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# Mitigating Nitrogen Oxides Exhaust Emissions from Petrol Vehicles by Application of a Fuel Additive

Dr Roman Kudin, Prabhat Chand and Anura Bakmeedeniya

### Abstract

This research has been commissioned by Eco Fuel Global Limited, a New Zealand-based company, to further evaluate the effects of their fuel-additive product on the tailpipe exhaust emissions of petrol cars. At the time this research was conducted (end of 2018), the product was still in development and had not been released to the market. Prior to the testing in this research, an initial pilot test was done for the same product on a single car (Nissan Pulsar 1998), which showed favourable results, with a reduction in hydrocarbons and oxides of nitrogen at the tailpipe by more than 70%.

The current research included five test cars, all running on RON 95 fuel, with the years of manufacture ranging between 1994 and 2006, and the odometer readings between 112,004 km and 264,001 km. The effects of the fuel-additive product were assessed by comparing the emissions from a car running on standard fuel with the emissions from the same car after it completed a road run ( $250\pm20$  km) on the additive-treated fuel.

The exhaust emissions were measured using the AVL series 4000 Emission Tester, which analyses five components: carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), oxides of nitrogen (NO<sub>x</sub>), hydrocarbons (HC) and oxygen (O<sub>2</sub>).

The most noticeable outcome of using the fuel-additive product was the reduction in the concentration of oxides of nitrogen in the tailpipe exhaust (by up to 27.7%), when compared with the same cars running on standard fuel. In addition, the results showed a decrease in residual oxygen concentration, which normally indicates more complete utilisation of  $O_2$  as an oxidising agent.

The changes for other emission parameters were either relatively small (below 1%) or were not statistically significant.

The application of such fuel-additive products could be beneficial for mitigating nitrogen oxides exhaust emissions from petrol vehicles in countries with ageing car fleets. These include New Zealand, which has a relatively high proportion of old cars in use, with no government-run scrappage scheme, and without a mandatory objective emissions testing.

## Background

The pollutant emissions generated by internal combustion engines (ICE) include carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), oxides of nitrogen (NO<sub>x</sub>), hydrocarbons (HC) and particulate matter (PM). Over the past several decades, due to technology improvements and government regulations, vehicle tailpipe emissions have decreased significantly. The emission intensities for a typical passenger car manufactured in 2019 can be up to 100 times lower than they would have been 30–40 years ago (Winkler et al., 2018).

Specialists are still looking for possible ways to further reduce tailpipe emissions, especially for older engines that are already in service. For large diesel engines, for example, retro-fitment of the Selective Catalytic Reduction (SCR) system is a cost-effective solution that can reduce  $NO_x$  exhaust emissions by up to 70% (Association for Emissions Control by Catalyst, 2019). For petrol engines, however, the effectiveness and the application of current SCR technology is still significantly limited (Empa, 2015). One of the possible ways to reduce emissions for old and/or high-mileage petrol vehicles is the use of fuel additives.

The Technical Committee of Petroleum Additive Manufacturers in Europe defines a fuel additive as "a chemical substance or preparation, added to fuel in concentration typically of less than 1% to impart or enhance desirable properties or to suppress undesirable properties" (2013, p. 7). Such substances can be added at three different stages: at the refinery, at the marketing terminal, or by the consumer.

The chemical composition and the mode of action for the fuel-additive product tested in this research was not disclosed by the company, as such confidentiality is common in the additive industry (Technical Committee of Petroleum Additive Manufacturers in Europe, 2013). This has significantly limited the authors' ability to establish the relevant theoretical backgrounds and to review the existing solutions in this area. However, the following test conditions were requested by the company representatives and agreed to by the research team:

- 1. Selecting vehicles with high odometer readings.
- 2. Running each of the vehicles 250 km on the additive-treated fuel before performing the final emission test.

Such test conditions indicate that a probable mode of action for the additive could be removing detrimental deposits from either engine, fuel system and/or exhaust-emission control system. This assumption allowed

the research team to narrow the area of theoretical analysis and to focus the review of the existing solutions on one particular group of fuel additives.

Currently there is one group of fuel additives with proven efficacy in reducing exhaust emissions by working with deposits in engines designed to run on unleaded petrol – Deposit Control Additives (DCAs), also known by the generic term 'detergents' (Technical Committee of Petroleum Additive Manufacturers in Europe, 2013).

As the name suggests, Deposit Control Additives (DCAs) are designed to keep the entire engine fuel system clean, preventing the formation of deposits (particularly on intake valve and fuel injectors). Those deposits deteriorate the air/fuel flow through the engine, increasing emissions. However, DCAs are more than just 'detergents' cleaning the engine; they inhibit deposit creation by forming a protective film which prevents deposit precursors accumulating to form deposits. DCAs help to keep metal surfaces clean and close to their 'as-manufactured' condition (Technical Committee of Petroleum Additive Manufacturers in Europe, 2013).

The importance of DCAs for maintaining low emissions has been recognised by the US Environmental Protection Agency (EPA). As part of the Federal Clean Air Act, the EPA requires all automotive gasoline sold in the USA to contain a minimum amount of deposit-control additives. Several major automobile manufacturers in 2004 introduced the TOP TIER Detergent Gasoline programme – the initiative for retailers to use a higher level of DCAs than the minimum required by the EPA. Such gasoline is widely available from over 50 licensed fuel retail brands and has proven its efficiency in preserving an engine's "original performance and emissions over time" (Bartlett, 2019, para. 5).

One of the most authoritative studies of fuel additives was commissioned by the German Environmental Protection Agency and completed by the Fraunhofer Institute. In regard to DCAs and dispersant substances, it states that "By appropriately structured test programmes, advantages in the area of the CO, HC,  $NO_x$  and particulates formation can be proven. Fuel savings between 2 and 3% appear realistic" (Keller, Boehncke, & Mangelsdorf, 1999, as cited in Technical Committee of Petroleum Additive Manufacturers in Europe, 2013, p. 57).

The chemistry of DCAs typically comprises amides, amines, polybutene succinimides, polyether amines, polyolefin amines and Mannich amines. DCAs are mostly added at refinery or marketing terminal stage (100–1000 mg/kg) and are supposed to be used continuously, preventing deposits from forming (Technical Committee of Petroleum Additive Manufacturers in Europe, 2013).

In addition, there is a wide range of aftermarket fuel-additive products that consumers can add to automotive fuel to lower exhaust pollutant levels and to improve fuel economy. Some of those products are registered with the US Environmental Protection Agency (EPA) and reviewed in Table 1. However, the EPA itself warns the potential consumers of such products: "Do not assume that because a fuel additive has been registered with EPA that this implies anything about the safety, benefits, or claims made by the manufacturer" (EPA, 2019, p. 2).

The purpose of this research is to evaluate the effects of a new fueladditive product on the tailpipe exhaust emissions for petrol cars. At the time of testing, the product was still under the development, and neither the chemical composition nor the mode of action was disclosed by the developing company.

### Table 1. Aftermarket fuel-additive products with claimed positive effects on tailpipe emissions.

Brand	Product	Mode of action postulated by the manufacturer of the product	Application process recommended by the manufacturer	Positive effects on tailpipe emissions claimed by the manufacturer of the product
Efficient Fuel Solutions, LLC	FuelSpec® combustion catalysts	Extends the combustion process, producing a more uniform and complete combustion of the fuel.	Continuous use of treated fuel.	Up to 90% reduction in carbon monoxide, up to 30% reduction in NOX and up to complete elimination of visible black smoke can be expected for diesel engines.
		·		(Efficient Fuel Solutions, 2016)
Cataclean Global	Cataclean ® Petrol Cataclean ® Diesel	Removal of deposits from the surface of the catalytic converter core, which increases the catalyst's ability to remove harmful exhaust emissions such as carbon monoxide & nitrogen oxides.	Adding the product to ¼ full fuel tank and driving for at least 15 minutes before refuelling. Re-applying every three months.	Bringing down a vehicle's emissions by up to 60%.
				(Cataclean, n.d.)
LIQUI MOLY	Injection Cleaner (#5110)	Removes deposits on injection valves, intake valves, spark plugs and in the combustion chamber and prevents them from reforming.	Adding to the fuel tank every 2000 km.	Optimises the emission test values.
	Fuel System Treatment (#5108)	Maintains and protects the entire fuel system from wear, deposits and corrosion. Improves engine running and prevents performance decrease.		Clean engines need less fuel and reduce emissions.
	Carburetor and Valve Cleaner (#5100)	Removes deposits in carburettor, in valves, spark plugs and in the combustion chamber and prevents renewed formation.		
			(Liqu	i-Moly Motor Oils Additives Car Care, n.d.)
CRC	Guaranteed To Pass®	Removes harmful deposits from the fuel system and emission-control components in gas-powered vehicles.	Pouring the entire contents of the bottle into full tank of gas, and driving until tank is empty. Refilling with regular (untreated) gasoline right before the emission test.	The company promises vehicle will pass emissions test or double money back.
			To be used every 3000 miles to improve fuel economy and acceleration, and reduce emissions.	
				(CRC Industries, 2017)
BlueSky Clean Air	Advanced BlueSky 3-in-1 Fuel Conditioner	Combination of low molecular cleaning esters and high molecular lubricating esters, aids in improving the combustion characteristics of commercial pump fuels, including gasoline and diesel.	Similar to the above product, but company recommends its product to be used continuously after passing the smog test.	Reduces the emissions of hydrocarbons (HC), nitrogen oxides (NOX), carbon monoxide (CO), particulate matter (PM) and other harmful by-products of combustion, while increasing the emission of O2.
				, (BlueSky Clean Air, 2017)

# **Research methods**

The research was conducted in accordance with the following protocol:

- 1. The AVL series 4000 Emission Tester was calibrated by the manufacturer's authorised equipment supplier and maintenance agent (the need for the periodic calibration is automatically calculated by the tester via its internal memory and demanded through the display screen).
- Five test cars were provided by the company who commissioned the research. Each test car was delivered at an agreed date and kept in the research facility for the whole period required to complete the testing. Before the delivery, the cars chosen for the research were regularly running on a standard fuel.
- 3. Prior to the testing, each car was checked to verify that it was in a reasonable mechanical condition and without any obvious defects related to the emission-control components.
- 4. The car manufacturer's emission specifications for each test car were obtained.
- 5. The RON 95 fuel was purchased from one petrol station, in a single transaction for all five test cars to avoid any confusion of results due to brand or batch changes.
- 6. Tailpipe emissions for the standard fuel were tested first at idle engine speed and then at 2500±50 RPM in accordance with steps 7–8.
- The engine of the test car was brought to normal running temperature. Required temperature was verified by AVL tester engine-oil temperature probe (minimum 80° C) and by letting the radiator cooling fan come 'ON' at least once for each test process.
- The tailpipe exhaust-emission test was repeated five times with the time interval of 2 minutes (minimum) in between tests, by using the AVL series 4000 Emission Tester, each time simultaneously measuring the concentration of the following components: carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), oxides of nitrogen (NO<sub>x</sub>), hydrocarbons (HC) and oxygen (O<sub>2</sub>).
- 9. Emissions results for the standard fuel were printed in duplicate, recorded and were taken as base values.
- 10. The remaining standard fuel in the system was used out by running the engine, before the additive-treated fuel was introduced.
- 11. The fuel-additive product was provided by a representative of the company, in an unsealed and unlabelled container (the product had not yet been released to the market). The process of the fuel treatment was performed separately for each car, in accordance with the verbal instructions from the company's representative. The liquid additive product (1 litre) was poured into a transparent plastic container, the standard fuel (30 litres) was added, and the container was shaken for at least 1 minute and then left to rest for at least 30 minutes.
- 12. The fuel and the additive product did not show any visible signs of creating a stable mixture, and remained in separate layers due to the density difference. The treated fuel (as the upper, less dense layer) was pumped

out from the container into the car's fuel tank without disturbing the actual additive layer.

- 13. Each vehicle was taken for a drive (250±20 km, under the direct supervision of a member of the research team) on the additive-treated fuel before repeating the emission tests. A drive of this length was stipulated by the company who commissioned the research, for the fuel additive to take an effect on the car's emissions. The drive run was performed in normal driving conditions on a highway.
- 14. Tailpipe emissions for the additive-treated fuel were tested first at idle engine speed and then at 2500±50 RPM in accordance with steps 7–8.
- 15. Emissions results for the additive-treated fuel were printed in duplicate, recorded and were compared to the base values of the standard fuel.

# Results

### DATA PROCESSING METHODS

Obtained tests results for each vehicle, and each exhaust parameter, were processed in the following steps:

- 1. The 'Average,' as the arithmetic mean of five test results, was calculated separately for the standard and treated fuel.
- 2. The 'Actual change' was calculated by subtracting the standard fuel average from the treated fuel average, keeping the original unit of measurement for each parameter.
- 3. The 'Relative change' was calculated as the ratio of the actual change to the standard fuel average and expressed as percentages for all exhaust parameters.
- P-value was calculated and checked against the chosen significance threshold of 0.05 to verify whether the observed changes in tailpipe emission levels for the treated fuel were statistically significant. An online data analysis software was applied (Stangroom, 2018).
- Air/Fuel Ratio or Lambda (λ) parameter was not analysed by P-value, since it is not an independent emission parameter – it is derived from the HC, CO, CO<sub>2</sub> and O<sub>2</sub> concentrations.
- 6. In the following discussion, all percentage changes of the exhaust parameters between treated and untreated fuels correspond to the 'Relative change' unless otherwise specified.

# Toyota Camry 2000

			ldle engi	ne speed					Cruising en	gine speed			
Parameter	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	
λ	1.0362	1.0172	- 0.019	- 1.8¹	-	_	1.0086	0.9928	- 0.0158	- 1.6	_	-	
CO %vol	0.454²	0.490	+ 0.036	+ 7.9	No	0.07359	0.444 <sup>6</sup>	0.458	+ 0.014	+ 3.1	No	0.339518	
CO <sub>2</sub> %vol	14.48 <sup>3</sup>	14.56	+ 0.08	+ 0.5	Yes	0.035265	15.02	15.04	+ 0.02	+ 0.1	No	0.544737	
O <sub>2</sub> %vol	1.1744	0.784	- 0.39	- 33.2	Yes	0.043593	0.506	0.162	- 0.344	- 68.0	No	0.205782	
HC ppm HEX	127.0 <sup>5</sup>	117.0	- 10.0	- 7.9	Yes	0.016683	33.0	24.8	- 8.2	- 24.8	Yes	0.000029	
NO <sub>x</sub> ppm vol	108.2	93.8	- 14.4	- 13.3	No	0.067166	56.4	42.0	- 14.4	- 25.5	Yes	0.008871	

Table 2.	Statistical	analysis of	f tailpipe exhau	ıst emissions	test results	for the	Toyota	Camry	2000.

1. " + " indicates increase, " - " indicates decrease of an emission parameter for the treated fuel.

2. Manufacturer's specification for CO limit at idle speed - 0.5% vol. max.

3. Manufacturer's specification for CO<sub>2</sub> at idle speed – between 14.5% and 16.0% vol.

4. Manufacturer's specification for  $O_2$  at idle speed – within 0.1–0.5% vol.

5. Manufacturer's specification for HC limit at idle speed – 100 ppm HEX max.

6. Manufacturer's specification for CO content at increased idle speed – 0% vol. max (increased idle speed for CO test – 2400–2600 RPM).

- 1. The level of  $NO_x$  with the treated fuel was reduced by 25.5% at cruising engine speed.
- 2. The level of O<sub>2</sub> with the treated fuel was reduced by 33.2% at idle engine speed.
- 3. The level of HC with the treated fuel was reduced by 7.9% at idle engine speed and by 24.8% at cruising engine speed. However, these results carry a limited importance because the actual change of the parameter was within the allowed environmental level of HC (below 20 ppm, see Appendix A).
- The changes for other emission parameters were either relatively small (less than 2%) or were not statistically significant (P-values exceeding threshold of 0.05).

# Volkswagen Golf 2001

			ldle engi	ne speed			Cruising engine speed						
Parameter	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	
λ	1.0214	1.0188	0.0026	+ 0.31	-	-	1.0062	1.0074	+ 0.0012	+ 0.1	-	-	
CO %vol	0.462 <sup>2</sup>	0.434	- 0.028	- 6.1	Yes	0.018385	0.052 <sup>6</sup>	0.036	- 0.016	- 30.8	Yes	0.019256	
CO <sub>2</sub> %vol	14.48 <sup>3</sup>	14.54	+ 0.06	+ 0.4	No	0.09435	15.22	15.20	- 0.02	- 0.1	No	0.607511	
O <sub>2</sub> %vol	0.8524	0.772	- 0.08	- 9.4	Yes	0.000058	0.182	0.200	+ 0.018	+ 9.9	No	0.498286	
HC ppm HEX	110.0⁵	102.2	- 7.8	- 7.1	No	0.054744	7.6	7.0	- 0.6	- 7.9	No	0.751822	
NO <sub>x</sub> ppm vol	93.6	86.4	- 7.2	- 7.7	Yes	0.011196	87.2	85.4	- 1.8	- 2.1	No	0.63979	

Tahla 3 Statio	etical analysis	of tailning exhau	ist amissions tas	t regulte for	Volkewagan	Golf 2001
	Sucai anaiysis	or tampipe exitat	121 61112210112 162		voikswayen	3011 2001.

1. "+" indicates increase, "-" indicates decrease of an emission parameter for the treated fuel.

2. Manufacturer's specification for CO limit at idle speed - 0.5% vol. max.

3. Manufacturer's specification for CO<sub>2</sub> at idle speed – between 14.5% and 16.0% vol.

4. Manufacturer's specification for O<sub>2</sub> at idle speed – within 0.1–0.5% vol.

5. Manufacturer's specification for HC limit at idle speed – 100 ppm HEX max.

6. Manufacturer's specification for CO content at increased idle speed – 0.3% max (increased idle speed for CO test – 2500–2800 RPM).

- 1. The level of  $NO_x$  with the treated fuel was reduced by 7.7% at idle engine speed.
- 2. The level of  $O_2$  with the treated fuel was reduced by 9.4% at idle engine speed.
- The level of CO with the treated fuel was reduced by 6.1% at idle engine speed. At cruising engine speed, the reduction was 30.8%. However, this result carries a limited importance as the registered values approached the lower limit of the measurement range and the actual change was close to the resolution capability of the testing equipment (0.01% for CO, see Appendix A).
- 4. The changes for other emission parameters were either relatively small (less than 1%) or were not statistically significant (P-values exceeding threshold of 0.05).



Figure 1. Emissions test setup for Toyota Camry 2000.



Figure 2. Emissions test setup for Volkswagen Golf 2001.

# Mitsubishi Chariot 1994

			ldle engi	ne speed <sup>7</sup>			Cruising engine speed						
Parameter	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	
λ	1.1212	1.0522	- 0.0690	- 6.1 <sup>1</sup>	-	-	1.0208	1.0106	- 0.0102	- 1.0	-	_	
CO %vol	0.240²	0.422	0.182	+ 75.8	Yes	below 0.00001	0.512 <sup>6</sup>	0.504	- 0.08	- 15.6	No	0.849676	
CO <sub>2</sub> %vol	13.14 <sup>3</sup>	13.98	+ 0.84	+ 6.4	Yes	below 0.00001	14.44	14.56	+ 0.12	+ 0.8	No	0.101222	
O <sub>2</sub> %vol	2.794 <sup>4</sup>	1.594	- 1.200	- 43.0	Yes	below 0.00001	0.870	0.618	- 0.252	- 29.0	Yes	below 0.00001	
HC ppm HEX	343.85	278.4	- 65.4	- 19.0	Yes	0.001059	90.8	72.2	- 18.6	- 20.5	Yes	0.030256	
NO <sub>x</sub> ppm vol	70.4	85.0	+ 14.6	+ 20.7	Yes	0.000114	178.0	152.6	- 25.4	- 14.3	Yes	0.005423	

Table 4.	Statistical	analysis of	f tailpipe exh	aust emission	is test resul	lts for N	litsubishi	Chariot '	1994.
		,							

1. " + " indicates increase, " - " indicates decrease of an emission parameter for the treated fuel.

2. Manufacturer's specification for CO limit at idle speed - 0.5% vol. max.

3. Manufacturer's specification for CO<sub>2</sub> at idle speed – between 14.5% and 16.0% vol.

4. Manufacturer's specification for O<sub>2</sub> at idle speed – within 0.1–0.5% vol.

5. Manufacturer's specification for HC limit at idle speed – 100 ppm HEX max.

6. Manufacturer's specification for CO content at increased idle speed – 0.3% vol. max (increased idle speed for CO test – 2500–2800 RPM).

7. Results for idle engine speed are limited in comparability because after the test run the engine could not maintain the required 750 RPM.

(Manufacturer's specifications - Autodata, n.d.)

- 1. The level of  $NO_x$  with the treated fuel was reduced by 14.3% at cruising engine speed.
- 2. The level of  $O_2$  with the treated fuel was reduced by 29.0% at cruising engine speed.
- 3. The level of HC was reduced by 20.5% at cruising engine speed. However, this result carries a limited importance because the actual change of the parameter was within the allowed environmental level of HC (below 20 ppm, see Appendix A).
- The changes for other emission parameters were either relatively small (below 1%) or were not statistically significant (P-values exceeding threshold of 0.05).
- 5. Results at idle engine speed are limited in comparability because after the test run the engine could not maintain the required 750 RPM.

# Mitsubishi Galant 1999

			ldle engi	ne speed		Cruising engine speed						
Parameter	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value
λ	1.0138	1.0096	- 0.0042	- 0.41	-	-	1.0066	1.0050	- 0.0016	- 0.2	-	-
CO %vol	0.104²	0.112	+ 0.008	+ 7.6	No	0.518027	0.114 <sup>6</sup>	0.124	+ 0.01	+ 8.8	No	0.586825
CO <sub>2</sub> %vol	15.04 <sup>3</sup>	15.00	- 0.04	- 0.3	No	0.346594	15.12	15.08	- 0.04	- 0.3	No	0.373375
O <sub>2</sub> %vol	0.4584	0.362	- 0.096	- 30.0	Yes	0.01392	0.242	0.214	- 0.028	- 11.6	Yes	0.004178
HC ppm HEX	97.45	86.6	- 10.8	- 11.1	No	0.084194	20.2	16.4	- 3.8	- 18.8	Yes	0.001895
NO <sub>x</sub> ppm vol	26.0	18.8	- 7.2	- 27.7	Yes	0.007166	110.2	91.4	- 18.8	- 17.1	Yes	0.00027

1. " + " indicates increase, " - " indicates decrease of an emission parameter for the treated fuel.

2. Manufacturer's specification for CO level at idle speed - 0.5% vol. max.

3. Manufacturer's specification for CO<sub>2</sub> level at idle speed – between 14.5 and 16.0% vol.

4. Manufacturer's specification for  $O_2$  level at idle speed – within 0.1–0.5% vol.

5. Manufacturer's specification for HC level at the idle speed – 100 ppm HEX max.

6. Manufacturer's specification for CO content at increased idle speed – 0.3% vol. max (increased idle speed for CO test – 2500–2800 RPM).

(Manufacturer's specifications – Autodata, n.d.)

- 1. The level of  $NO_x$  with the treated fuel was reduced by 27.7% at idle engine speed and by 17.1% at cruising engine speed.
- 2. The level of  $O_2$  with the treated fuel was reduced by 30.0% at idle engine speed, and by 11.6% at cruising engine speed.
- 3. The level of HC with the treated fuel was reduced by 18.8% at cruising engine speed. However, this result carries a limited importance because the actual change of the parameter was within the allowed environmental level of HC (below 20 ppm, see Appendix A).
- 4. The changes for other emission parameters were not statistically significant (P-values exceeding threshold of 0.05).



Figure 3. Emissions test setup for Mitsubishi Chariot 1994.



Figure 4. Emissions test setup for Mitsubishi Galant 1999.

# Volkswagen Passat 2006

			ldle engi	ne speed			Cruising engine speed						
Parameter	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	Standard fuel average	Treated fuel average	Actual change	Relative change, %	Statistical significance	P-value	
λ	1.0020	1.0022	+ 0.00021	below 0.02	-	-	1.0022	1.0006	- 0.0016	- 0.2	-	-	
CO %vol	0.0122	0.006	- 0.006	- 50.0	No	0.09435	0.012 <sup>6</sup>	0.014	+ 0.002	+ 16.7	No	0.544737	
CO <sub>2</sub> %vol	15.4 <sup>3</sup>	15.3	- 0.1	- 0.6	Yes	0.00395	15.40	15.36	- 0.04	- 0.3	No	0.141113	
O <sub>2</sub> %vol	0.0744	0.076	+ 0.002	+ 2.7	No	0.788543	0.078	0.054	- 0.024	- 30.8	Yes	0.020875	
HC ppm HEX	15.05	12.4	- 2.6	- 17.3	No	0.056343	11.2	19.8	+ 8.6	+ 76.8	Yes	0.000105	
NO <sub>x</sub> ppm vol	0.8	1.0	+ 0.2	+ 25.0	No	0.740439	4.0	4.6	+ 0.6	+15.0	No	0.273139	

Table 6. Statistica	l analysis of ta	ilpipe exhaust	emissions test	results for	Volkswagen	Passat 2006.
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1. " + " indicates increase, " - " indicates decrease of an emission parameter for the treated fuel.

2. Manufacturer's specification for CO level at idle speed - 0.5% vol max.

3. Manufacturer's specification for CO<sub>2</sub> level at idle speed – between 14.5 and 16.0% vol.

4. Manufacturer's specification for  $O_2$  level at idle speed – within 0.1–0.5% vol.

5. Manufacturer's specification for HC level at idle speed – 100 ppm HEX max.

6. Manufacturer's specification for CO content at increased idle speed – 0.3% vol. max (increased idle speed for CO test – 2500–2800 RPM).

(Manufacturer's specifications – Autodata, n.d.)

- 1. The level of  $O_2$  with the treated fuel was reduced by 30.8% at cruising engine speed.
- The level of HC with the treated fuel increased by 76.8% at cruising engine speed. However, this result carries a limited importance because the actual change of the parameter was within the allowed environmental level of HC (below 20 ppm, see Appendix A).
- The changes for other emission parameters were either relatively small (no more than 1%) or were not statistically significant (P-values exceeding threshold of 0.05).



Figure 5. Emissions test setup for Volkswagen Passat 2006.



Figure 6. Emissions test setup – the AVL 4000 tester.

# Discussion

### COMPARATIVE ANALYSIS OF RESULTS FOR TEST CARS

Table 7 represents the relative changes in tailpipe exhaust emissions after each test car completed its road run (250±20 km) on the additive-treated fuel.

# Table 7. Relative changes in tailpipe exhaust emissions of test cars with the additive-treated fuel in comparison to the standard fuel.

Test car model, year of manufacturing, odometer reading	Fuel		ld	le engine spe	ed			Crui	sing engine s	peed		
						Parar	meter					
		CO %vol	CO <sub>2</sub> %vol	O2 %vol	HC ppm HEX	NO <sub>x</sub> ppm vol	CO %vol	CO <sub>2</sub> %vol	O2 %vol	HC ppm HEX	NO <sub>x</sub> ppm vol	
			Relative change, % and its statistical significance, Yes / No									
Toyota Camry 2000 246,487 km		+ 7.91 No	+ 0.5 Yes	-33.2 Yes	- 7.9 Yes	- 13.3 No	+ 3.1 No	+ 0.1 No	- 68.0 No	- 24.8 Yes	- 25.5 Yes	
Volkswagen Golf 2001 186,299 km		- 6.1 Yes	+ 0.4 No	- 9.4 Yes	- 7.1 No	- 7.7 Yes	- 30.8 Yes	- 0.1 No	+ 9.9 No	- 7.9 No	- 2.1 No	
Mitsubishi Chariot 1994 239,131 km	RON 95		After the tes maintain	st run the engi the required 7	ne could not 750 RPM		- 15.6 No	+ 0.8 No	- 29.0 Yes	- 20.5 Yes	- 14.3 Yes	
Mitsubishi Galant 1999 264,001 km		+ 7.6 No	- 0.3 No	-30.0 Yes	- 11.1 No	- 27.7 Yes	+ 8.8 No	- 0.3 No	- 11.6 Yes	- 18.8 Yes	- 17.1 Yes	
Volkswagen Passat 2006 112,004 km		- 50.0 No	- 0.6 Yes	+ 2.7 No	- 17.3 No	+ 25.0 No	+ 16.7 No	- 0.3 No	- 30.8 Yes	+ 76.8 Yes	+15.0 No	

1. "+" indicates increase, "-" indicates decrease of an emission parameter for the treated fuel.

Results do not carry an importance due to statistical insignificance (P-values exceeding the threshold of 0.05).

Results do not carry an importance because the relative change of the parameter was too small (less than 1%).

Results carry a limited importance as the registered values approached the lower limit of the measurement range and the actual change was close to the resolution capability of the testing equipment (0.01% for CO, see Appendix A).

Results carry a limited importance because the registered actual change was within the allowed environmental level of the parameter (below 20 ppm for HC, see Appendix A).

Results are important and statistically verified.

The changes in tailpipe exhaust emissions are discussed in the order of their importance:

### REDUCTION IN OXIDES OF NITROGEN AND OXYGEN

The fuel-additive product has demonstrated the ability to reduce the concentration of oxides of nitrogen (NO<sub>X</sub>). At idle engine speed, two out of five test cars had the concentration of this pollutant reduced by between 7.7% and 27.7%. At cruising engine speed, three out of five test cars had the concentration of NO<sub>X</sub> reduced by between 14.3% and 25.5%. At the same time, the concentration of oxygen (O<sub>2</sub>) in the tailpipe exhaust was also reduced considerably. At idle engine speed, three out of five cars had the concentration of O<sub>2</sub> reduced by between 9.4% and 33.2%. At cruising engine speed, three out of five and 11.6% and 30.8%.

According to Faiz, Weaver and Walsh (1996), the main nitrogen oxide, normally emitted from internal combustion engines, is nitric oxide (around 90% of the total oxides of nitrogen). This gas is formed by nitrogen and free oxygen reacting at high temperatures. The rate of formation depends on oxygen availability, and exponentially increases with temperature (Faiz et al., 1996, p. 82). The observed decrease of both NO<sub>x</sub> and O<sub>2</sub> in tailpipe emissions in the test cars indicates that the fuel additive may have reduced the amount of free oxygen available to form nitric oxide during the combustion process. The mechanism in which free oxygen was utilised remains unknown – there was no corresponding increase in  $CO_2$  emissions. The other possible mode of action for the fuel additive could be a decrease in combustion temperature. The direct measurement of combustion temperature requires special equipment and involves sophisticated methods, therefore this parameter was not monitored during the tests in this study.

### **HYDROCARBONS**

Levels of hydrocarbons (HC) in the tailpipe exhaust also changed. At idle engine speed, one car had the concentration of HC reduced by 7.9%. At cruising engine speed, three out of five cars had the concentration of HC reduced by between 18.8% and 24.8%, and one car had the concentration of HC increased by 76.8%. However, all these results for hydrocarbons carry a limited importance because the actual changes of the average concentration of hydrocarbons were between 3.8 ppm and 18.6 ppm. According to the testing equipment manufacturer (see Appendix A), such small actual changes could be caused by differences in the workshop environment (ambient temperature, pressure, relative humidity, air circulation) after the car arrived from the test run.

### CARBON MONOXIDE

Only one car demonstrated changes in the level of carbon monoxide (CO) with the treated fuel. At idle engine speed it was reduced by 6.1% and at cruising engine speed, the reduction was 30.8%. However, the result at cruising engine speed carries a limited importance as the measured values (between

0.03% and 0.07% of CO) approached the lower limit of the measurement range, and the actual change was close to the resolution capability of the testing equipment (0.01% for CO, see Appendix A).

### OTHER EMISSION PARAMETERS

The changes for other emission parameters were either relatively small (below 1%) or were not statistically significant (P-values exceeding the threshold of 0.05).

### RECOMMENDATIONS FOR FURTHER RESEARCH

A further, more extensive study is needed to determine the full impact of this fuel-additive application. It may include the following components:

- a. Emissions tests in controlled laboratory conditions (on a rolling road, or on a chassis dynamometer) under various speeds and loads.
- b. Assessment of transitional effects of the fuel additive, after an engine resumes running on the standard fuel.
- c. Measurement of an engine's torque/power output, fuel consumption and knock resistance.
- d. Inspection of deposit removal and/or deposit formation processes in the engine, fuel system and exhaust system.
- e. Evaluation of long-term positive/negative effects on a vehicle, including impact on the engine's reliability and serviceability.
- f. Testing of the fuel additive to ensure that its application is safe for human health and the environment.

If any further emissions tests are undertaken for this fuel additive, it is recommended these are performed on old cars with high-mileage engines, as modern cars are already highly efficient in reducing exhaust emissions.

# Conclusion

The results of the conducted experiments demonstrate that the use of the fuel additive had positive effects on tailpipe emissions of the tested cars, manufactured between 1994 and 2006, with high odometer readings. The most important result is the reduction of the concentration of oxides of nitrogen (NO<sub>x</sub>). When compared with the cars running on standard fuel, the concentration of this hazardous pollutant was reduced by between 7.7% and 27.7%.

The concentration of  $O_2$  in tailpipe emissions was reduced (between 9.4% and 33.2%) for the majority of the test cars running on the treated fuel. Oxygen is not a hazardous pollutant, but its decreased concentration in the tailpipe emissions normally indicates more complete utilisation of  $O_2$  as an oxidising agent.

The observed decrease of both  $NO_x$  and  $O_2$  in tailpipe emissions of the test cars indicates that the fuel additive may have reduced the amount of free oxygen available to form nitric oxide during the combustion process. The

mechanism in which free oxygen was utilised remains unknown, as there was no corresponding increase in  $CO_2$  emissions. The other possible mode of action for the fuel additive could be a decrease in combustion temperature.

Changes of other tested parameters of the tailpipe emissions (carbon monoxide, carbon dioxide and hydrocarbons) were not considered to be conclusive.

The chemical composition of the tested product was unknown (such confidentiality is a common requirement in the additive industry to protect commercially sensitive information) and the exact mechanism by which this fuel additive worked was uncertain. A further, more extensive study is required to determine the full impact of this fuel-additive application.

### LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

Percent by volume	NO <sub>x</sub>	Oxides of nitrogen	
Carbon dioxide	O <sub>2</sub>	Allotrope of oxygen	
Carbon monoxide	PM	Particulate matter	
Deposit-control additives	PPM	Parts per million	
United States Environmental	P-value	Probability value	
Protection Agency	RON	Research octane number	
Hydrocarbons	RPM	Revolutions per minute	
Internal combustion engine	λ	Air/Fuel ratio or Lambda	
	Percent by volume Carbon dioxide Carbon monoxide Deposit-control additives United States Environmental Protection Agency Hydrocarbons Internal combustion engine	Percent by volumeNOxCarbon dioxideO2Carbon monoxidePMDeposit-control additivesPPMUnited States EnvironmentalP-valueProtection AgencyRONHydrocarbonsRPMInternal combustion engineλ	

FIGURE A1. AVL 4000 TESTER SPECIFICATION AND MEASUREMENTS CHARACTERISTICS (AVL DITEST, 2002).

### MEASUREMENT DATA:

	Measurement Range	Resolution
AVL DiGas 4000/AVL DiCom 4000		
CO:	0 10 % Vol.	0.01 % Vol.
CO <sub>2</sub> :	0 20 % Vol.	0.1 % Vol.
HC:	0 20 000 ppm Vol.	1 ppm
NOx:	0 5 000 ppm Vol.	1 ppm
02:	0 25 % Vol.	0.01 % Vol.
λ-calculation:	0 9.999	0.001
λ-sensor voltage:	0 5.0 V	0.04 V
Engine Speed:	250 9 990 rpm	10 rpm
Oil Temperature:	0 150 °C	1 °C
Ignition Angle TDC Sensor:	- 60 100 °c.a.	0.1 °c.a.
Ignition Angle Stroboscope:	0 60 °c.a.	0.1 °c.a.
Dwell Angle:	0 100 %	1.0 %

# FIGURE A2. THE ALLOWED MAXIMUM VALUE OF HYDROCARBONS (HC) IN THE TESTING ENVIRONMENT BY THE AVL TESTER MANUFACTURER (AVL DITEST OPERATING MANUAL, 2001).

The tester automatically checks the HC residue in the sampling hose and lines. The probe must be in the fresh air and not in the exhaust pipe!

#### HC RESIDUE



If the probe is not in the exhaust gas flow and the HC concentration is greater than 20 ppm, there may be a high level of petrol residue in the air. Make sure the probe intake is fresh air - move to another location if necessary or ventilate the room.

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