point. The cetane improvers only showed  $\text{NO}_x$  reduction at cylinder gas



**Fig. 9**  $\text{NO}_x$ -PM trade-off for FTP tests

densities below 35 kg/m<sup>3</sup> and 2-EHN is known to be more effective at reducing ignition delay at low pressures and temperatures from fundamental combustion studies.

The data from this study show that cetane-improving additives are beneficial in reducing NO<sub>x</sub> in engines with low compression ratios (typically legacy engines) but have less opportunity for NO<sub>x</sub> reduction in newer-technology engines (higher compression ratio and EGR). The increased compression ratio of the 1991 DDC, 1999 Cummins, and 2004 Cummins engines increased the cylinder gas density at all operating points, creating less opportunity for NO<sub>x</sub> reduction. Although the increased NO<sub>x</sub> production with the addition of cetane improvers for the newer engines is less than 3 per cent at high engine powers, this increase negates some of the newer, and possibly future, engine technology benefits.

The B20 did have an increase in NO<sub>x</sub> production, but there was a decrease in all the other regulated emissions. Some NO<sub>x</sub> reduction (about 1 per cent) was noticeable below a normalized engine power of 0.42 in the 1992 rebuilt DDC engine and below 0.18 in the 1999 Cummins engine, suggesting that the increased cetane number of the biodiesel created a 'cetane effect', but the NO<sub>x</sub> increased approximately 2–4 per cent at high engine powers. These NO<sub>x</sub> results for B20 are in agreement with the data obtained by Eckerle *et al.* [8], which showed no change or a reduction in NO<sub>x</sub> at low loads and an NO<sub>x</sub> increase at high loads. This emissions impact can be seen as being beneficial considering only NO<sub>x</sub> is being increased and, if a cetane-improving additive were used, the NO<sub>x</sub> production is only slightly higher than with the petroleum-based diesels from which the blends were created on the basis of the additive treat rates used in this work.

© Authors 2009

## REFERENCES

- 1 Code of Federal Regulations. CFR Title 40 Part 86-89, Office of Federal Register National Archives and Records Administration, Washington, DC, 2006.
- 2 Notice of filing of consent decree under the clean air act. Federal Register, vol. 63, no. 212, Office of the Federal Register, National Archives and Records Administration, Washington, DC, 1998.
- 3 Majewski, W. A. and Khair, M. K. *Diesel emissions and their control*, 1st edition, 2006 (SAE International, Warrendale, Pennsylvania).
- 4 Tamanouchi, M., Morihisa, H., Yamada, S., Iida, J., Sasaki, T., and Sue, H. Effects of fuel properties on exhaust emissions for diesel engines with and without oxidation catalyst and high pressure injection. SAE paper 970758, 1997.
- 5 Owen, K. and Coley, T. *Automotive fuels reference book*, 2nd edition, 1995 (SAE International, Warrendale, Pennsylvania).
- 6 Ullman, T. L., Mason, R. L., and Montalvo, D. A. Effects of fuel aromatics, cetane number, and cetane improver on emissions from a 1991 prototype heavy-duty diesel engine. SAE paper 902171, 1990.
- 7 Mann, N., Kvinge, F., and Wilson, G. Diesel fuel effects on emissions – towards a better understanding. SAE paper 982486, 1998.
- 8 Eckerle, W., Lyford-Pike, E., Stanton, D., La-Pointe, L., Whitacre, S., and Wall, J. Effects of methyl ester biodiesel blends on NO<sub>x</sub> emissions. SAE paper 2008-01-0078, 2008.
- 9 Alam, M., Song, J., Acharya, R., Boehman, A., and Miller, K. Combustion and emissions performance of low sulfur, ultra low sulfur and biodiesel blends in a DI diesel engine. SAE paper 2004-01-3024, 2004.
- 10 Shih, L. Comparison of the effects of various fuel additives on the diesel engine emissions. SAE paper 982573, 1998.
- 11 Kullnowski, A., Henly, T., and Growcott, P. Diesel fuel additives to meet worldwide performance and emissions requirements. SAE paper 932737, 1993.
- 12 Lange, W., Cooke, J., Gadd, P., Zurner, H., Schlogl, H., and Richter, K. Influence of fuel properties on exhaust emissions from advanced heavy-duty engines considering the effect of natural and additive enhanced cetane number. SAE paper 972894, 1997.
- 13 Ryan III, T., Buckingham, J., Dodge, L., and Olikara, C. The effects of fuel properties on emissions from a 2.5 gm NO<sub>x</sub> heavy-duty diesel engine. SAE paper 982491, 1998.
- 14 Barbier, P. Evaluation of cetane improver effects on regulated emissions from a passenger car equipped with a common rail diesel engine. SAE paper 2000-01-1853, 2000.
- 15 McCormick, R., Alvarez, J., Graboski, M., Tyson, K., and Vertin, K. Fuel additive and blending approaches to reducing NO<sub>x</sub> emissions from biodiesel. SAE paper 2002-01-1658, 2002.
- 16 McCormick, R., Tennant, C., Hayes, R., Black, S., Ireland, J., McDaniel, T., Williams, A., Frailey, M., and Sharp, C. Regulated emissions from biodiesel tested in heavy-duty engines meeting 2004 emission standards. SAE paper 2005-01-2200, 2005.
- 17 Sheehan, J., Dunahay, T., Benemann, J., and Roessler, P. A look back at the U.S. Department of Energy aquatic species program – biodiesel from algae. Report NREL/TP-580-24190, National Renewable Energy Laboratories, Golden, Colorado, USA, 1998.
- 18 Sharp, C. A. The effect of biodiesel fuels on transient emissions from modern diesel engines. Part I, regulated emissions and performance. SAE paper 2000-01-1967, 2000.

- 19 Graboski, M. S., Ross, J. D., and McCormick, R. L. Transient emissions from No. 2 diesel and biodiesel blends in a DDC series 60 engine. SAE paper 961166, 1996.
- 20 Szybist, J. and Boehman, A. Behavior of a diesel injection system with biodiesel fuel. SAE paper 2003-01-1039, 2003.
- 21 Tat, M., Van Gerpen, J., Soylu, S., Canakci, M., Monyem, A., and Wormley, S. Speed of sound and isentropic bulk modulus of biodiesel at 21 °C from atmospheric pressure to 35 MPa. *J. Am. Oil Chemists' Soc.*, 2000, **77**(3), 285–289.
- 22 Cheng, A., Upatnieks, A., and Mueller, C. Investigation of the impact of biodiesel fuelling on NO<sub>x</sub> emissions using an optical direct injection diesel engine. *Int. J. Engine Res.*, 2006, **7**(4), 297–319. DOI: 10.1243/14680874JER05005.
- 23 Ban-Weiss, G., Chen, J., Buchholz, B., and Dibble, R. A numerical investigation into the anomalous slight NO<sub>x</sub> increase when burning biodiesel; a new (old) theory. *Fuel Processing Technol.*, 2007, **88**, 659–667.
- 24 Higgins, B., Siebers, D., Mueller, C., and Aradi, A. Effects of an ignition-enhancing, diesel-spray evaporation, mixing, ignition, and combustion. In *Proceedings of the 27th International Symposium on Combustion*, 1998, pp. 1873–1880 (Combustion Institute, Pittsburgh, Pennsylvania).
- 25 Kobori, S., Kamimoto, T., and Aradi, A. A study of ignition delay of diesel fuel sprays. *Int. J. Engine Res.*, 2000, **1**, 29–39. DOI: 10.1243/1468087001545245.
- 26 Gibble, J. C. *Comparison of heavy-duty engine emissions between an on-road route and engine dynamometer simulated on-road cycle*. MS Thesis, Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, West Virginia, USA, 2003.