

AECC, CLEPA, EUROMOT and OICA proposal

Recommendation concerning Guidelines for Market Fuel Quality

in R.E.3 and/or S.R.1

Justification

The objective of this document is to provide recommendations for the **minimum quality of market fuels** (i.e. gasoline and diesel) **that should be introduced in parallel, and at the same time, to complement the level of motor vehicle and non-road mobile machinery pollutant emission standards that a country or region may be considering to introduce.**

For the purpose of these recommendations, the motor vehicle and non-road mobile machinery pollutant emissions standards are those identified in the various series of UNECE Regulation No 83, UNECE Regulation No 49 and UNECE Regulation No 96⁽¹⁾ that might be considered by countries or regions introducing for the first time, or strengthening, motor vehicle emission standards.

Scope of the recommendation

This Recommendation applies to fuel quality parameters that directly affect the performance and durability of engine and exhaust emission control equipment and influence the content of exhaust emissions.

Definitions and Abbreviations

AQIRP	Air Quality Improvement Research Program
CEN	European Committee for Standardization
DPF	Diesel Particulate Filter
HC	Hydrocarbons
JCAP	Japan Clean Air Programme
OBD	On-board diagnostics
PM	Particulate matter
TEL	Tetra Ethyl Lead

⁽¹⁾ See Annex C for the correlation between the series of Regulation No 83, Regulation No 49 and Regulation No 96 and the respective European emission standards.

Introduction

It is acknowledged that market fuel quality plays a key role in the level and type of pollutant emissions from motor vehicles. Regulations and specifications for market fuel quality are not yet well harmonized (even in the same region) and they are not always fully aligned with the needs of engine technology to help meet pollutant emission regulations in force. As many world regions and cities suffer from poor air quality and move towards more stringent motor vehicle emission regulations, this requires the use of more advanced emission control technology on engines - which drives the crucial need for improved market fuel quality.

This recommendation defines a list of key fuel parameters linked to legally required emissions levels and suggests the minimum fuel quality requirements corresponding to vehicle technologies necessary to help achieve and maintain such emission levels. It has to be recognised that other parameters can influence tailpipe pollutant emissions and thus adherence to this list may not be sufficient to enable durable compliance to the relevant emissions standards for all vehicle concepts.

The list of parameters has been herewith linked to emission limits set in the various series of UNECE Regulations No 83 and No 49 up to the versions of R83.05 (row B) and R49.03 (row B1) and UNECE Regulation No 96 up to the version R96.02. An extension to cover more recent and more stringent emission limits may be needed in due time in order to keep this recommendation updated to technical progress.

Considering that the annex to the Consolidated Resolution on the Construction of Vehicles (R.E.3)⁽²⁾ set, as a first step, limited recommendations concerning lead and sulphur in gasoline and sulphur, ash and total contamination in diesel, a fuller set of fuel parameters should now be included that impact:

- a) On the performance and durability of engines and emission control equipment and,
- b) Parameters that have an impact on human health and the environment.

The position of OICA, EUROMOT, CLEPA and AECC is, in general, that a recommendation to WP29 to definitively link emissions standards and necessary fuel quality should be based on the World Wide Fuel Charter (WWFC) which, in the 5th version being completed now, sets 5 categories of petrol and 5 categories of diesel fuel characteristics that are appropriate for various emission control technology mixes.

However, international fuel standards (e.g. CEN) have been developed from the emission technology-fuel specifications that have been driven by European legislation. These CEN standards, developed on a technical basis between the various stakeholders in CEN, provide for European market fuels that are, essentially, fit for purpose.

The parallel application of appropriate market fuel standards must be an important part of an integrated approach by Contracting Parties to enable improved and long-lasting emission reductions during the lifetime of all motor vehicles.

For information:

- Annex A shows the historical development of on-road and non-road emission standards and fuel quality (based on CEN standards).

⁽²⁾ ECE-TRANS-WP29-2011-127e.pdf

- Annex B details the fuel parameters that have been changed in alignment with the progression of the UNECE emission standards that require the use of more advanced exhaust after-treatment control technology that are affected by market fuel quality.
- Annex C shows the correlation between the series of UNECE Regulation No 83, UNECE Regulation No 49 and UNECE Regulation No 96 and the parallel Euro standards.
- Annex D gives details of gasoline parameters – extract of the latest draft of the 5th edition of the World Wide Fuel Charter (published September 2013).
- Annex E gives details of diesel parameters - extract of the latest draft of the 5th edition of the World Wide Fuel Charter (published September 2013).
- Annex F gives details of recommended housekeeping for fuel management.

Recommendation

The clearly demonstrated link between emission standards and market fuel quality – which the European Union, Japan and the USA have all followed - should followed in those world areas that are now introducing for the first time, or adopting more stringent emission standards, for on-road motor vehicles and non-road mobile machinery.

The short-list of parameters outlined in annex to the Consolidated Resolution on the Construction of Vehicles (RE3) and in SR1 is insufficient for this purpose and for ensuring in-service performance and durability of emission control systems. Therefore, OICA proposes that the list of fuel parameters be extended.

In this respect, OICA, EUROMOT, CLEPA and AECC propose that the parameters shown in the following tables (gasoline and diesel for on-road engines and diesel for non-road mobile machinery) be included in RE3 and SR1.

Fuel Quality Recommendations – on road vehicles:

Unleaded Gasoline:	R83.03	R83.05 (row A)	R83.05 (row B)	Test method
Lead [g/l] ⁽¹⁾	No intentional addition, with a max $\leq 0,013^{(1)}$	No intentional addition, with a max $\leq 0,005^{(1)}$	No intentional addition, with a max $\leq 0,005^{(1)}$	EN 237
Sulphur [mg/kg] ⁽¹⁾	$\leq 500^{(1)}$	$\leq 150^{(1)}$	$\leq 50^{(1)}$	EN ISO 20846 EN ISO 20884
Metal Additives [mg/l]	----- Not permitted -----			
Oxygen [%m/m]	[$\leq 2,7$]	$\leq 2,7$	$\leq 2,7$	EN 1601 EN 13132
Oxygenates [%v/v]				
- methanol	$\leq 3,0^{(2)}$	$\leq 3,0^{(2)}$	$\leq 3,0^{(2)}$	
- ethanol	$\leq 5,0$	$\leq 5,0$	$\leq 5,0$	
- iso-propyl alcohol	$\leq 10,0$	$\leq 10,0$	$\leq 10,0$	
- iso-butyl alcohol	$\leq 10,0$	$\leq 10,0$	$\leq 10,0$	EN 1601 EN 13132
- tert-butyl alcohol	$\leq 7,0$	$\leq 7,0$	$\leq 7,0$	
- ethers	$\leq 15,0$	$\leq 15,0$	$\leq 15,0$	
- other oxygenates	$\leq 10,0$	$\leq 10,0$	$\leq 10,0$	
RVP [kPa]	35 - 100	45 – 100	45 – 100	EN 13016/ DVPE
Density [kg/m ³]	725 – 780	720 – 775	720 – 775	EN ISO 3675 EN ISO 12185
RON	[≥ 95]	[≥ 95]	[≥ 95]	EN ISO 5164
MON	[≥ 85]	[≥ 85]	[≥ 85]	EN ISO 5163
Benzene [%v/v]	≤ 5	≤ 1	≤ 1	EN 238 EN 14517
Aromatics [%v/v]	-	≤ 42	≤ 35	EN 14517 EN15553
Olefins [%v/v]	-	≤ 21 & 18	≤ 18	EN 14517 EN15553
VLI (10VP + E70)	-	1050 – 1250	1050 - 1250	
Residue [%v/v]	< 2	<2	<2	EN ISO 3405

⁽¹⁾ Already agreed in annex to the Consolidated Resolution on the Construction of Vehicles (RE3). Industry recommends maximum 50ppm sulphur.

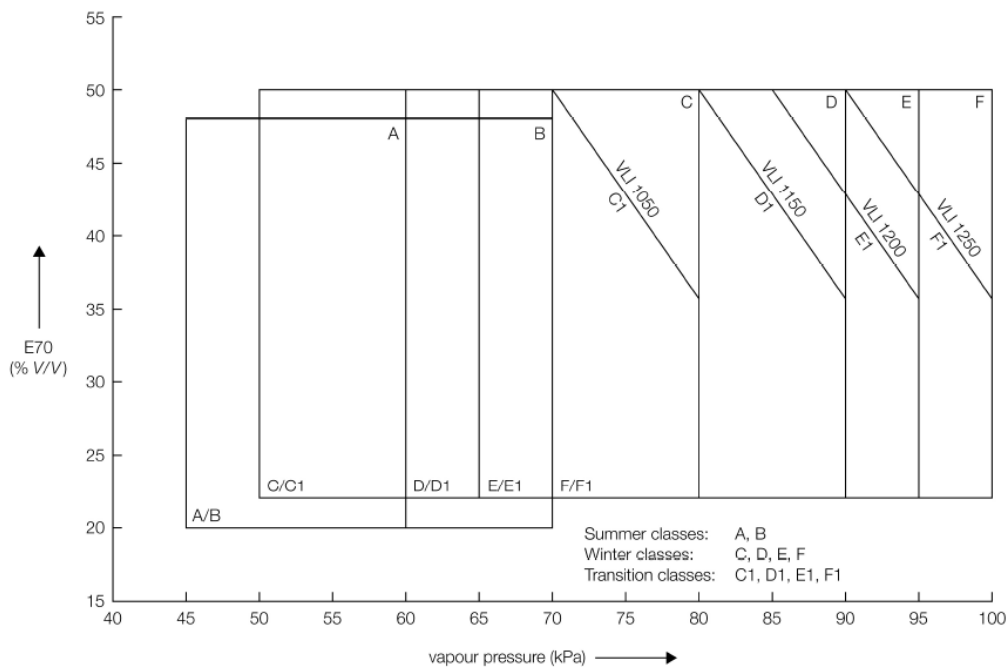
⁽²⁾ Industry recommends no methanol content (non-detectable).

Volatility Classes for Unleaded Gasoline:

Class ^(*)	A	B	C/C1	D/D1	E/E1	F/F1
Vapour pressure (kPa)	45 – 60	45 - 70	50 - 80	60 - 90	65 - 95	70 - 100
E70 (%) ⁽¹⁾	20 - 48	20 - 48	22 - 50	22 - 50	22 – 50	22 – 50
E100 (%) ⁽¹⁾	46 - 71	46 - 71	46 - 71	46 - 71	46 - 71	46 - 71
E150 (% min) ⁽¹⁾	75	75	75	75	75	75
Final boiling point (°C max) ⁽¹⁾	210	210	210	210	210	210
T10 (°C, max) ⁽¹⁾	65	60	55	50	45	45
T50 (°C, max) ⁽¹⁾	77-100	77-100	75-100	70-100	65-100	65-100
T90 (°C, max) ⁽¹⁾	130-175	130-175	130-175	130-175	130-175	130-175
Distillation residue (% V/V)	2	2	2	2	2	2
Vapour Lock Index (VLI) (10 VP + 7 E70) (index max)	-	-	C	D	E	F
Vapour Lock Index (VLI) (10 VP + 7 E70) (index max)			C1 1050	D1 1150	E1 1200	F1 1250

(*) 'Class' is based on the minimum expected ambient temperature of the market and will vary by season.

(1) E-values or T-values as alternatives.



Relation between VP, E70 and VLI for the ten different volatility classes for unleaded gasoline

Diesel – on-road vehicles:

	R83.03 and R49.02 (Stage II)	R83.05 (row A) and R49.03 (row A)	R83.05 (row B) and R49.03 (row B)	Test method
Sulphur [mg/kg] ⁽¹⁾	≤ 500 ⁽¹⁾	≤ 350 ⁽¹⁾	≤ 50 ⁽¹⁾	EN ISO 20846 EN ISO 20884
Ash [%m/m] ⁽¹⁾	≤ 0,01 ⁽¹⁾	≤ 0,01 ⁽¹⁾	≤ 0,01 ⁽¹⁾	EN/ISO 6245
Total Contamination [mg/kg] ⁽¹⁾	≤ 24 ⁽¹⁾	≤ 24 ⁽¹⁾	≤ 24 ⁽¹⁾	EN 12662
Cetane Number ⁽²⁾	[≥ 49]	[≥ 51]	[≥ 51]	EN ISO 5165
Cetane Index ⁽²⁾	[≥ 46]	[≥ 46]	[≥ 46]	EN ISO 4264
Density [kg/m ³] ⁽²⁾	820 – 860	820 – 845	820 – 845	EN ISO 3675 EN ISO 12185
Viscosity [mm ² /s] ⁽²⁾	2,0 - 4,5	2,0 - 4,5	2,0 – 4,5	EN ISO 3104
Flash Point [°C]	> 55	> 55	> 55	EN ISO 2719
T50 [°C]	-	T65 = 250 min	T65 = 250 min	EN ISO 3405
T85 [°C]	≤ 350	≤ 350	≤ 350	EN ISO 3405
T95 [°C]	≤ 370	≤ 360	≤ 360	EN ISO 3405
PAH [%m/m]	≤ 11	≤ 11	≤ 11	EN 12916
Carbon residue [%m/m]	≤ 0,3	≤ 0,3	≤ 0,3	EN ISO 10370
CFPP [°C] ⁽²⁾	-44 to +5	-44 to +5	-44 to +5	EN 116
Cloud Point [°C] (severe winter conditions) ⁽²⁾	-34 to -10	-34 to -10	-34 to -10	EN 23015
Copper strip corrosion (3h at 50°C) [rating]	Class 1			EN ISO 2160
Water [mg/kg]	≤ 200	≤ 200	≤ 200	EN ISO 12937
Lubricity [micron]	≤ 460	≤ 460	≤ 460	EN ISO 12156-1
Oxidation stability [hours] ⁽³⁾	> 20	> 20	> 20	EN15751
FAME [%v/v]	(4)	(4)	(4)	EN14214 ASTM D6751
Appearance	Clear and bright, no free water or particulates			D4176 visual inspection
Ethanol/Methanol [%v/v]	Non-detectable ⁽⁵⁾			

(1) Already agreed in annex to the Consolidated Resolution on the Construction of Vehicles (RE3). Industry recommends maximum 50ppm sulphur.

(2) Implementing country to choose value appropriate within range for arctic or severe winter conditions. More detailed arctic or severe winter specifications for these parameters to be considered.

(3) Applicable for diesel containing more than 2%v/v FAME.

(4) Up to 5%v/v FAME permitted if FAME complies with ASTM D6751. Up to 7%v/v FAME permitted if FAME complies with EN14214. Industry recommends that vehicle owners refer to their vehicle handbook.

(5) At or below detection limit of method used.

Diesel – non-road mobile machinery:

	R96 Power bands A to C	R96.01 Power bands D to G	R96.02 Power bands H to K	Test method
Sulphur [mg/kg] ⁽¹⁾	≤ 2000 ⁽¹⁾	≤ 2000 ⁽¹⁾	≤ 300 ⁽¹⁾	ASTM D5453
Ash [%m/m] ⁽¹⁾	≤ 0,01 ⁽¹⁾	≤ 0,01 ⁽¹⁾	≤ 0,01 ⁽¹⁾	EN/ISO 6245
Total Contamination [mg/kg] ⁽¹⁾	≤ 24 ⁽¹⁾	≤ 24 ⁽¹⁾	≤ 24 ⁽¹⁾	EN 12662
Cetane Number ⁽²⁾	[≥ 45]	[≥ 45]	[≥ 52]	EN ISO 5165
Density [kg/m ³] ⁽²⁾	835 – 845	835 – 845	833 – 837	EN ISO 3675 ASTM D4052
Viscosity [mm ² /s] ⁽²⁾	2,0 - 4,5	2,0 - 4,5	2,0 – 4,5	EN ISO 3104
Flash Point [°C]	> 55	> 55	> 55	EN ISO 2719
T50 [°C]	-	-	> 250	EN ISO 3405
T95 [°C]	≤ 370	≤ 370	345-350	EN ISO 3405
Final boiling point [°C]	-	-	≤ 370	EN ISO 3405
PAH [%m/m]	≤ 11	≤ 11	≤ 11	EN 12916
Carbon residue [%m/m]	≤ 0,3	≤ 0,3	≤ 0,3	EN ISO 10370
CFPP [°C] ⁽²⁾	-44 to +5	-44 to +5	-44 to +5	EN 116
Cloud Point [°C] (severe winter conditions) ⁽²⁾	-34 to -10	-34 to -10	-34 to -10	EN 23015
Copper strip corrosion (3h at 50°C) [rating]	Class 1			EN ISO 2160
Water [mg/kg]	≤ 500	≤ 500	≤ 500	EN ISO 12937
Lubricity [micron]	≤ 460	≤ 460	≤ 460	EN ISO 12156-1
Oxidation stability [hours] ⁽³⁾	> 20	> 20	> 20	EN15751
FAME [%v/v]	(4)	(4)	(4)	EN14214 ASTM D6751
Appearance	Clear and bright, no free water or particulates			D4176 visual inspection
Ethanol/Methanol [%v/v]	Non-detectable ⁽⁵⁾			

(1) Already agreed in annex to the Consolidated Resolution on the Construction of Vehicles (RE3) for on-road engines only. Industry recommends maximum 50ppm sulphur.

(2) Implementing country to choose value appropriate within range for arctic or severe winter conditions. More detailed arctic or severe winter specifications for these parameters to be considered.

(3) Applicable for diesel containing more than 2%v/v FAME.

(4) Up to 5%v/v FAME permitted if FAME complies with ASTM D6751. Up to 7%v/v FAME permitted if FAME complies with EN14214. Industry recommends that vehicle owners refer to their vehicle handbook.

(5) At or below detection limit of method used.

ANNEX A - Evolution of the UNECE emission standards:

Emission standards have been linked with a revision of the respective European market fuel standards (EN228 and EN590):

On-road standards:

UNECE Emission Levels	Gasoline				Diesel				Date of application	
	CO (g/km)	HC+NOx (HC/NOx) (g/km)		PM (g/km)	Fuel standard	CO (g/km)	HC+NOx (HC/NOx) (g/km)	PM (g/km)		Fuel standard
R83.03	2.2	0.5		-	EN228: 1993	1.0	0.7	0.08	EN590: 1993	1996
R83.05 (level A)	2.3	0.2	0.15	-	EN228: 1999	0.64	0.50	0.05	EN590: 2000	2000
R83.05 (level B)	1.0	0.1	0.08	-	EN228: 2004	0.5	0.30	0.025	EN590: 2004	2005
R83.06	1.0	0.1	0.60	0.0045	EN228: 2008	0.5	0.23	0.0045	EN590: 2008	2009

UNECE Emission Levels	Diesel						Date of application
	CO (g/kWh)	NMHC (g/kWh)	THC (g/kWh)	NOx (g/kWh)	PM (g/kWh)	Fuel standard	
R49.02 (level B) ⁽¹⁾	4.0	-	1.1	7.0	0.15	EN590: 1993	1995
R49.03 (level A) ⁽²⁾	5.45	0.78	1.6	5.0	0.03	EN590: 2000	2000
R49.03 (level B1) ⁽²⁾	4.0	0.55	1.1	3.5	0.03	EN590: 2004	2005
R49.03 (level B2) ⁽²⁾	4.0	0.55	1.1	2.0	0.02	EN590: 2008	2008

⁽¹⁾ Limits shown for the 13-mode test.

⁽²⁾ Limits shown for the ETC test only.

Non-road standards:

UNECE Emission Levels	Power band	Net power (P) (kW)	CO (g/kWh)	HC (g/kWh)	NOx (g/kWh)	PM (g/kWh)	Date of application
R96	A	$P \geq 130$	5	1,3	9,2	0,54	1995
	B	$75 \leq P < 130$	5	1,3	9,2	0,7	
	C	$37 \leq P < 75$	6,5	1,3	9,2	0,85	
R96.01	E	$130 \leq P \leq 560$	3,5	1,0	6,0	0,2	2001
	F	$75 \leq P < 130$	5,0	1,0	6,0	0,3	
	G	$37 \leq P < 75$	5,0	1,3	7,0	0,4	
	D	$18 \leq P < 37$	5,5	1,5	8,0	0,8	

UNECE Emission Levels	Power band	Net power (P) (kW)	CO (g/kWh)	HC + NOx (g/kWh)	PM (g/kWh)	Date of application
R96.02	H	$130 \leq P \leq 560$	3,5	4,0	0,2	2008
	I	$75 \leq P < 130$	5,0	4,0	0,3	
	J	$37 \leq P < 75$	5,0	4,7	0,4	
	K	$19 \leq P < 37$	5,5	7,5	0,6	

ANNEX B

Evolution of stringency of gasoline market fuel quality standards:

On-road standards:

Gasoline	R83.03	R83.05 (row A)	R83.05 (row B)
RON	95	95	95
MON	85	85	85
Lead	0,013	0,005	0,005
Sulphur	500	150	50 [10]
Benzene	5	1	1
Aromatics	-	42	35
Olefins	-	21 & 18	18
Oxygen	-	2,7	2,7
RVP	35 - 100	45 - 100	45 - 100
VLI	-	1050 - 1250	1050 - 1250
Density	725 - 780	720 - 775	720 - 775
FBP	215	210	210
E70	15 - 47	20 - 50	20 - 50
E100	40 - 70	46 - 71	46 - 71
E180	85	-	-
Residue	2	2	2

Evolution of stringency of diesel market fuel quality standards:

On-road standards:

Diesel	R83.03 R49.03	R83.05 (level A) R49.05 (level A)	R83.05 (level B) R49.05 (level B1)
Cetane Number	49	51	51
Cetane Index	46	46	46
Sulphur	500	350	50 & 10
Density	820 - 860	820 - 845	820 - 845
Viscosity	2,0 - 4,5	2,0 - 4,5	2,0 – 4,5
T50	Report	T65 = 250 min	T65 = 250 min
T85	350 max	350 max	350 max
T95	360 max	360 max	360 max
PAH	11	11	11
Flash Point	55	55	55
CCR	0,3	0,3	0,3
CFPP	[-44] to +5	[-44] to +5	[-44] to +5
Cloud Point	-34 to -10	-34 to -10	-34 to -10
Water and sediment	-	0,0024	0,0024
Water	0,02	0,02	0,02
Ash	0,01	0,01	0,01
Lubricity	-	460	460

ANNEX C

On-road:

Correlation between the series of Regulation 83 and Regulation 49 and Euro emission standards.

UNECE Regulation 49	Euro standard
R49.02 level B	Euro II
R49.03 level A	Euro III
R49.03 level B1	Euro IV

UNECE Regulation 83	Euro standard
R83.03	Euro 2
R83.05 level A	Euro 3
R83.05 level B	Euro 4

Non-road:

Correlation between the series of Regulation 96 and Euro emission standards.

UNECE Regulation 96	NRMM Directive 97/68/EC
R96	Stage I
R96.01	Stage II
R96.02	Stage IIIA

ANNEX D - GASOLINE TECHNICAL ANNEX

OCTANE NUMBER

Octane number is a measure of a gasoline's ability to resist auto-ignition; auto-ignition can cause engine knock, which can severely damage engines. Two laboratory test methods are used to measure octane: one determines the Research Octane Number (RON) and the other determines the Motor Octane Number (MON). RON correlates best with low speed, mild-knocking conditions and MON correlates with high-temperature knocking conditions and with part-throttle operation. RON values are typically higher than MON, and the difference between these values is the sensitivity, which should not exceed 10. In North America, $(RON + MON)/2$ is typically used to specify the octane rating, while many other markets typically specify RON.

Vehicles are designed and calibrated for a certain octane rating. When a customer uses gasoline with an octane rating lower than required, knocking may result. Engines equipped with knock sensors can handle lower octane ratings by retarding the spark timing, but this will increase fuel consumption, impair driveability and reduce power, and knock may still occur. Using gasoline with an octane rating higher than recommended will not cause problems.

Gasoline sold at higher altitudes should have the same octane ratings as gasoline sold at lower altitudes. Historically, for older model engines, lower octanes provided the same anti-knock performance at high altitudes as higher octanes provided at sea level. Since 1984, however, most vehicles have been equipped with sophisticated electronic control systems that adjust to changes in air temperature and barometric pressure, and these vehicles require the same octane levels at all altitudes.

Ash-forming (metal-containing) additives sometimes used for boosting octane are not recommended (see Ash-Forming Additives discussion below). Certain oxygenates, on the other hand, also can boost octane but can do so more safely.

Increasing the minimum octane rating available in the marketplace has the potential to help vehicles significantly improve fuel economy and, consequently, reduce vehicle CO₂ emissions. While the improvement will vary by powertrain design, load factor and calibration strategy, among other factors, vehicles currently designed for 91 RON gasoline could improve their efficiency by up to 3% if manufacturers could design them for 95 RON instead. Octane rating is becoming an especially important limiting factor in future efficiency improvements because new, more efficient engine designs, such as smaller displacement turbo-charged engines, are approaching their theoretical knock limits when using lower octane rated gasoline. Raising the minimum market octane to 95 RON will enable manufacturers to optimize powertrain hardware and calibrations for thermal efficiency and CO₂ emissions. All of these technologies and actions will be needed to meet the highly challenging fuel economy and CO₂ requirements emerging in many countries.

SULPHUR

Sulphur naturally occurs in crude oil. If the sulphur is not removed during the refining process it will remain in the vehicle fuel. Cross-contamination also can occur in the fuel distribution system. Sulphur has a significant impact on vehicle emissions by reducing the efficiency of catalysts. Sulphur also adversely affects heated exhaust gas oxygen sensors. Reductions in sulphur will provide immediate reductions of emissions from all catalyst-equipped vehicles on the road.

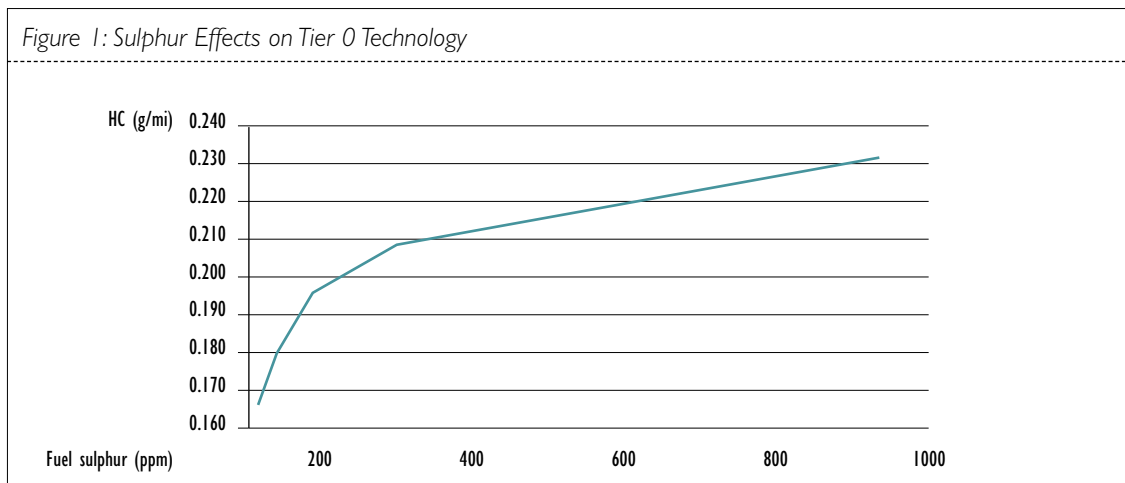
There has been extensive testing done on the impact of sulphur on vehicle emissions. The following studies (see Table 1) indicate the emission reductions that occur with different vehicle technologies as sulphur is reduced from the 'high' sulphur gasoline to the 'low':

Table 1: Impact of Sulphur on Emissions

Study	Vehicle Technology	Sulphur Range (ppm)		Emission Reduction, % (high to low sulphur)		
		high	low	HC	CO	NO _x
AQIRP	Tier 0	450	50	18	19	8
EPEFE	EURO 2+	382	18	9 (43*)	9 (52*)	10 (20*)
AAMA/AIAM	LEV & ULEV	600	30	32	55	48
CRC	LEV	630	30	32	46	61
JARI	1978 Regulations	197	21	55	51	77
Alliance/AIAM	LEV/ULEV	100	30	21	34	27
	LEV/ULEV	30	1	7	12	16
JCAP	DI/NO _x cat.	25	2			37

* Reduction achieved during hot EUDC (extra-urban) portion of test.

Figure 1, which depicts the HC reductions from the US AQIRP study, indicates the typical emission reduction for the different studies as the sulphur level changes, including the significant reduction when sulphur is reduced from about 100ppm to 'low' sulphur fuel. The data illustrate the importance of a very low sulphur limit for advanced technology vehicles.

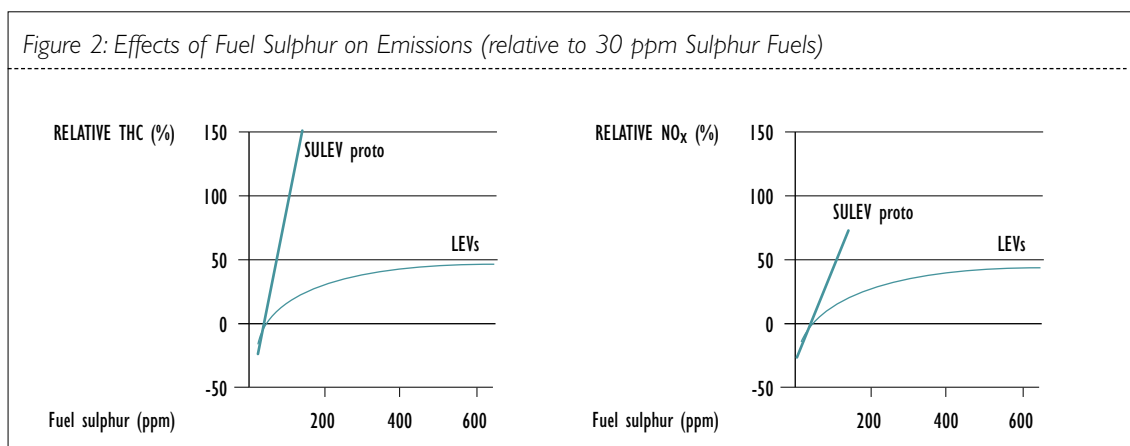


In addition, laboratory research of catalysts has demonstrated delays in light-off time, increase in light-off temperature and reductions in efficiency resulting from higher sulphur fuels across a full range of air/fuel ratios. Studies have also demonstrated that sulphur slows the rich to lean transition, thereby introducing an unintended rich bias into the emission calibration.

Stringent Emission Standard Challenges

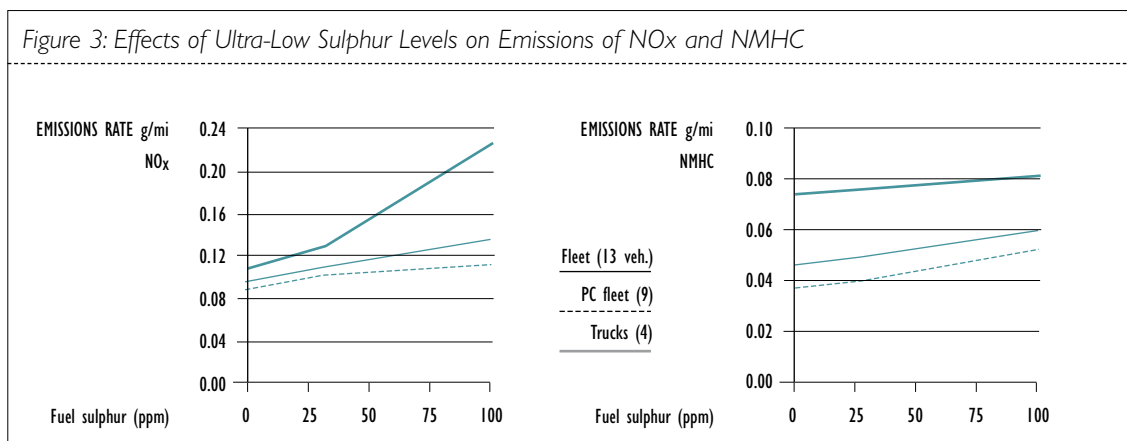
Stringent emission requirements, combined with long-life compliance, demand extremely efficient, and durable, after-treatment systems. For example, it is generally recognised that catalyst hydrocarbon efficiency at 100,000 miles must be at least 93% for a vehicle meeting Low Emission Vehicle (LEV)/EURO 3 standards, and about 97% for a vehicle meeting Ultra-LEV/EURO 4 standards. Studies on LEVs indicate that warmed-up catalyst HC efficiency (i.e. excluding the start-up portion) must be 98% or better for 120,000 miles to ensure that new US Tier 2 emission limits are met. These standards represent significant technological hurdles, even in markets with high quality (Category 3) gasoline.

Figure 2 indicates the significant HC and NO_x sensitivity to sulphur content. Advanced technologies indicate an even higher response to sulphur.



In 2001, the Alliance and AIAM completed a joint test program to evaluate the emission effects of decreasing fuel sulphur levels ranging from 100 to 30 to 1ppm S in a California Phase 2 reformulated gasoline containing 11% MtBE. The test fleet consisted of 13 vehicles with LEV and ULEV technology, including nine passenger cars and four light trucks. Vehicles were tested using the U.S. EPA Federal Test Procedure (FTP). The relative rate of emissions reduction in the 30 to 1ppm S range may have been due to a sulphur contribution from the engine lubricant.

Figure 3 shows how the emissions of NO_x and non-methane hydrocarbons (NMHC) continue to decline significantly at ultra-low sulphur levels for advanced technology vehicles.



Sulphur also will affect the feasibility of advanced on-board diagnostic system requirements. Existing California on-board diagnostic (OBD II) regulations require vehicles to be equipped with catalyst monitors that determine when catalyst efficiency changes and tailpipe emissions increase by 1.5 times the standard. The loss of catalyst efficiency resulting from high sulphur fuels could cause some catalyst monitors to indicate a problem code resulting in the illumination of a malfunction indicator light to signal the driver. Similarly, some LEV data demonstrate that the catalysts monitor could fail to identify when a catalyst operated on high sulphur fuel is no longer able to function.

Advanced and Future Technology

NO_x emission control to the limits required by more advanced emission standards - considering the concurrent needs of maintaining the control for the life of the vehicle and operating under very lean conditions - is among the biggest challenges for emerging

emission control technologies, especially when sulphur is present in the fuel. Three way catalysts and lean NO_x adsorbers are both highly sensitive to sulphur, albeit to different degrees, and the reversibility of the impact remains a concern for both types of emission control systems. Publicly available data are just beginning to emerge as vehicles with these technologies are becoming more widely available.

One study published in 2011 documented the effect of sulphur on a 2009 Model Year mid-sized sedan with three-way catalyst technology meeting California's PZEV standards (see SAE 2011-01-0300) The study compared the effects of a 3ppm sulphur gasoline with those of a 33ppm sulphur gasoline. One of the objectives was to determine whether 3 ppm fuel would cause NO_x emission control to deteriorate during repeated testing, similar to the test-to-test deterioration seen with 33ppm fuel ('NO_x creep'). The study first confirmed that, at the low level of emissions being measured from PZEV technology, sulphur levels as low as 33 ppm can indeed contaminate the emission control system and affect test-to-test NO_x stability during compliance (FTP) testing. Special procedures not typically found during real world driving can be applied prior to testing to nearly recover the original emission system efficiency, but the contamination and emission system degradation do not occur when 3ppm sulphur fuel is used. The study also found that using a 3ppm sulphur fuel can reduce tailpipe NO_x emissions by 40% over the emissions produced when the vehicle is operated using a 33ppm sulphur fuel.

A different type of emission control technology (lean-NO_x adsorbers or traps) is required for lean-burn engines to meet emission standards for NO_x that are associated with more advanced emission standards. Manufacturers are working toward ambitious goals for improved fuel consumption/reduced CO₂ emissions, and operation at lean air-fuel ratio is one of the most promising means to achieve these reductions in gasoline-powered vehicles. Manufacturers estimate lean-burn engines have the potential to reduce fuel consumption by up to 10 to 15%, but lean operation introduces a new challenge: while three-way catalysts effectively remove unburned HC and CO during lean operation, they can remove NO_x only during stoichiometric or rich operation.

Lean-NO_x traps can operate in a lean exhaust environment, but they are highly sensitive to sulphur. Lean NO_x adsorber catalysts function by trapping NO_x chemically during lean engine operation. NO_x can then be released and destroyed over a catalyst by a few seconds of rich operation. However, sulphur oxides are more strongly trapped, and as a competitor to NO_x, they reduce the NO_x capacity of the adsorber. Sulphur removal requires prolonged rich operating conditions, but the original NO_x reduction efficiency level can never be fully recovered. Also, allowing any rich engine operation significantly negates the fuel efficiency benefits of the lean burn engine technologies used with these catalysts. Sulphur-free gasoline is therefore necessary to maximise the benefits of lean-burn, fuel-efficient technology.

Figure 4 and Figure 5 provide examples of the adverse effect of sulphur on storage-type NO_x reduction catalysts. With increased exposure time, the lower sulphur gasoline allow the catalysts to retain a higher NO_x conversion efficiency. Further tests in vehicles (Figure 6 and Figure 7) confirm the critical need for very low sulphur gasoline. Maintaining a high level of NO_x conversion efficiency over a long period of time - e.g. for the life of the vehicle - is another major concern due to sulphur's cumulative impact in the field. Figure 8 shows how ultra-low sulphur gasoline can maintain much higher NO_x conversion efficiencies over time compared with higher sulphur levels. Thus, ultra-low or sulphur-free gasoline is required to achieve and maintain high NO_x conversion efficiencies over years of vehicle use.

Figure 4: Sulphur Effect on Low Emission Vehicles – Direct Fuel Injection Engines (Japan Clean Air Program)

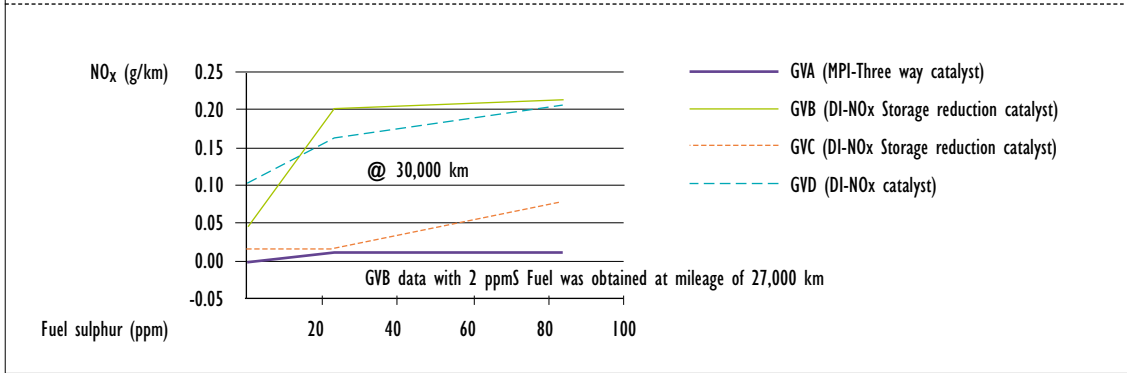


Figure 5: Effect of Fuel Sulphur on Lean NO_x Traps Flow Reactor Study

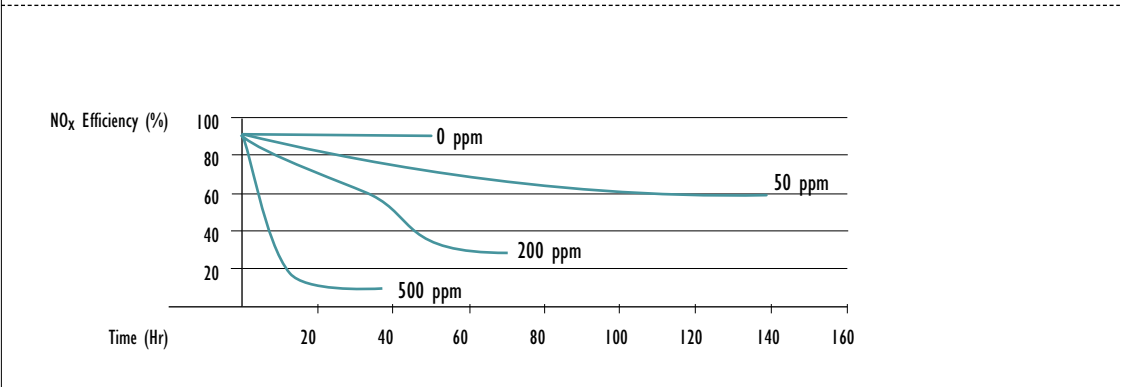


Figure 6: Influence of Sulphur Concentration in Gasoline on Vehicle Aftertreatment System Durability

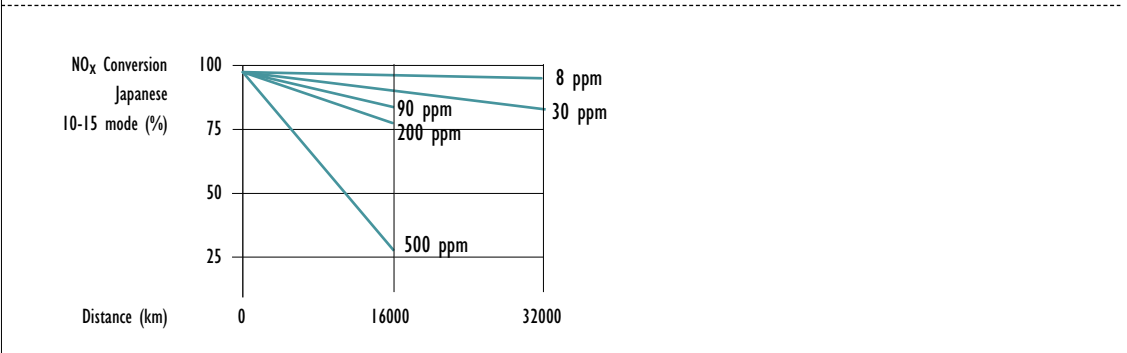


Figure 7: Lean NO_x Adsorber Catalyst Data – Catalyst NO_x Breakthrough vs. Fuel Consumed & Fuel Sulphur Content

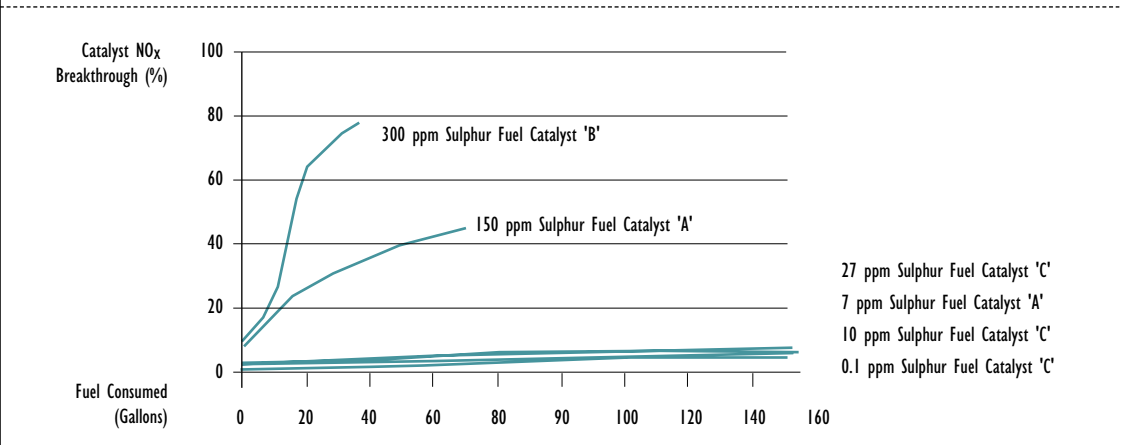
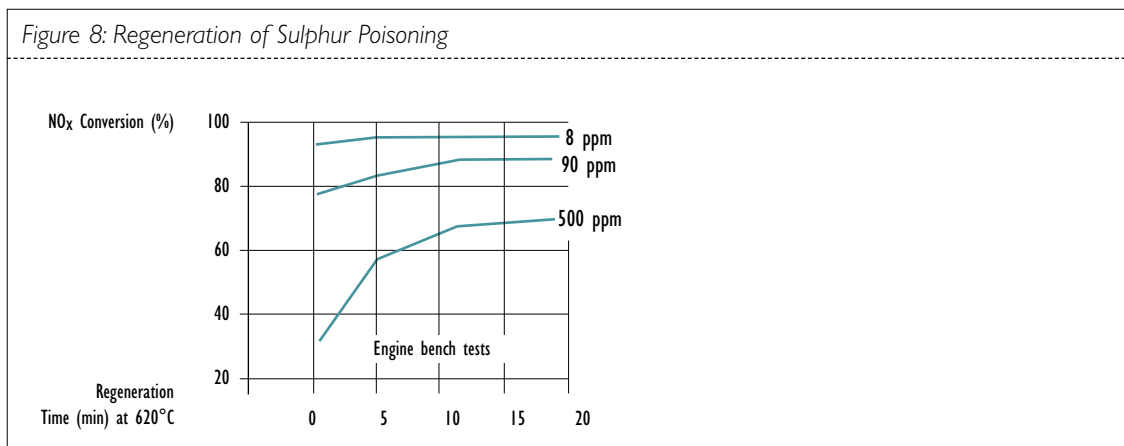


Figure 8: Regeneration of Sulphur Poisoning



ASH-FORMING (METAL-CONTAINING) ADDITIVES

Today's vehicles employ sophisticated exhaust emission control equipment and strategies, such as close-coupled high cell density three-way catalysts, ceramic oxygen sensors and computerized engine control modules that provide precise closed-loop control. These systems must be kept in optimal condition to maintain the vehicle's low emissions capability. Ash-forming fuel additives, such as organo-metallic compounds, and metallic contaminants, such as calcium, copper, phosphorous, sodium and zinc, can adversely affect the operation of these systems in an irreversible way that increases emissions. Thus, high-quality gasoline should be used and ash-forming additives and contaminants must be avoided.

Lead

Tetra-ethyl lead has been used historically as an inexpensive octane enhancer for gasoline, but it will poison vehicle emission control systems. The lead binds to active sites within the catalyst and oxygen sensor, greatly reducing their effectiveness. The tolerance to lead contamination has steadily declined as catalyst efficiencies and sensors have improved, so even a slight amount of lead in the fuel will irreversibly disable the emission control system. As a result, vehicle hydrocarbon and NOx emissions will increase even when the vehicle returns to using lead-free gasoline. Unleaded gasoline must be available wherever catalyst-equipped vehicles refuel; increasingly, this means every market around the world. A global lead-free market also is essential for public health, given lead's well known adverse health effects. These concerns have led most countries to require lead-free gasoline; the few that have not yet done so should eliminate the use of this fuel additive as soon as possible.

Manganese (MMT)

Manganese is a key component of methylcyclopentadienyl manganese tricarbonyl (MMT), which also is marketed as an octane-enhancing fuel additive for gasoline. Like lead, manganese in the fuel will irreversibly reduce the efficiency of exhaust emission control systems.

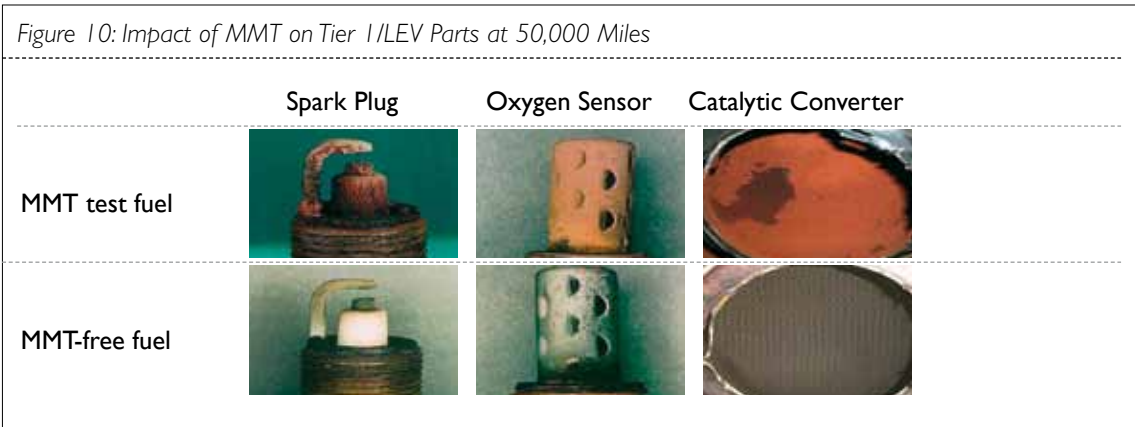
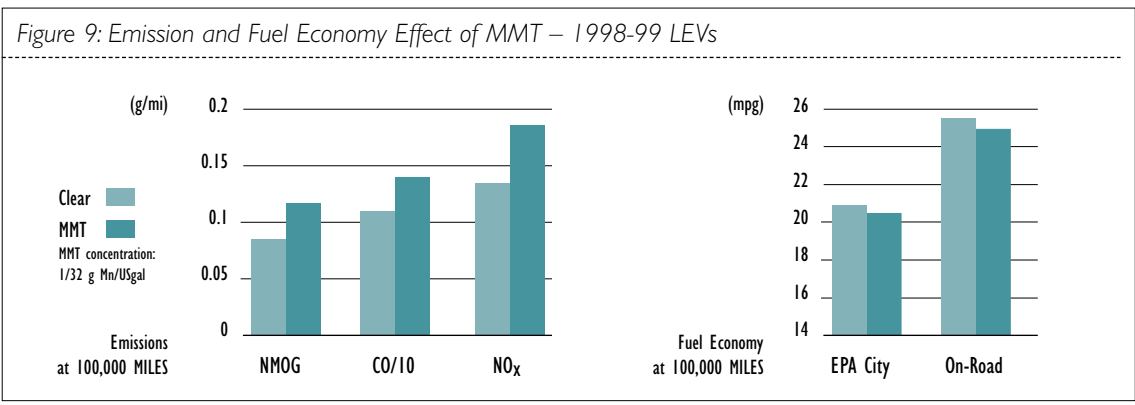
Studies have shown that most of the MMT-derived manganese in the fuel remains within the engine, catalyst and exhaust system. The oxidized manganese coats exposed surfaces throughout the system, including spark plugs, oxygen sensors and inside the cells of the catalytic converter. These effects result in higher emissions and lower fuel economy. The effect is irreversible and cumulative.

- The coating of internal engine components, such as spark plugs, can cause in-cylinder combustion misfire, which leads to increased HC and CO emissions, increased fuel consumption, poor vehicle driveability and possible physical damage to the catalyst.

These conditions result in increased owner dissatisfaction and expensive repairs for consumers and vehicle manufacturers.

- MMT’s combustion products also accumulate on the catalyst. In some cases, the front face of the catalyst can become plugged with deposits, causing increased back pressure, poor vehicle operation and increased fuel consumption in addition to reduced emission control.

In 2002, automobile manufacturers jointly completed a multi-year study of the real-world impact of MMT on Low Emission Vehicles (LEVs). After 100,000 miles of driving with fuel containing 1/32 g Mn/gal, the test fleet showed significantly increased non-methane organic gases (NMOG), CO and NO_x emissions. MMT also significantly decreased fuel economy; on average, on-road (highway) fuel economy was about 0.5 miles per gallon (mpg) lower than with a clear test gasoline (Figure 9). Similar results were found in another part of the study with earlier model vehicles equipped with Tier 1 emission control technology, where HC emissions increased after 50,000 miles of driving. Figure 10 provides visual evidence of MMT’s impact on parts used in some Tier 1 and LEV vehicles. The spark plug and oxygen sensor came from vehicles used in the 2002 joint automaker study, and the catalytic converters came from market vehicles, one driven in Canada when MMT was in widespread use and the other driven in California where MMT is not allowed. The reddish-brown deposits were identified as oxidized manganese.



Around the time when this study was released (2002), North American automakers began to notice increased warranty claims in Canada, where MMT was in widespread use, compared to claims in the U.S., where MMT was not in widespread use. The growth in claims was occurring just as new emission control technologies were being introduced. Beginning in the late 1990s, automakers had been introducing vehicles with high cell density catalysts, close-coupled catalysts, catalysts with new washcoats, more sophisticated computerized engine-control systems and engine design modifications, in

anticipation of more stringent emission standards. By the early 2000s, the newer technologies were penetrating the Canadian fleet at increasing rates, varying by manufacturer and model. Today, in the EU, Japan, North America and many other developed markets, these highly advanced technologies now dominate the fleets because they are needed to meet stringent emission standards.

Sierra Research, Inc., compiled and analysed these observations in Sierra Report SR2008-08-01, Impacts of MMT Use in Unleaded Gasoline on Engines, Emission Control Systems and Emissions (available at www.autoalliance.org). The report revealed cases of severe catalyst plugging, driveability problems, illumination of the dashboard engine malfunction indicator light (MIL) and increased tailpipe emissions, among other adverse effects (Table 2). The automakers conducted laboratory tests to confirm the in-use findings, investigated causative factors and measured the emission impacts. The data confirmed their suspicions: MMT had adversely affected at least 25 different models, including both advanced and older technologies of 1999-2003 model year vintage produced by nine different manufacturers and accounting for about 85% of Canadian light-duty vehicle sales in 2006. The magnitude of this statistic fails to reflect the full potential impact, however, due to unknowns and varying conditions such as changing vehicle technologies, fuel quality, vehicle mileage, MMT concentrations and actual use of MMT-containing gasoline. The report's Executive Summary includes the following statement:

There is no demonstrated method, other than eliminating MMT® from the fuel, to ensure that an emission control system that allows a vehicle to comply with the requirements of the Tier 2/LEV II regulations will not experience catalyst plugging caused by manganese oxides as well as one or more of the observed problems of degraded driveability, MIL illumination, and increased emissions.

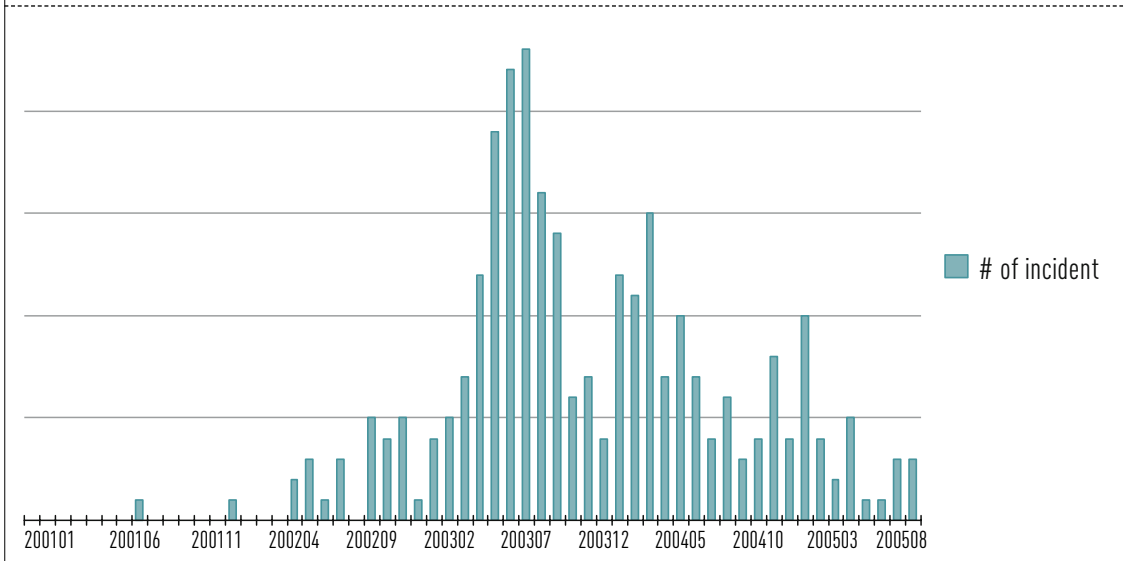
Table 2. Source of Evidence of Adverse MMT® Impacts on Exhaust Emissions, Operation and Performance of In-Use Canadian Vehicles with Advanced Emission Control Technologies and Systems

MFR	Warranty Claims	In-Use Vehicle Inspection	Laboratory Testing	Emissions Testing	Number of Models Impacted by MMT® Identified	Model Years
A	YES	YES	NO	NO	1	1999
C	YES	YES	YES	YES	4	2000-2002
D	YES	YES	YES	YES	2	2003
I	NO	YES	NO	NO	1	2002
J	YES	YES	YES	YES	7	2002-2003
K	YES	YES	YES	YES	1	2003
L	NO	YES	YES	YES	3	2001
M	YES	YES	YES	YES	5	2001-2003
O	NO	NO	YES	NO	1	2001

After Canadian refiners voluntarily halted MMT use between 2003 and 2005 (most use had ended by the summer of 2004), automakers then observed a rapid decline in the incidence of catalyst plugging. Figure 11 shows one manufacturer's month-by-month warranty analysis for the period between 2001 and 2005.

Other manufacturers found similar impacts, including the reversal of the monitored effect as MMT was phased out in most of Canada.

Figure 11. Warranty Analysis: Number of Catalyst Replacement Incidences per Month due to MMT Plugging (Manufacturer C)



Automakers consider the above statistics to be very conservative and believe the true vehicle impact was actually greater than recorded. Since the vehicle impairment also meant the emission control systems were functioning poorly, automakers conservatively estimate that VOC, CO and NOx emissions would have increased by 77%, 51% and 12%, respectively, by 2020, if MMT had been reintroduced into Canada in 2008.

The reader is referred to the Sierra Report for more detail concerning this analysis.

The real-world evidence of adverse impacts continues to grow. In addition to the above studies and experience in North America, several major companies have reported failed emission components in China, South Africa, parts of Eastern Europe, parts of Asia, and/or Argentina. South African vehicles, which have less advanced control systems than in Canada but use fuel with higher levels of MMT, also have been adversely affected (Figure 12). Given this overwhelming body of information, automobile manufacturers remain extremely concerned about MMT's impact, especially on the highly sensitive technologies that are being or will be used in markets around the world. Most major auto manufacturers state in their Owner Guides that they recommend against the use of MMT, advising further that any damage caused by MMT may not be covered by the warranty.

Figure 12: Evidence of MMT's Impact on Canadian and South African Vehicles



A: Canada

B: South Africa

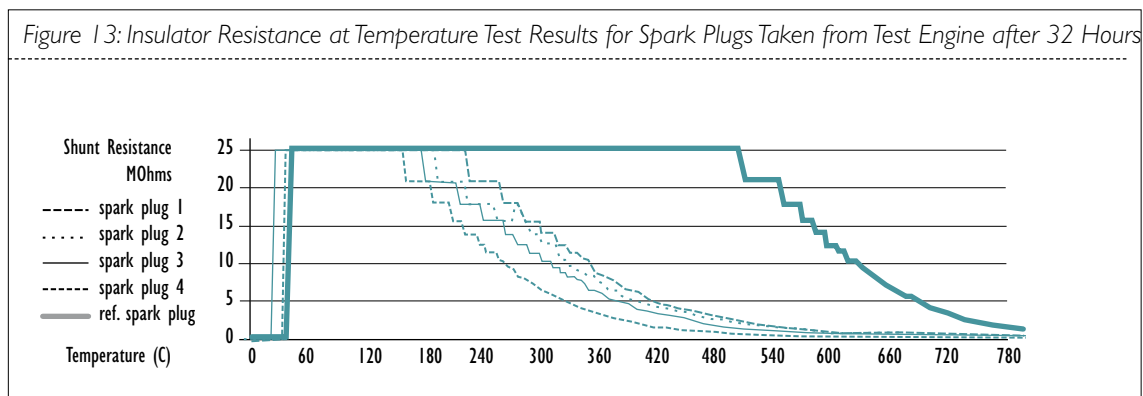
Information on the amount of MMT consumed worldwide is not publicly available, although fuel surveys suggest frequent use in several countries outside of Europe, Japan and North America. In other markets, surveys show that manganese is virtually absent from market gasoline, either as a result of regulation or voluntary action by fuel providers. U.S. law, for example, prohibits MMT use in federal reformulated gasoline (RFG), which constitutes more than one third of the U.S. gasoline pool, and the State of California also bans use in that state. Even outside RFG and regulated areas, the fuel is voluntarily MMT-free. Fuel providers in Canada, India, Indonesia and Japan also are voluntarily providing MMT-free

gasoline. In 2009, the European Parliament adopted market restrictions on MMT that were upheld in 2011 against a legal challenge. South Africa adopted a dual fuel approach where gasoline with MMT may legally be sold for use in older vehicles (as Lead Replacement Petrol), but that market has been declining. China is among the regions where MMT use has been growing. In 2011, however, the government adopted a rule imposing tight limits nationwide beginning in 2014. For markets where at least some gasoline contains MMT, appropriate pump labelling is imperative to inform the consumer.

Iron (Ferrocene)

Ferrocene has been used to replace lead as an octane enhancer for unleaded fuels in some markets. It contains iron, which deposits on spark plugs, catalysts and other exhaust system parts as iron oxide, and may also affect other engine components. The deposits will cause premature failure of the spark plugs, with plug life being reduced by up to 90% compared to normal service expectations. Failing spark plugs will short-circuit and cause misfiring when hot, such as under high load condition. This may cause thermal damage to the exhaust catalyst.

Figure 13 shows the reduction in spark plug insulator resistance as a function of temperature. The results compare plugs using fuel with a ferrocene additive after only 32 hours of testing, with a reference plug using conventional gasoline after 300 hours of testing.



Iron oxide also acts as a physical barrier between the catalyst/oxygen sensor and the exhaust gases, and also leads to erosion and plugging of the catalyst. As a result, the emission control system is not able to function as designed, causing emissions to increase. Additionally, premature wear of critical engine components such as the pistons and rings can occur due to the presence of iron oxide in the vehicle lubrication system.

CONTAMINANTS

Contaminants, including some from additives, whether intentionally or inadvertently added during fuel production or distribution, can cause significant harm to the powertrain, fuel, exhaust or emission control systems. Good housekeeping practices can help minimize or prevent inadvertent contamination. No detectable levels of the elements listed below should exist in gasoline, nor should they be used as components of any fuel additive package intended to improve gasoline and engine performance. These elements should be strictly controlled, and it may prove necessary to check and control the fuel quality at the pump.

- Phosphorus, which is sometimes used as a valve recession additive, can foul spark plugs and will deactivate catalytic converters.
- Silicon is not a natural component of gasoline but has been found in commercial

gasoline in several instances. The source usually is silicon-containing waste solvents added to the gasoline after the fuel has left the refinery. Such contamination has significant adverse effects on the engine and emission control systems. Silicon, even in low concentrations, can cause failure of the oxygen sensors and high levels of deposits in engines and catalytic converters. These impacts can lead to catastrophic engine failures in less than one tankful of contaminated fuel.

- Chlorine, which is not naturally contained in petroleum, has been found in gasoline in both inorganic and organic forms. Inorganic chlorine usually enters the fuel as a result of contamination by sea water ballast during shipping or from salt water intrusion during storage. Such contamination occurs more readily in gasoline-ethanol blends than in E0 due to the blends' ability to dissolve more water. Organic chlorine may enter the fuel through adulteration with chemical or waste solvents. Chlorine forms highly corrosive acids during combustion, which can reduce significantly the durability of the engine, fuel system and emission control system. In the worst case, the presence of chlorine may lead to catastrophic engine failure as injectors fail to operate or operate improperly after various periods and levels of exposure.

OXYGENATES

Oxygenated organic compounds, such as MtBE and ethanol, often are added to gasoline to increase octane or extend gasoline supplies. Oxygenating the fuel also may affect vehicle emissions (tailpipe, evaporative or both), performance and/or durability. Adding ethanol also affects the distillation of the gasoline blend. See Volatility, below.

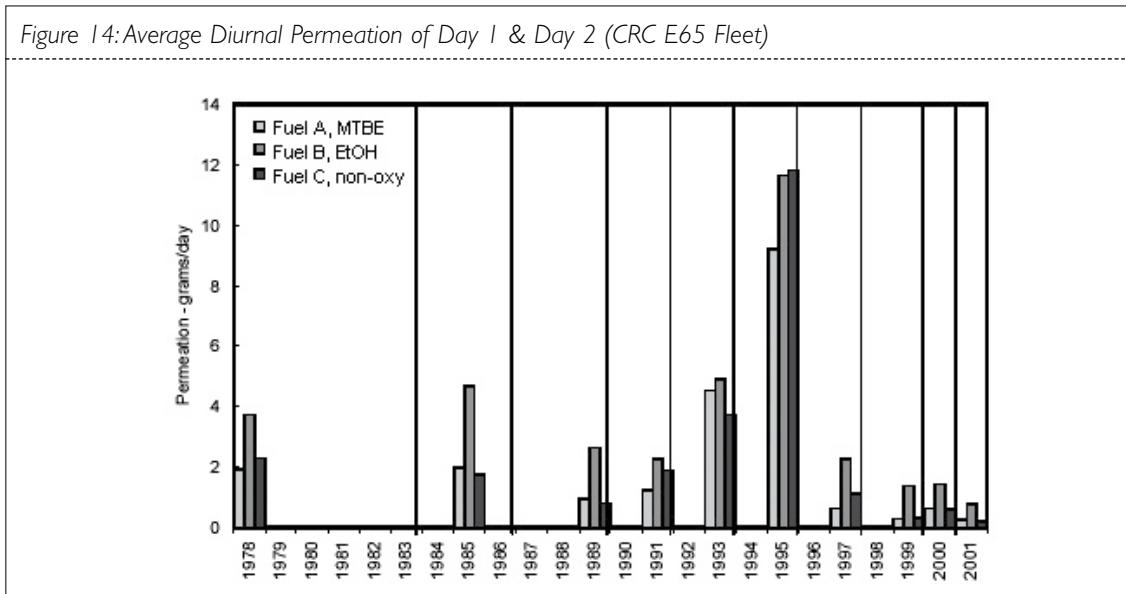
Adding oxygenates to gasoline will induce a lean shift in engine stoichiometry, which, in turn, will reduce carbon monoxide (CO) emissions, especially from carburetted vehicles without electronic feedback-controlled fuel systems. These emission benefits are smaller in modern electronic feedback-controlled vehicles, however, because the leaning effect only occurs during cold operation or during rapid accelerations. In fact, fuel-leaning caused by oxygenates can cause tailpipe emissions to increase, depending on the leanness of the engine's base calibration with non-oxygenated gasoline. The California Air Resources Board (CARB) found in emission tests on 14 1990-1995 model year vehicles that a gasoline containing 10% ethanol by volume decreased toxic emissions by 2% and CO by 10% but increased NO_x by 14%, total HC by 10% and ozone-forming potential by 9%, relative to a gasoline containing 11% MtBE by volume. More recent testing by the Coordinating Research Council (CRC) on newer vehicles has produced similar results (CRC E-67).

This over-leaning also can degrade driveability, and it is well documented that ethanol-blended gasoline, in particular, can cause an offset in driveability performance. Increased exhaust hydrocarbon emissions are likely to accompany this offset in driveability performance. Because ethanol has a higher heat of vaporisation than ethers, some of the driveability and emissions degradation of gasoline-ethanol blends can be attributed to the additional heat needed to vaporise the gasoline.

The use of ethanol-blended gasoline also may affect evaporative emissions. LEV vehicles, for example, have been found to emit approximately 12 percent more evaporative emissions when using 10% ethanolblended gasoline than when using a hydrocarbon-only fuel (General Motors, 2000). This emissions impact may be due, in part, to the permeation of fuel molecules through elastomeric materials (rubber and plastic parts) used in the vehicle's fuel and fuel vapor handling systems. In a study conducted from January 2003 to June 2004, the CRC in cooperation with CARB found that permeation emissions increased on all 10 vehicle-fuel systems in the study when ethanol replaced MtBE as the test fuel oxygenate (both oxygenated fuels contained 2% oxygen by weight). The ethanol-blended

fuel increased the average diurnal permeation emissions by 1.4 g/day compared to the MtBE fuel, and by 1.1 g/day compared to the non-oxygenated fuel (see Figure 14). The study also confirmed previous estimates that permeation of these gasoline-ethanol blends doubles for each 10°C rise in temperature.

Figure 14: Average Diurnal Permeation of Day 1 & Day 2 (CRC E65 Fleet)



The study further examined specific ozone reactivity and found the non-oxygenated fuel to have a statistically higher reactivity than either the MtBE- or ethanol-containing fuels. The average specific reactivities of the two oxygenated fuel permeates were not statistically different. The data support the hypothesis that ethanol-blends tend to increase the permeation of other hydrocarbon species in addition to ethanol. The study is continuing with 2004 model year vehicles, which have to meet more stringent emission standards than those used in the first part of the study.

Based on past experience with impurities in ethanol that have led to degradation of fuel systems, fuel ethanol must have a specification to control pH and its blending properties (ASTM D 4806). Also, the limits and restriction on the oxygenates permitted in each Category were developed on the basis of emission benefits, vehicle performance and existing regulations. Based on these criteria, when oxygenates are used, ethers are preferred. Also, the use of ethanol-blended gasoline may require other fuel changes to mitigate evaporative and exhaust emission impacts. Maintaining the availability of protection-grade fuel (up to E5) may be necessary in some markets to protect older vehicles designed for ethanol-free gasoline.

Methanol is not permitted. Methanol is an aggressive material that can cause corrosion of metallic components of fuel systems and the degradation of plastics and elastomers.

OLEFINS

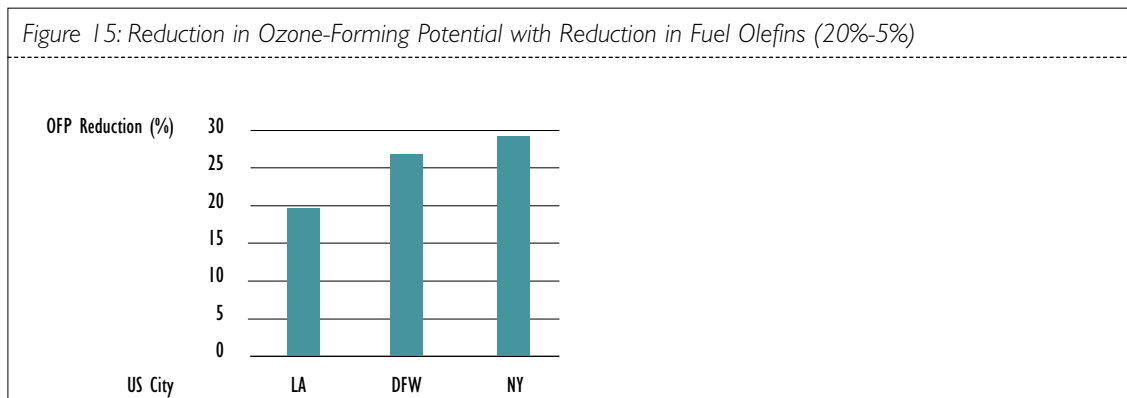
Olefins are unsaturated hydrocarbons and, in many cases, are also good octane components of gasoline.

However, olefins in gasoline can lead to deposit formation and increased emissions of reactive (i.e. ozone-forming) hydrocarbons and toxic compounds.

Effect of Olefins on Emissions

Olefins are thermally unstable and may lead to gum formation and deposits in an engine's intake system. Furthermore, their evaporation into the atmosphere as chemically reactive species contributes to ozone formation and their combustion products form toxic dienes.

The effect on ozone-forming potential was clearly demonstrated by the US Auto/Oil programme. The programme concluded that reducing total olefins from 20% to 5% would significantly decrease ozone forming potential in three critical cities: Los Angeles, Dallas-Fort Worth, and New York City (Figure 15).



The model also showed that the same reduction in gasoline olefin level would reduce the light-duty vehicle contribution to peak ozone by 13% to 25% in future years for the cities shown in Figure 15. About 70% of this effect was due to reducing low molecular weight olefins.

AROMATICS

Aromatics are fuel molecules that contain at least one benzene ring. In general, aromatics are good octane components of gasoline and high-energy density fuel molecules. Fuel aromatic content can increase engine deposits and increase tailpipe emissions, including CO₂.

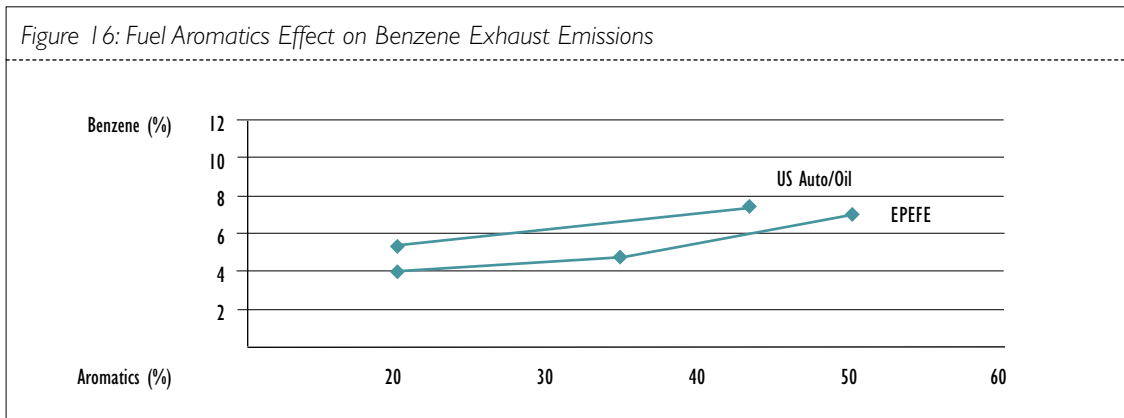
Influence of Aromatics on Engine Deposits

Heavy aromatics, and other high molecular weight compounds, have been linked to engine deposit formation, particularly combustion chamber deposits. As discussed below ('Deposit Control Additives'), these deposits increase tailpipe emissions, including HC and NO_x. Since it is not feasible to specify limits for individual hydrocarbon compounds in the fuel, the total aromatic limit in Category 1 and the final boiling point limits in Categories 2 and 3 provide the best means to limit heavy aromatics.

Influence of Aromatics on Tailpipe Emissions

Combustion of aromatics can lead to the formation of carcinogenic benzene in exhaust gas and increased combustion chamber deposits which can increase tailpipe emissions. Lowering aromatic levels in gasoline significantly reduces toxic benzene emissions in exhaust from vehicles as shown in both the US AQIRP and the European EPEFE studies. (Figure 16).

Figure 16: Fuel Aromatics Effect on Benzene Exhaust Emissions



Findings from the US AQIRP programme showed that, of all the fuel properties tested, aromatic level had the largest effect on total toxics, largely due to its effect on exhaust benzene emissions as shown in the above figure. Reducing total aromatics from 45% to 20% caused a reduction in total exhaust air toxics of 28% (74% of the total toxic emissions was benzene).

Influence of Aromatics on CO2 Emissions

Gasoline aromatic content also has a direct effect on tailpipe CO2 emissions. The European EPEFE programme demonstrated a linear relationship between CO2 emissions and aromatic content. The reduction of aromatics from 50 to 20% was found to decrease CO2 emissions by 5%.

BENZENE

Benzene is a naturally occurring constituent of crude oil and a product of catalytic reforming that produces high octane gasoline streams. It is also a known human carcinogen.

The control of benzene levels in gasoline is the most direct way to limit evaporative and exhaust emissions of benzene from automobiles. The control of benzene in gasoline has been recognised by regulators in many countries as an effective way to reduce human exposure to benzene. These gasoline recommendations recognise the increasing need for benzene control as emission standards become more stringent.

VOLATILITY

Proper volatility of gasoline is critical to the operation of spark ignition engines with respect to both performance and emissions. Volatility may be characterised by various measurements, the most common of which are vapour pressure, distillation and the vapour/liquid ratio. The presence of ethanol or other oxygenates may affect these properties and, as a result, performance and emissions as well.

Vapour Pressure

The vapour pressure of gasoline should be controlled seasonally to allow for the differing volatility needs of vehicles at different ambient temperatures. The vapour pressure must be tightly controlled at high temperatures to reduce the possibility of hot fuel handling problems, such as vapour lock or excessive evaporative emissions due to carbon canister overloading, especially at higher temperatures. At lower temperatures, a sufficiently high vapour pressure is needed to allow ease of starting and good warm-up performance. Therefore, both minimum and maximum vapour pressures are specified.

New data have become available on the effects of vapour pressure. Figures 17 and 18

provide the hydrocarbon slip from canisters for two sample vehicles tested during study of the effects of 48, 62 and 69 kPa E10 (10% ethanol gasoline blend) fuels on canister breakthrough emissions over 14 days of SHED testing using the temperature profile from the U.S. Federal Diurnal Cycle. The data collected throughout the testing provides a correlation between the hydrocarbon slip from the vehicle canister and the fuel vapour pressure. The data indicate that the lower vapour pressure fuels, such as 48 kPa, are imperative during warm ambient temperatures for achieving very low evaporative emissions. The full report, with additional data, can be found at SAE 2013-01-1057. The study provided additional empirical evidence to a previous SAE study (Clontz, SAE Technical Paper No. 2007-01-1929) that showed the most important property of the fuel blend for canister performance is the vapour pressure. More importantly, the vapour pressure, not ethanol concentration, is the determining factor for vapour generation in the fuel tank.

Figure 17: Effect of Vapour Pressure on LEV II PZEV Vehicle Canister During 14-day Diurnal

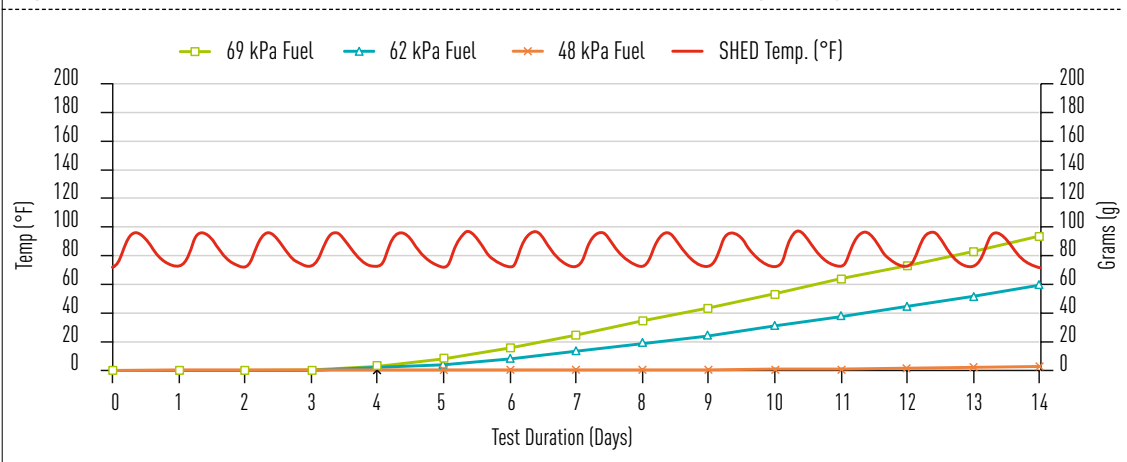
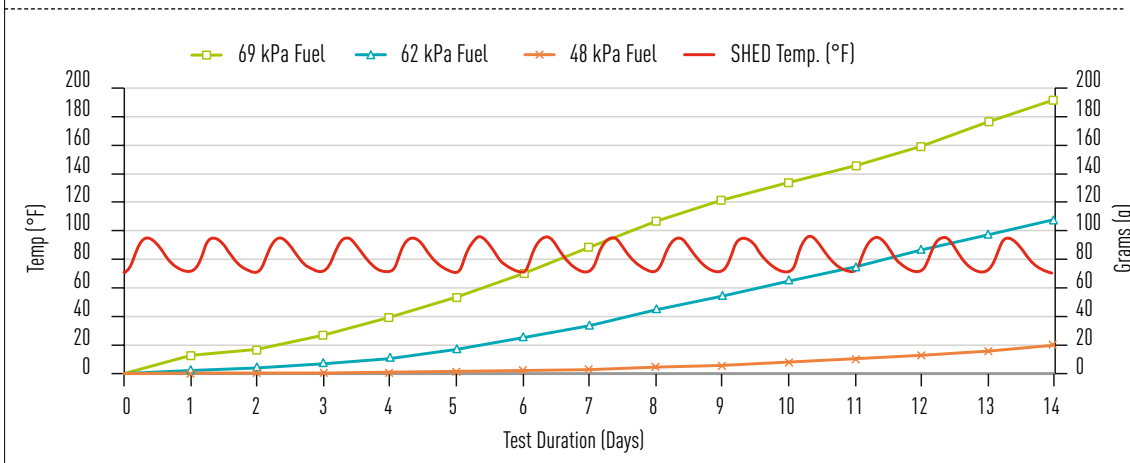


Figure 18: Effect of Vapour Pressure on Tier 2 Vehicle Canister During 14-day Diurnal

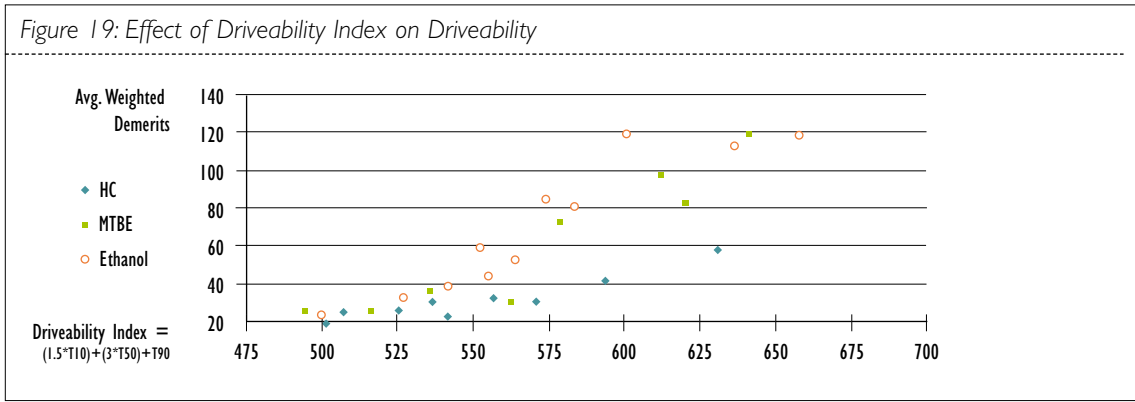


Distillation

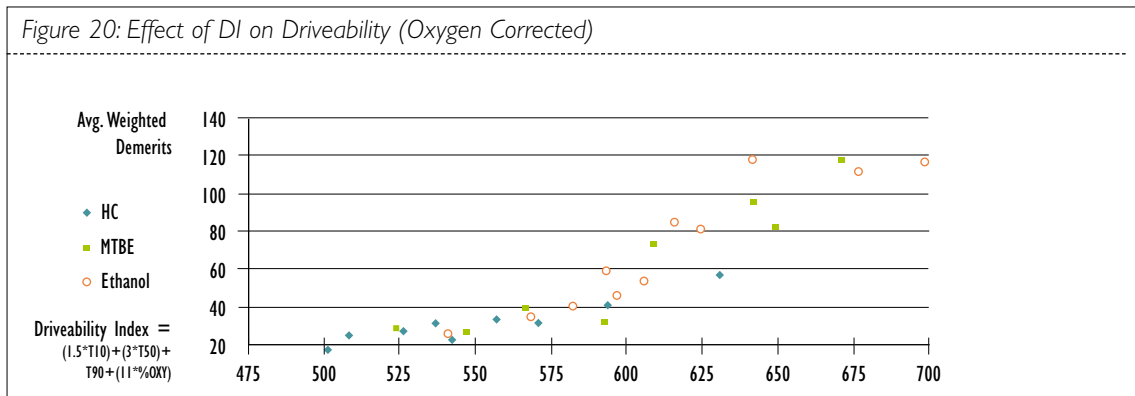
Distillation of gasoline yields either a set of 'T' points (T50 is the temperature at which 50% of the gasoline distills) or 'E' points (E100 is the percentage of a gasoline distilled at 100 degrees). Excessively high T50 (low E100) can lead to poor starting and warm-up performance at moderate ambient temperatures. Control of the Distillation Index (DI), derived from T10, T50, T90, and oxygen content, also can be used to assure good cold start and warm-up performance.

Driveability concerns are measured as demerits. Figure 19 provides the test results from

one CRC study of the impact of the Driveability Index on driveability. This study tested 29 fuels: 9 all hydrocarbon, 11 with 10% ethanol and 9 with 15% MtBE. The data indicate that driveability problems increase for all fuel types as the Driveability Index increases. At Driveability Index levels higher than those specified in these recommendations, driveability concerns increase dramatically.



An oxygen correction factor is required to correct for higher driveability demerits for oxygenated fuels as compared to all-HC gasoline. Figure 20 indicates how the correction factor smooths the data presented in Figure 19.



DI also is directly related to tailpipe HC emissions, as shown in Figure 21. As with driveability demerits, HC emissions increase significantly at DI levels higher than those specified in these recommendations.

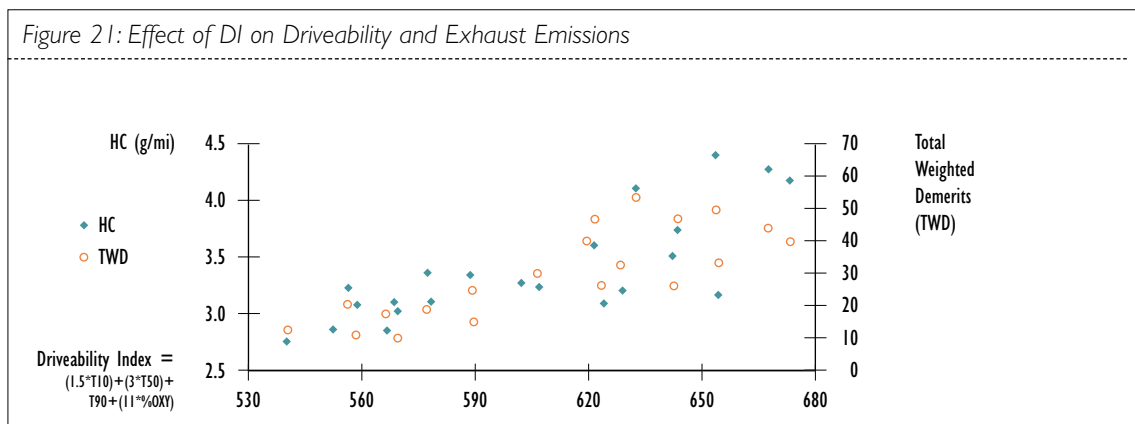
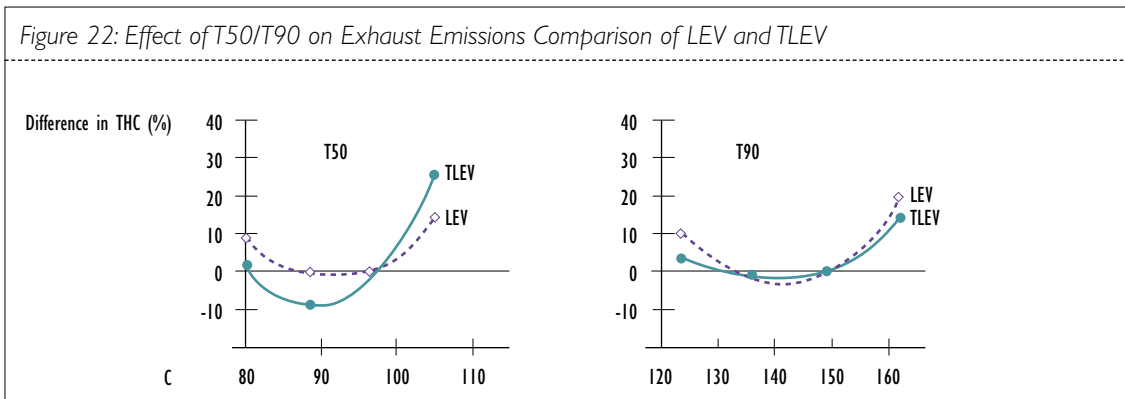


Figure 22 indicates that optimum values for T50 and T90 exist to achieve lower exhaust THC emissions.

Figure 22: Effect of T50/T90 on Exhaust Emissions Comparison of LEV and TLEV



Vapour/Liquid Ratio

Excessively high gasoline volatility can cause hot fuel handling problems such as vapour lock, canister overloading, and higher emissions. Vapour lock occurs when too much vapour forms in the fuel system and decreases or blocks fuel flow to the engine. This can result in loss of power, rough engine operation or engine stalls. Since controls on vapour pressure and distillation properties are insufficient to prevent this problem, a Vapour/Liquid Ratio specification is necessary.

Ethanol's Impact on Volatility

As a pure compound, ethanol exhibits straightforward behaviour regarding vapour pressure and distillation.

When added to a base gasoline, however, the behaviour of the mixture is anything but straightforward.

As a result, the vapour pressure and distillation of ethanol-gasoline blends, at a minimum, must be carefully regulated to ensure proper vehicle operation and emissions control. Ethanol also will make vapour lock more likely, so controlling the vapour-liquid ratio is even more important when ethanol is present.

Ethanol by itself has a very low vapour pressure, but adding it to gasoline has a non-linear and synergistic effect. Importantly, the final vapour pressure of the blend could be either higher or lower than the base gasoline, depending on temperature and ethanol concentration. At lower ethanol concentrations (below about 10% by volume) and typical temperatures, ethanol will cause the blend's vapour pressure to exceed that of the base gasoline. To prevent excess evaporative emissions, the vapour pressure of the finished blend, not just the base gasoline, must be controlled. Figure 23 illustrates this effect.

Figure 23: Impact of Ethanol Level on Vapour Pressure at 37.8 °C

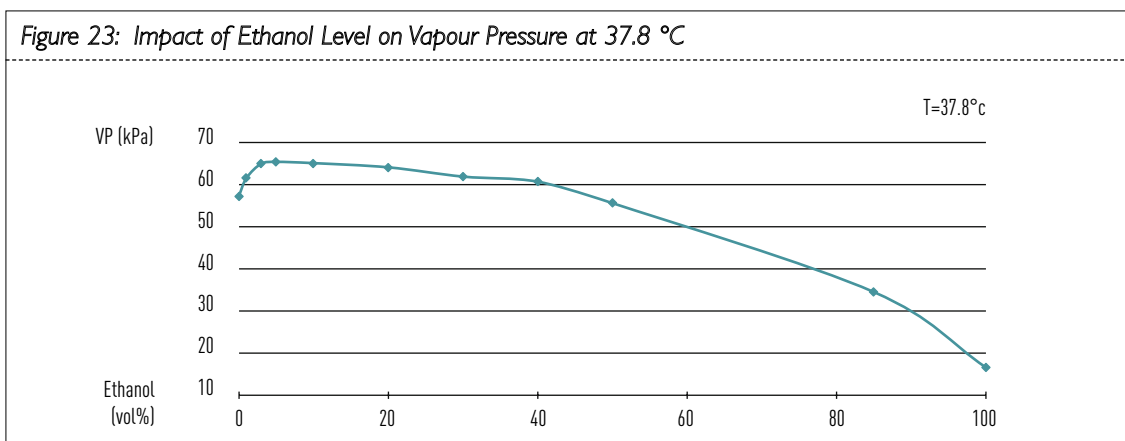
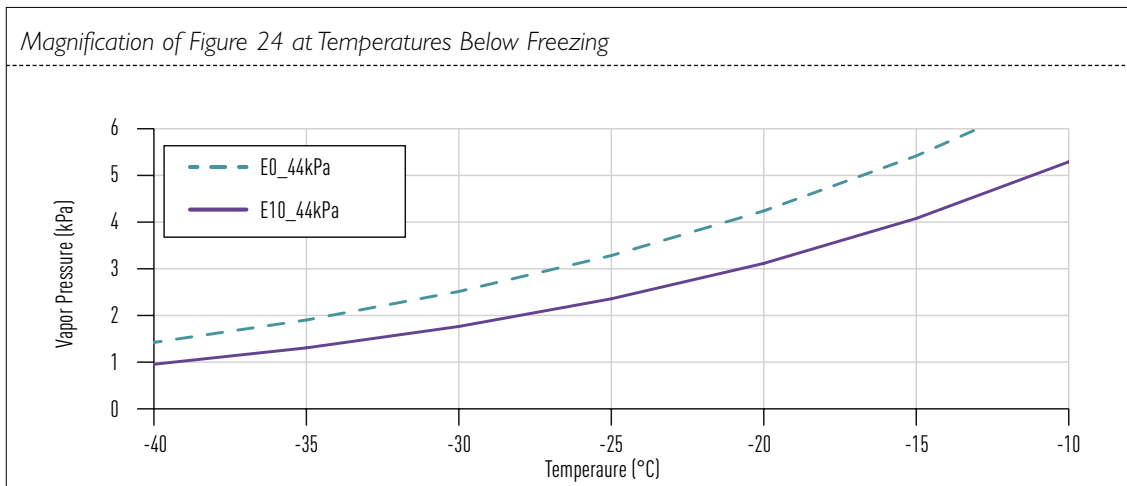
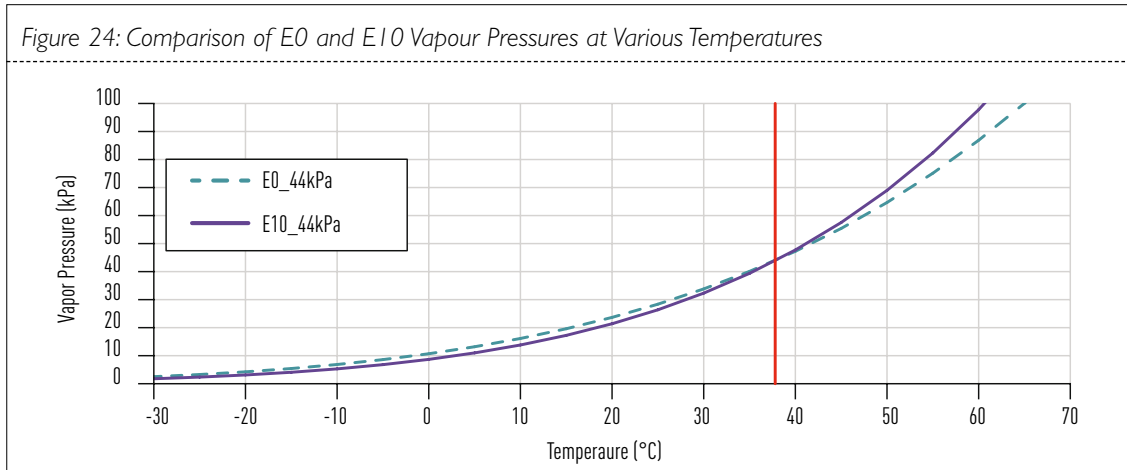


Figure 24, below, looks more closely at the variation for an E10 and its base gasoline (E0),

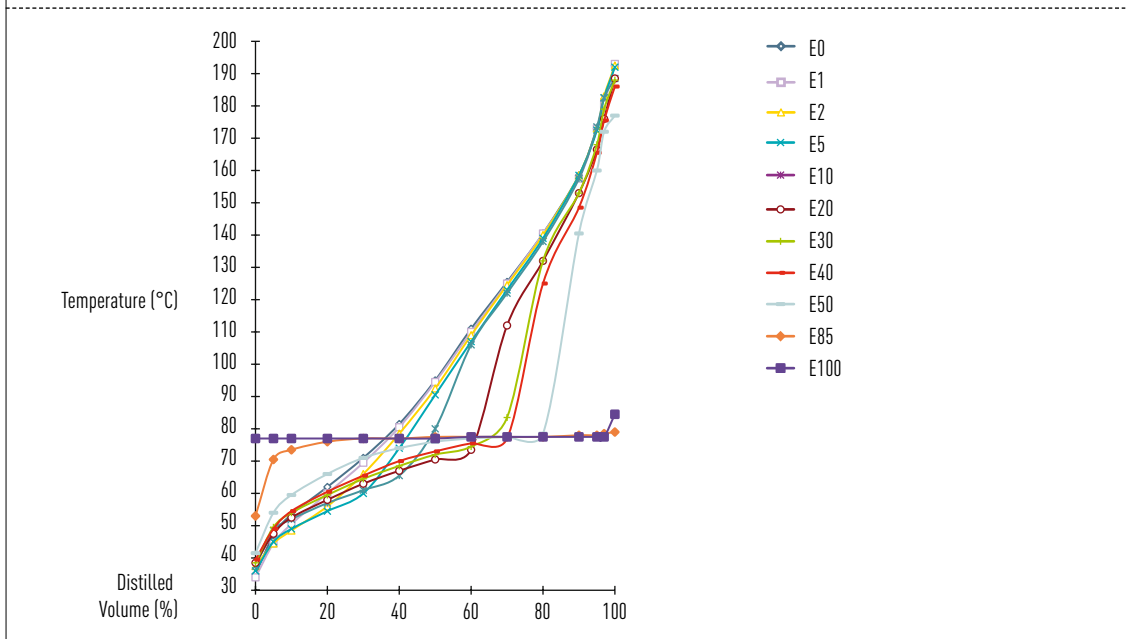
showing the impact for a wider range of temperatures. Importantly, at temperatures above 37.8°C, the E10 has a higher vapour pressure relative to E0, but at lower temperatures, the vapour pressure goes below that of E0.

The effect could be significant and prevent an engine from starting at very cold temperatures. Therefore, a higher minimum vapour pressure is required for ethanol-gasoline blends than would be needed for the base gasoline alone at these very low temperatures.



Ethanol's impact on the distillation curve is just as complex, if not more so. Figure 25 shows how different ethanol levels in gasoline can cause dramatic changes in distillation, especially as the ethanol concentration goes above 10% by volume and near the middle of the distillation curve. The distillation measurement must be adjusted to account for the impact, and the blend's distillation must be well-controlled.

Figure 25: Influence of Ethanol on Gasoline Distillation



DEPOSIT CONTROL ADDITIVES

Combustion of even good quality gasoline can lead to deposit formation. Such deposits will increase engine-out emissions and affect vehicle performance. High quality fuel contains sufficient deposit control additives to reduce deposit formation to acceptable rates.

Carburettors

First generation additives based on amine chemistry were developed in the early 1950's and are still used in some countries at levels of 50 parts per million treat rate. Many of these additives were multifunctional, providing anti-icing protection, corrosion inhibition and carburettor detergency performance.

Port Fuel Injectors

US gasoline marketers introduced port fuel injector deposit control additives around 1985 to overcome problems with fuel injector fouling that led to driveability problems. However, treat rates were nearly double those for carburettor detergents resulting in increased intake valve deposits in many cases.

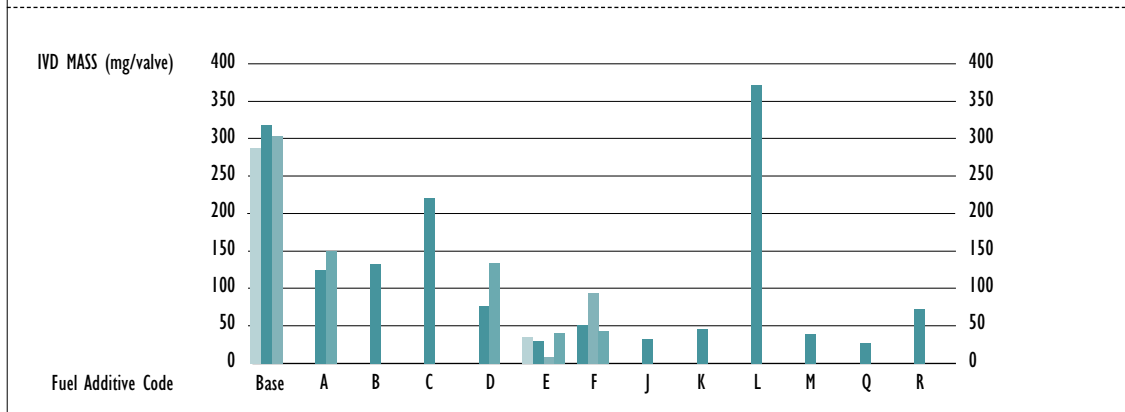
Detergent technology and test procedures must be developed to protect the more advanced injectors being introduced in direct injection engines.

Intake Valves

Various tests are available to evaluate the gasoline's capability of maintaining acceptable intake valve cleanliness.

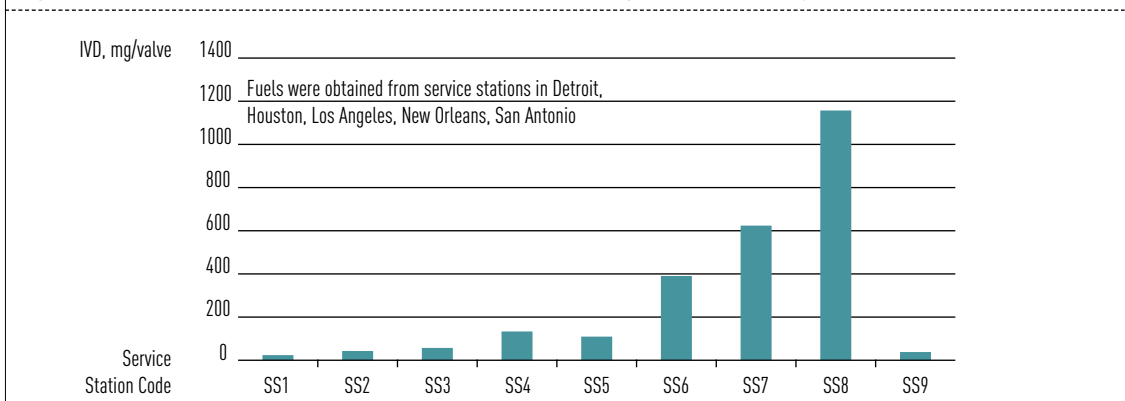
Figure 26 shows the performance of base fuel without detergent additives and fuels with various detergent additive chemistries in the Ford 2.3L IVD test (ASTM D6201). Moderate additive treat rates combined with effective carrier fluids help avoid intake valve sticking. Passing the VW Wasserboxer Intake Valve Sticking Test minimises the likelihood of this problem occurring.

Figure 26: IVD Performance of Gasolines With and Without Detergents, Using the Ford 2.3L Dynamometer Test



The impact of intake valve deposits on driveability in both North America and Europe has been severe enough in recent years to prompt vehicle manufacturers to steer customers to gasoline known to contain adequate detergency for minimizing and reducing intake valve deposits. Figure 27 shows the results of a Ford study of US market gasoline performance regarding intake valve deposits conducted in 1999-2000 and presented to ASTM in 2003. One third of the fuel samples caused unacceptable IVD rates ranging from 392 mg/valve to 1157 mg/valve. This problem is continuing to cause concern in 2012.

Figure 27: IVD Performance of Service Station Gasolines, using the Ford 2.3L Dynamometer Test



Combustion Chambers

As combustion chamber deposits (CCDs) form, they reduce the space available in the chamber for combustion while adding small crevices that increase the surface area of the chamber. This phenomenon has three undesirable effects: 1) higher compression ratios and end gas temperatures that increase the octane requirements higher than the engine was designed for, 2) increased exhaust emissions, and 3) mechanical interference between the piston top and cylinder head called 'carbon knock'.

Methods for measuring CCD could be improved. CEC F-20-A (Method 2), for example, produces technically relevant results when the engine operator has detailed knowledge about the measurement precision of the particular test stand, but in general, the method lacks precision data and cannot produce statistically valid CEC results for chamber deposits.

Engine Dynamometer Results

Detergent additives usually increase the level of CCDs relative to base fuel as shown in Figure 28 and Figure 29. Detergent packages with higher ratios of mineral oil carriers tend to increase CCDs, while detergent packages with optimised high-quality synthetic carrier

fluids and compounds like polyether amines (PEA) minimise CCD build-up. Additive packages should be optimised to minimise CCDs, which will allow engine designers to improve combustion chamber designs further for lower emissions and fuel consumption.

Figure 28: Engine Dynamometer Results

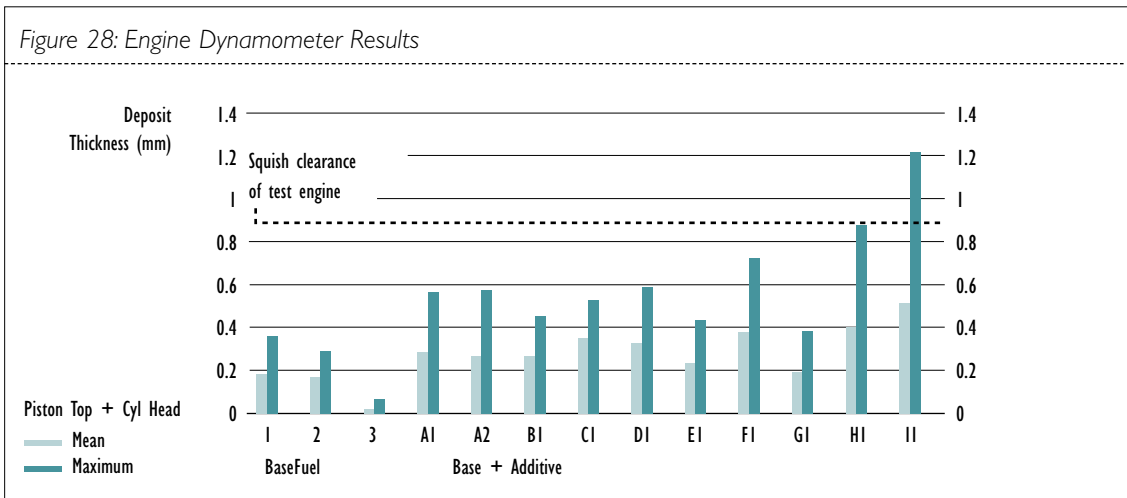
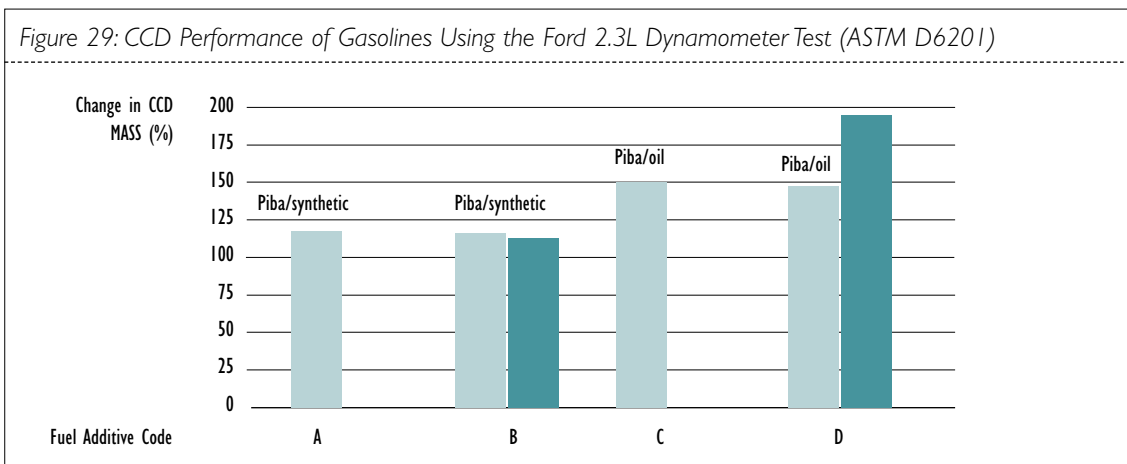


Figure 29: CCD Performance of Gasolines Using the Ford 2.3L Dynamometer Test (ASTM D6201)



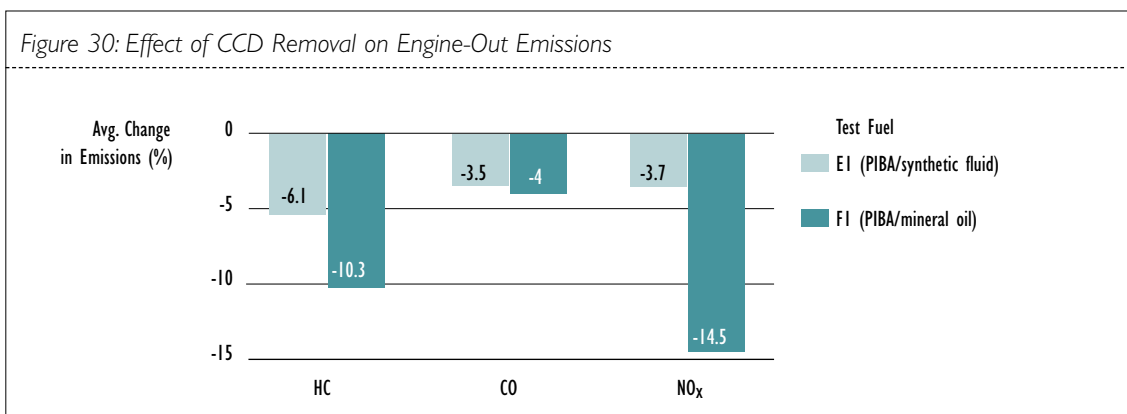
Note: Piba/Synthetic - polyisobutene amine/synthetic oil

Piba/Oil - polyisobutene amine/mineral oil

Effect of CCD Removal on Engine-Out Emissions

The removal of CCDs can reduce engine out HC emissions by up to 10%, CO by 4%, and NOx by 15% as shown in Figure 30 for fleet vehicles after accumulating 50,000 miles.

Figure 30: Effect of CCD Removal on Engine-Out Emissions



Carbon knock in modern engines did not occur even at high mileages in Japan. When these same engines were sold in the US, customers began objecting to the engine noise

after only a few thousand miles in some cases. Some customers required replacement of the cylinder heads because of the damage caused by the piston hitting the deposits. Other customers switched brands of gasoline or used after-market deposit control additives to help remove deposits causing carbon knock. The problem in the US was attributed to high-additive treat rates being used for IVD control.

Relationship of CCDs to TGA Test

A test procedure with the Mercedes M111 E engine is being developed to evaluate the CCD-forming tendency of gasoline. A thermogravimetric analysis (TGA) bench test method has been developed that provides a good correlation with CCDs in a dynamometer-based multi-cylinder engine test as shown in Figure 31 and Figure 32.

Figure 31: Correlation of CCD and TGA Results of Commercial Fuels in Ford 2.3L IVD Test (ASTM D6201)

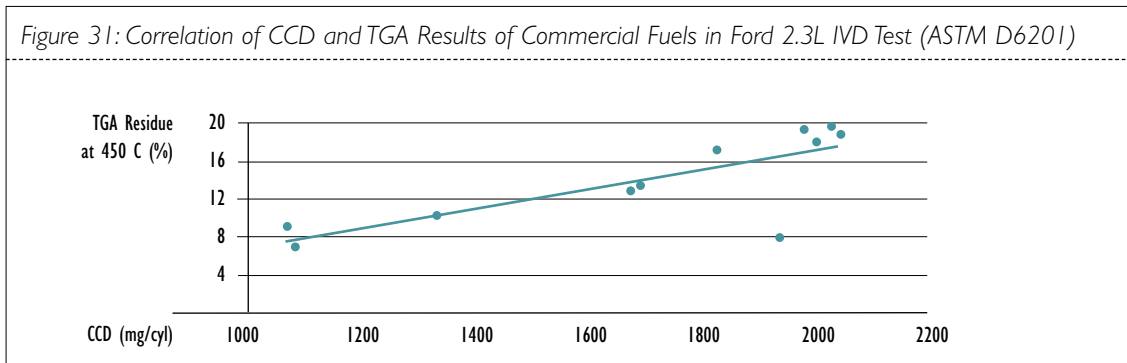
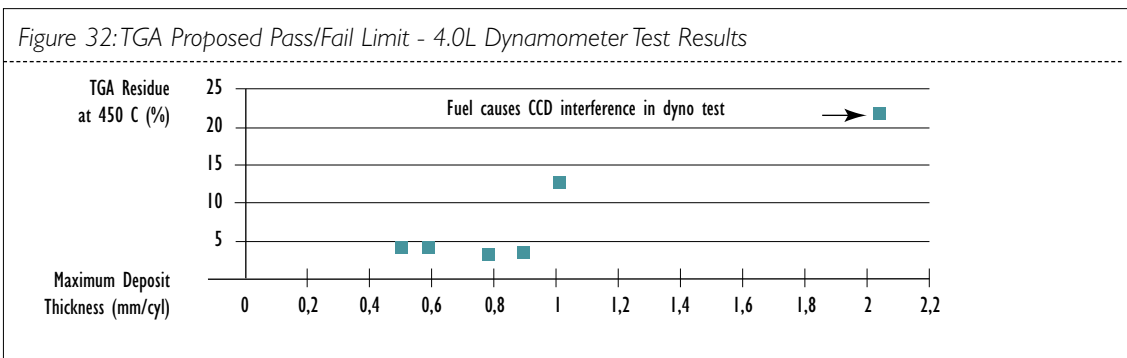


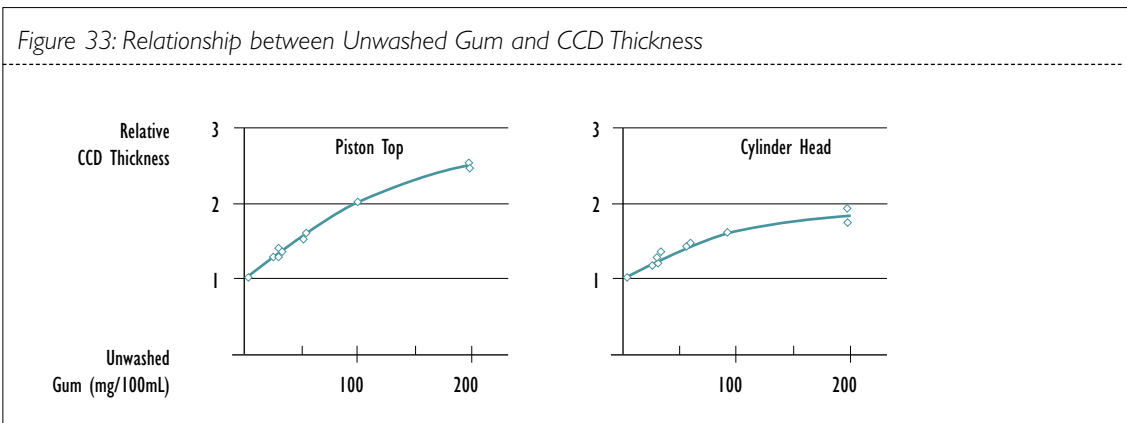
Figure 32: TGA Proposed Pass/Fail Limit - 4.0L Dynamometer Test Results



Relationship between Unwashed Gum and CCD Thickness

Figure 33 indicates the correlation between unwashed gums and CCD formation as compared to base gasoline without detergent. Thus, the Charter allows compliance to either an unwashed gum limit or a CCD requirement.

Figure 33: Relationship between Unwashed Gum and CCD Thickness



As emission standards become more stringent, it is critical for fuel quality to support improvements in emission control technology to meet these limits. Detergent additives that

prevent the formation of CCDs have the benefit of helping meet environmental standards while improving vehicle performance.

CORROSIVE (ACTIVE) SULPHUR

Certain fuel sulphur compounds, including elemental sulphur, hydrogen sulphide (H₂S), mercaptans and other sulphur-containing molecules, can tarnish silver- and copper-containing metals that are widely used in fuel system parts such as fuel level sender units and fuel pump bearings. Active sulphur compounds may be present in the fuel due to problems during gasoline production, such as improper operation of a refinery's desulphurization process or through accidental events. These compounds are highly reactive, and their presence even at very small levels (a few ppm) can cause harm. The sulphur compounds react with the metal parts to form silver or copper sulphides. In the case of fuel level sender units, which measure the amount of fuel in a fuel tank, the formation of silver sulphide on the electrical contacts interrupts the flow of current to the fuel gauge and causes the gauge to display erratic readings. In the case of fuel pump bearings, which enable the pump to operate smoothly, the formation of copper sulphide on the bearing surface causes the pump shaft to stick, interrupting the pump's smooth operation and potentially causing pump failure and vehicle stalling. To prevent the presence of these compounds in fuel, strict and continuous quality control is required.

ANNEX E – DIESEL TECHNICAL ANNEX

CETANE

Cetane is a measure of the compression ignition behaviour of a diesel fuel; higher cetane levels enable quicker ignition. Cetane influences cold startability, exhaust emissions and combustion noise. Higher cetane generally enables improved control of ignition delay and combustion stability, especially with modern diesel engines which use high amounts of exhaust gas recirculation (EGR). It does this by providing room for engine calibrators to tailor combustion for the best calibration compromise among combustion noise, emissions and fuel consumption goals across the engine operating range. Additives can enhance a fuel's cetane level; natural cetane refers to the cetane level when the fuel contains no additives, and artificial cetane refers to the cetane level in an additized fuel. Cetane levels achieved through additives affect vehicle performance differently than natural cetane levels, and sometimes they produce inconsistent results.

Cetane is measured or derived in various ways. The cetane number is produced by testing the fuel in a test engine (ASTM D613). When the fuel does not contain any cetane improver, the cetane number is the same as the fuel's natural cetane. The derived cetane number, which is produced using a combustion tester (see ASTM D6890 and D7170), is an indirect measure of combustion ignition behaviour that is equated to the cetane number. The cetane index (ASTM D4737) is calculated from certain measured fuel properties (fuel density and distillation temperatures); it is designed to approximate the natural cetane. Since the cetane number and the derived cetane number are measured by combusting the fuel, both may reflect the effects of cetane improver additives; by contrast, the cetane index does not. To avoid excessive additive dosage, the difference between the cetane index and the cetane number must be maintained as specified in the various categories.

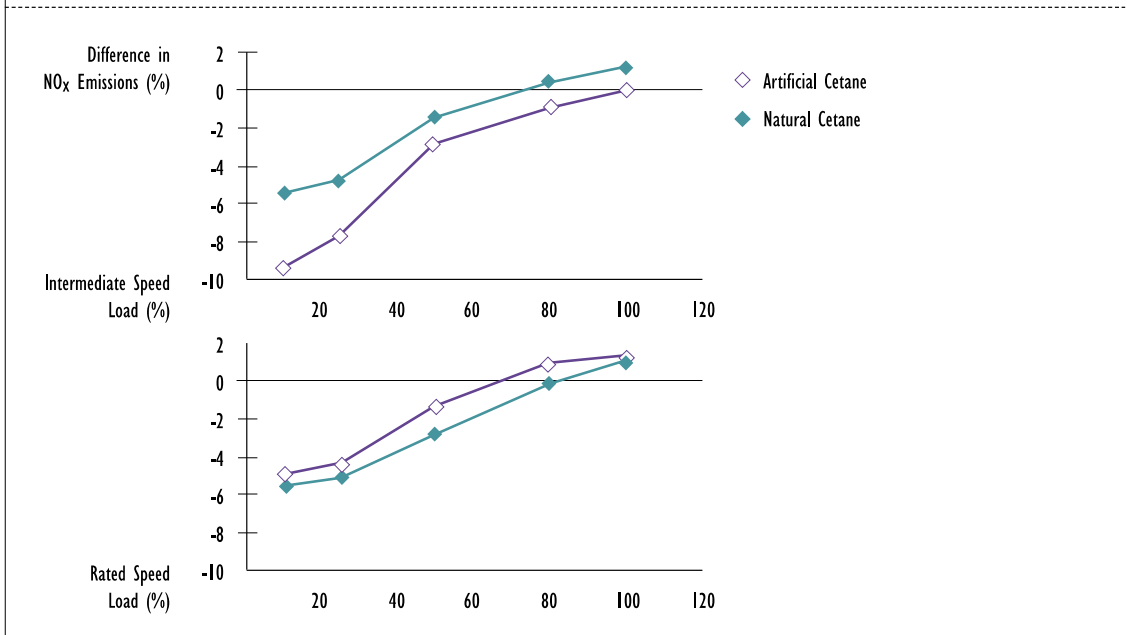
Influence of Cetane on Cold Startability

Increasing the cetane number will decrease engine crank time (the time before the engine reaches 'starter off') at a given engine speed. The ACEA EPEFE follow-up programme, which looked at the influence of diesel fuel quality on heavy-duty diesel engine emissions, demonstrated a significant (up to 40%) reduction in crank time for an increase in cetane number from 50 to 58. A shorter cranking cycle means fewer cycles with incomplete or partial combustion during 'crank to run' operation, and this leads to improved combustion stability and lower noise, vibration and harshness (NVH).

Influence of Cetane on Exhaust Emissions

The following figures show the influence of cetane on NO_x emissions as a function of engine load in heavy-duty engines (88/77/EEC 13-mode cycle). Cetane's influence on NO_x is very significant (Figure 1), particularly at low loads where reductions of up to 9% are achieved. (Note that each point in the graphs shows the NO_x reduction achieved for cetane increase at a given load.) The cetane increase also reduced HC emissions by 30-40%. For light-duty vehicles, EPEFE found that increasing the cetane number from 50 to 58 would reduce HC and CO each by 26%.

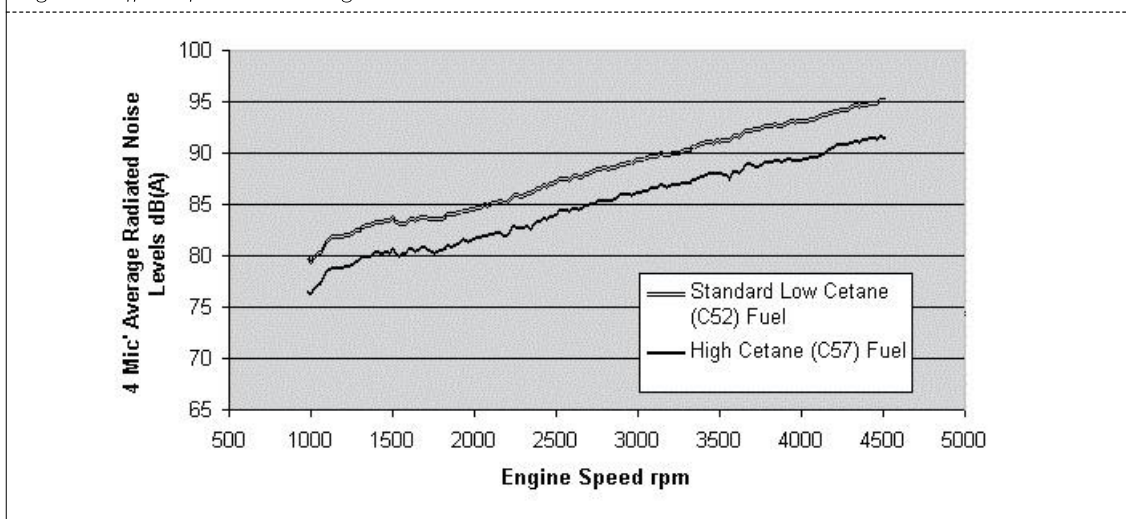
Figure 1: Effect of Cetane on NO_x Emissions 50 to 58 CN



Cetane Influence on Combustion Noise

Increased cetane will also reduce noise, as demonstrated by the results shown here (Figure 2). In this case, natural and artificial cetane have similar effects.

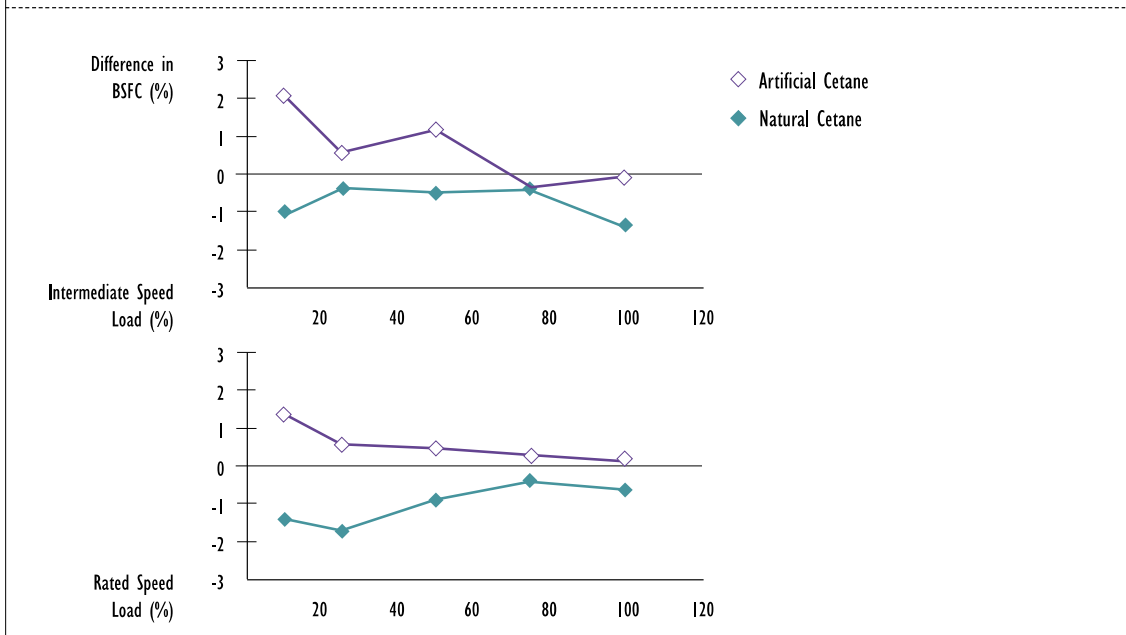
Figure 2: Effect of Cetane on Engine Noise, 52 to 57 CN



Influence of Cetane on Fuel Consumption

Existing data on the influence of cetane on fuel consumption in older technology heavy-duty engines are inconsistent. Figure 3 demonstrates this inconsistency through measurements of heavy-duty brake specific fuel consumption (BSFC): increasing natural cetane from 50 to 58 generally improved BSFC, but increasing artificial cetane had the opposite effect. On-going research may help resolve this uncertainty as well as provide better data for the impacts on more advanced heavy-duty and light-duty engines and vehicles.

Figure 3: Effect of Cetane on Fuel Consumption 50 to 58 CN



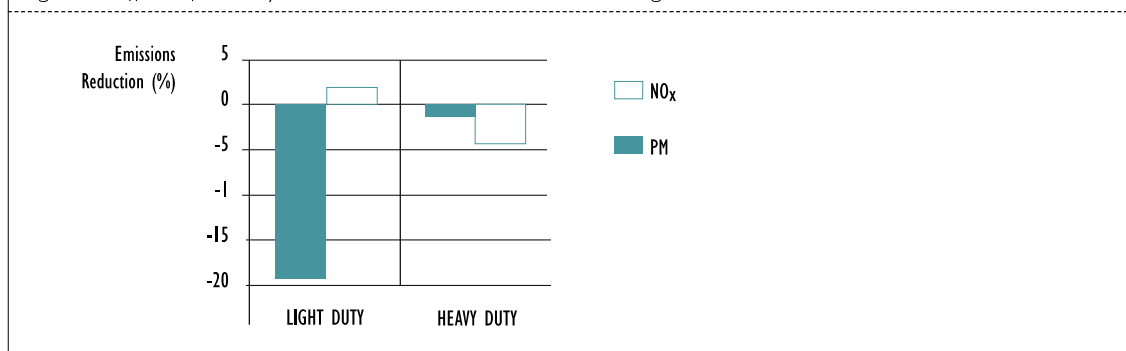
DENSITY and VISCOSITY

The diesel fuel injection is controlled volumetrically or by timing of the solenoid valve. Variations in fuel density (and viscosity) result in variations in engine power and, consequently, in engine emissions and fuel consumption. The European EPEFE programme found that fuel density also influences injection timing of mechanically controlled injection equipment, which also affects emissions and fuel consumption. Therefore, in order to optimise engine performance and tailpipe emissions, both minimum and maximum density limits must be defined in a fairly narrow range.

Effect of Density on Emissions and Engine Power

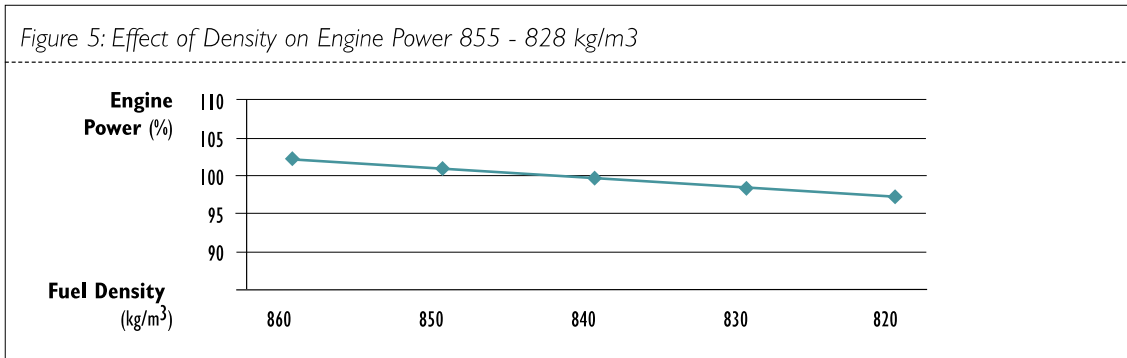
Emissions' testing has demonstrated that reduced density will reduce PM emissions from all diesel vehicles, and NO_x emissions from heavy-duty vehicles (Figure 4).

Figure 4: Effect of Density on Exhaust Emissions 855 to 828 kg/m³



However, due to the volumetric fuel injection of diesel engines, reduced density will also increase fuel consumption and reduce power output. EPEFE testing has shown that lowering fuel density decreases engine power output (Figure 5) and increases volumetric fuel consumption. Variations in fuel viscosity (i.e. reduced density generally reduces viscosity) may accentuate the density effects on power (not necessarily fuel consumption), particularly in combination with distributor-type injection pumps.

Figure 5: Effect of Density on Engine Power 855 - 828 kg/m³



Influence of Fuel Density on Emission Control Systems

Production diesel engines are set to a standard density, which determines the amount of fuel injected. The (volumetric) injection quantity is a control parameter for other emission control systems like exhaust gas recirculation (EGR). Variations in fuel density therefore result in non-optimal EGR-rates for a given load and speed point in the engine map and, as a consequence, influence the exhaust emission characteristics.

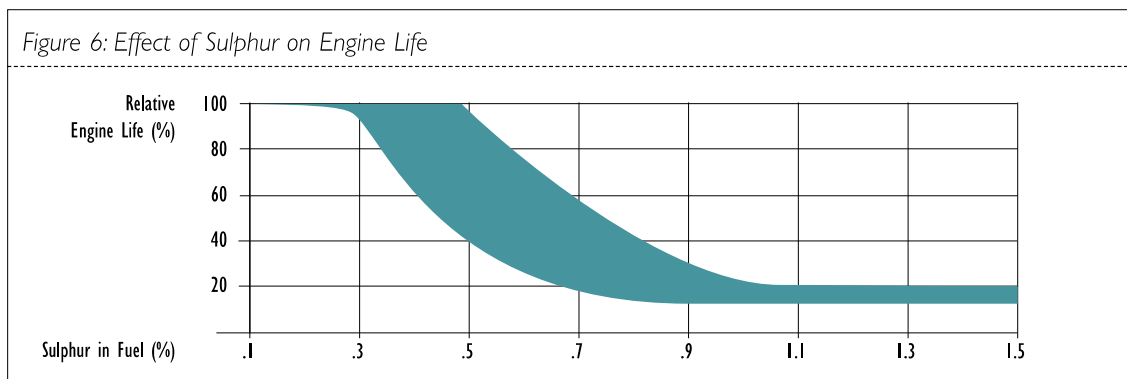
Influence of Fuel Viscosity on Injection System Performance

Fuelling and injection timing are also dependent on fuel viscosity. High viscosity can reduce fuel flow rates, resulting in inadequate fuelling. A very high viscosity may actually result in pump distortion. Low viscosity, on the other hand, will increase leakage from the pumping elements, and in worse cases (low viscosity, high temperature) can result in total leakage. As viscosity is impacted by ambient temperature, it is important to minimise the range between minimum and maximum viscosity limits to allow optimisation of engine performance.

SULPHUR

Sulphur naturally occurs in crude oil. If the sulphur is not removed during the refining process, it will remain in the vehicle fuel. Cross-contamination also can occur in the fuel distribution system. Sulphur can have a significant effect on engine life by leading to corrosion and wear of engine systems. As shown in Figure 6, relative engine life decreases as the sulphur level increases.

Figure 6: Effect of Sulphur on Engine Life



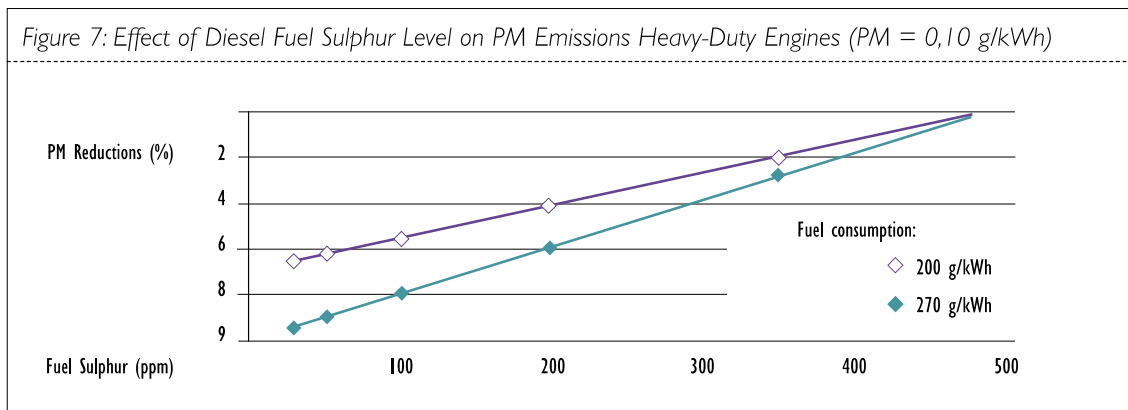
Diesel fuel sulphur also contributes significantly to fine particulate matter (PM) emissions, through the formation of sulphates both in the exhaust stream and later in the atmosphere. Furthermore, the efficiency of some exhaust after-treatment systems is reduced as fuel sulphur content increases, while others are rendered permanently ineffective through sulphur poisoning.

As sulphur levels are reduced, fuel stability requires special attention. The industry has

developed a 'Standard Test Method for High Temperature Stability of Distillate Fuels' (ASTM D 6468) for thermal oxidative stability. Inadequate thermal stability can result in fuel filter plugging by oxidised products (sludge). As fuel injection system pressures and temperatures increase, it may be more appropriate to measure the thermal oxidative stability of diesel fuel rather than only long-term storage stability.

Effect of Sulphur on Particulate Emissions

The impact of sulphur on particulate emissions is widely understood and known to be significant. In the European Auto Oil programme, it was predicted that a reduction in sulphur from 500ppm to 30ppm would result in PM emission reductions of 7% from light-duty vehicles and 4% from heavy-duty trucks. However, the predictive equations do not take into account the absolute PM level or the fuel consumption. A correction factor has been developed by European heavy-duty manufacturers to better reflect the relationship between PM emissions and fuel sulphur levels. This correction suggests that the real benefit from sulphur reductions will be more significant, as shown here (Figure 7) for heavy-duty trucks. Reductions in fuel sulphur will also provide particulate emission reductions in all engines, regardless of emission calibration.



Testing performed on heavy-duty vehicles using the Japanese diesel 13 mode cycle have shown significant PM emission reductions can be achieved with both catalyst and non-catalyst equipped vehicles. The testing showed that PM emissions from a non-catalyst equipped truck running on 400ppm sulphur fuel were about double the emissions when operating on 2ppm fuel. (JSAE 9831171)

Sulphur Contribution to Aerosols and Fine Particulate Emissions

When sulphur is oxidised during combustion, it forms SO₂, which is the primary sulphur compound emitted from the engine. Some of the SO₂ is further oxidised - in the engine, exhaust, catalyst or atmosphere - to sulphate (SO₄). The sulphate and nearby water molecules often coalesce to form aerosols or engulf nearby carbon to form heavier particulates that have a significant influence on both fine and total PM. Without oxidation catalyst systems, the conversion rate from sulphur to sulphate is very low, typically around 1%, so the historical sulphate contribution to engine-out PM has been negligible. However, oxidation catalysts dramatically increase the conversion rate to as much as 100%, depending on catalyst efficiency. Therefore, for modern vehicle systems, most of which include oxidation catalysts, a large proportion of the engine-out SO₂ will be oxidized to SO₄, increasing the amount of PM emitted from the vehicle. Thus, fuel sulphur will have a significant impact on fine particulate emissions in direct proportion to the amount of sulphur in the fuel.

The mass of sulphates emitted from the engine depends on the following parameters:

- The fuel consumption of the engine.

- The fuel sulphur content.
- The S to SO₄ conversion rate.

Both the fuel sulphur content and fuel consumption are measurable parameters; the conversion rate is predicted based on engine variability and the use of an oxidation catalyst. The following formula can provide an estimate of the impact:

$$\mathbf{BSSO_4} = \mathbf{BSFC} * \mathbf{FSC}/100 * \mathbf{PCSC}/100 * \mathbf{7}$$

Where

BSSO₄ = brake specific sulphate in mass/brake power-hour.

BSFC = brake specific fuel consumption in g/kWh.

FSC = fuel sulphur content in % mass.

PCSC = Percent sulphur conversion (to SO₄).

7 = S to (SO₄ + water) weight increase factor = Brake specific sulphate in mass/brake power-hour.

Overview of Sulphur's Effect on Highly Advanced Diesel Emission Control Systems

No single device can simultaneously reduce NO_x, PM, HC and other emissions from diesel engines. Furthermore, trade-offs historically have been required between and among emissions and fuel economy, especially for markets with higher sulphur diesel fuel. To meet the requirements of many new regulations, highly advanced emission control systems have been developed around combinations of engine and aftertreatment devices. Sulphur has a particularly strong impact on these newer NO_x controls, and many will stop working if the sulphur level becomes too high. Thus, these new systems require low or ultra-low sulphur fuels to maintain their operational capability.

The most advanced of these technologies includes De-NO_x catalyst systems, such as Lean NO_x traps (LNT) (also known as NO_x adsorbers) and Selective Catalytic Reduction (SCR) devices, which can remove a greater amount of NO_x emissions from the diesel's oxygen-rich exhaust than previously possible. Highly advanced particulate filters also have been developed to reduce PM emissions. Many of these devices are combined in various configurations to enable the vehicle to meet specific emission standards and to minimize impacts on fuel efficiency. Diesel oxidation catalysts (DOC), which reduce HC and CO emissions, and exhaust gas recirculation (EGR) systems, which reduce NO_x, are among the proven technologies that may be used in conjunction with newer technologies. More importantly, all emission control systems perform better and last longer with sulphur-free fuel.

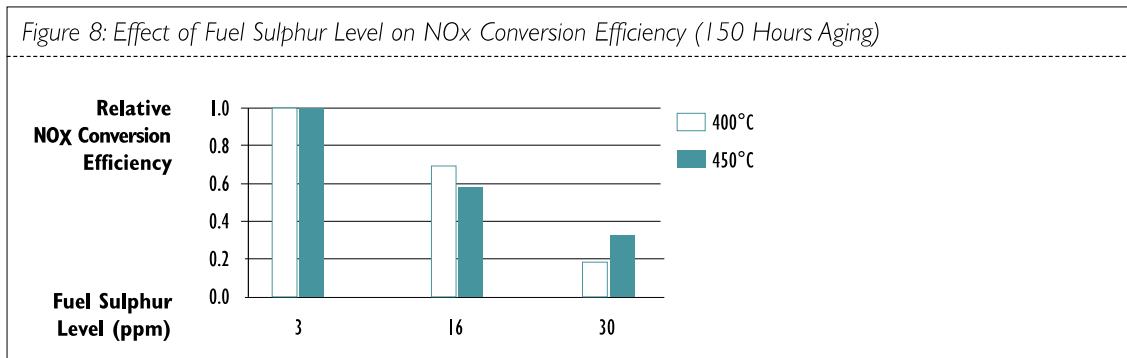
The Diesel Emission Control-Sulphur Effects (DECSE) project, a collaborative program conducted by the US Department of Energy (DOE), Engine Manufacturers Association (EMA) and Manufacturers of Emission Controls Association (MECA), studied the impact of diesel fuel sulphur levels of 3, 16, 30, 150 and 350ppm on a number of these technologies on both heavy-duty and light-duty engines. Reference: www.ott.doe.gov/decse.

The Advanced Petroleum Based Fuels - Diesel Emission Control (APBF-DEC) Program, another collaborative effort, has identified optimal combinations of low-sulphur diesel fuels, lubricants, diesel engines and emission control systems to meet projected emission standards for the 2001 to 2010 time period. Reference: <http://www.ott.doe.gov/apbf.shtml>. Research and development are continuing to refine and improve the systems now entering Category 4 and Category 5 markets.

NO_x Adsorber

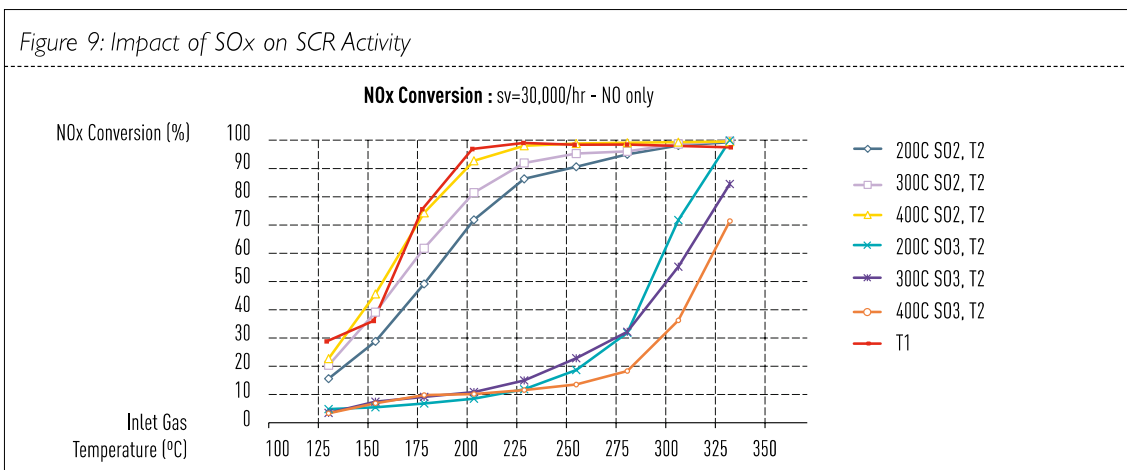
NOx adsorbers are poisoned and rendered ineffective by the presence of sulphur. These devices can be up to 90% efficient in NOx removal if operated on sulphur-free fuel. The SO₂ formed during combustion and released in the exhaust undergoes reactions in these devices that are similar to those of NOx, but the oxidized sulphur compounds adsorb more strongly to the catalyst surface than the NOx, thereby poisoning the catalyst.

The effect of fuel sulphur content on NOx adsorber conversion efficiency is shown in Figure 8 below. The figure illustrates the effect of fuel sulphur on relative NOx conversion efficiencies. Compared to 3ppm sulphur fuel, both 16 and 30ppm sulphur fuels resulted in a significant decline in performance.



Selective Catalytic Reduction

Selective Catalytic Reduction (SCR) emission control devices, which are being used on both light-duty and heavy-duty vehicles, are catalysts that work in conjunction with a specially formulated reactant (called Diesel Exhaust Fluid (DEF) in the U.S.) to convert NOx into nitrogen and water vapour. Like other catalysts, the effectiveness and durability of SCR systems can be adversely affected by fuel sulphur. The impact is exacerbated by the use of a diesel oxidation catalyst (DOC) in front of the SCR because DOCs convert much of the exhaust SO₂ to SO₃. While both SO₂ and SO₃ poison the SCR, research has shown SO₃ to have a stronger impact on SCR conversion efficiency. Figure 9 shows how SO₂ and SO₃ affect NOx conversion in SCRs at different temperatures (also see SAE 2009-01-0898).



Diesel Particulate Filter

The Diesel Particulate Filter (DPF), which first appeared in the market on production vehicles in mid-2000, allows vehicles to achieve extremely low particulate emissions. The filtration of exhaust gas particulates has been possible for many years, but the disposal of the accumulated particulate has remained a difficult problem to solve. Apart from removing the filter frequently for cleaning (which is not allowed in the U.S.), a reliable and cost-

effective system of on-board filter regeneration by combustion of the particulate was previously not available. The latest generation of common rail engines opened possibilities through electronic injection strategies for increasing exhaust gas temperatures, however, and this has enabled the combustion of the trapped particulate. A different strategy for regenerating filters uses a combination of catalytic additive mixed on-board with the fuel, or post-combustion fuel injection into the exhaust and an oxidation catalyst pre-filter.

The latest generation of common rail direct injection diesel engines emits 60% less particulate matter than its immediate pre-chamber predecessors, and when combined with a DPF system, these engines can reduce the number of particulate in the exhaust gas to the level of ambient air, which completely eliminates black smoke. What is more, this $10^3 - 10^4$ reduction magnitude in particulate emissions is constant over the whole range of particulate size. Thus, using DPF systems further enhances the potential of the diesel engine as a low-polluting power unit. The sulphur contained in diesel fuel is likely to be transformed into gaseous sulphur compounds in the oxidation catalyst included with the emission control system, and these compounds may be transformed through secondary reactions into sulphate particulates in the atmosphere. Therefore, the use of sulphur-free fuels in vehicles with DPF systems is highly recommended to avoid this phenomenon.

Continuously Regenerating and Catalysed Diesel Particulate Filters

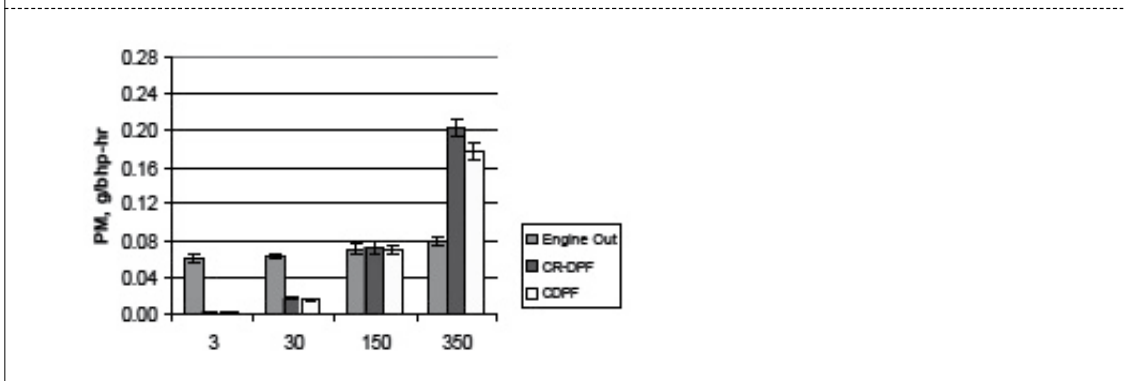
The Continuously Regenerating Diesel Particulate Filter (CR-DPF) and Catalysed Diesel Particulate Filter (CDPF) represent two different approaches to DPF regeneration.

The CR-DPF regenerates by continuously generating NO_2 from engine-emitted NO over a diesel oxidation catalyst placed upstream of the DPF. Proper vehicle calibration is necessary to ensure that sufficient NO_2 is generated for this purpose. NO_2 has been established as a more effective low-temperature oxidizing agent for diesel PM than oxygen. Sulphur in the exhaust is oxidised over the CR-DPF, however, forming sulphates that contribute to PM emissions. Sulphur oxides also compete for the critical NO and NO_2 reaction sites on the DPF, making trap regeneration less effective.

The CDPF regenerates by using a catalyst coating on the DPF element to promote oxidation of the collected PM using available oxygen in the diesel exhaust. Sulphur in the exhaust is oxidised over the CDPF to form sulphates. Exhaust-gas temperature and fuel-sulphur level are critical factors that affect the performance of both types of DPF (CR-DPF and CDPF).

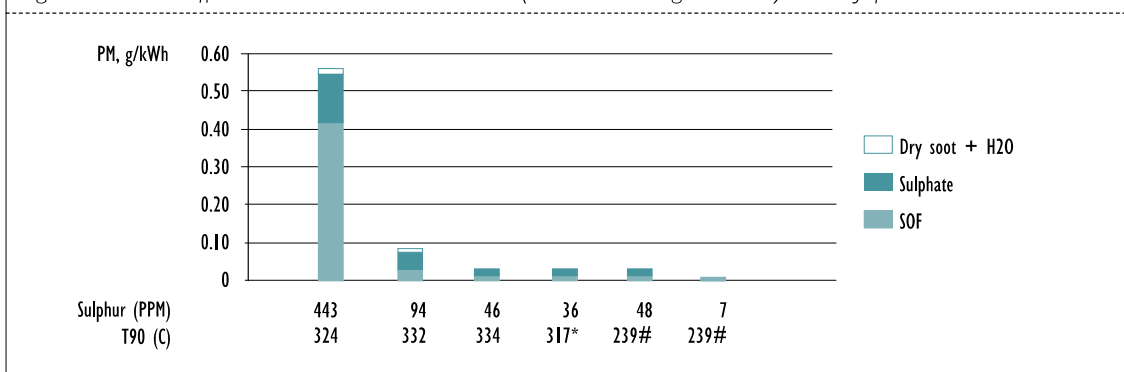
Fuel sulphur has a significant effect on PM emissions from these emission control devices. Both types of DPF effectively reduce PM emissions when fuel sulphur is very low, but when fuel sulphur increases, so do sulphate levels, which affects the amount of PM emitted. In one study, PM was reduced by 95% over the OICA cycle when the tested DPFs were used with 3ppm sulphur fuel (Figure 10a), but with 30ppm sulphur fuel, the PM reduction efficiencies dropped to 72 and 74% for the CR-DPF and CDPF, respectively. At the 150ppm sulphur test point, the sulphur content of the measured mass completely masked the reduction in carbonaceous particles, so that the measured total PM reductions were near zero. A similar outcome was seen in Japanese DPF testing (Figure 10b).

Figure 10a: Effect of Fuel Sulphur Level on PM Emissions – OICA Cycle



Engine tested: Caterpillar 3126, 7.2 litre, Inline 6 cylinder, 205 kW @2200 rpm

Figure 10b: Fuel effect on Diesel Particulate – CR (Continuous Regeneration) - DPF Japan Diesel 13 Mode



*Blend of diesel fuel and kerosene.

#Kerosene.

ASH

Fuel and lubricant derived ash can contribute to coking on injector nozzles (see Figure 16) and will have a significant effect on the life of diesel particulate filters. Ash-forming metals can be present in fuel additives, lubricant additives or as a by-product of the refining process.

Metallic ash constituents are incombustible, so when they are present in the fuel, they remain in the exhaust and become trapped within the DPF. Thus, the presence of ash-forming materials in the fuel will lead to a premature build-up of backpressure and other vehicle operability problems. Non-fuel solutions have been found unsatisfactory. Larger filters can reduce backpressure build-up but otherwise would be unnecessary and may be infeasible (for example, in smaller vehicles). Increased in-use maintenance or, in extreme cases, DPF replacement would help, but these steps may not be allowed in some markets. Therefore, keeping ash-forming compounds out of the fuel to the extent possible provides the best solution.

Ash-forming compounds may be present in fuel in four forms:

- Abrasive solids, such as suspended solids and organometallic compounds that contribute to injector, fuel pump, piston and ring wear and to the formation of engine deposits.
- Soluble metallic soaps, which have little effect on wear but may contribute to engine deposits.

- Soluble metals, which may be present in vegetable-derived fuels as a result of absorption by the plant source and inadequate removal during processing. Biodiesel fuel, for example, may contain metals that were left in the residue resulting from common catalytic production methods.
- Metals that originate in water entrained in the fuel.

Industry standards limiting ash to less than 0.01%, which were intended to protect close tolerance fuel injection equipment and reduce piston ring zone deposits, have addressed the first form of ash-forming compounds. Fuel surveys have confirmed that the ash content in most fuels has been near the detection limit of the currently available test procedure (0.001%). The remaining forms of metallic ash, however, may enter fuel during the distribution process and must be controlled before dispensing the fuel to the engine or vehicle.

Diesel fuel containing ash at the current detection limit (0.001%) may require the DPF to be serviced during the vehicle's useful life, but many jurisdictions do not allow this for engines or vehicles meeting strict particle emission regulations. Therefore, ash-forming metals must be controlled to very low levels to enable these emission control devices to operate properly over the lifetime of the vehicle. To allow the appropriate level for these ash compounds, a new test procedure capable of measuring lower levels of ash in diesel fuel should be developed.

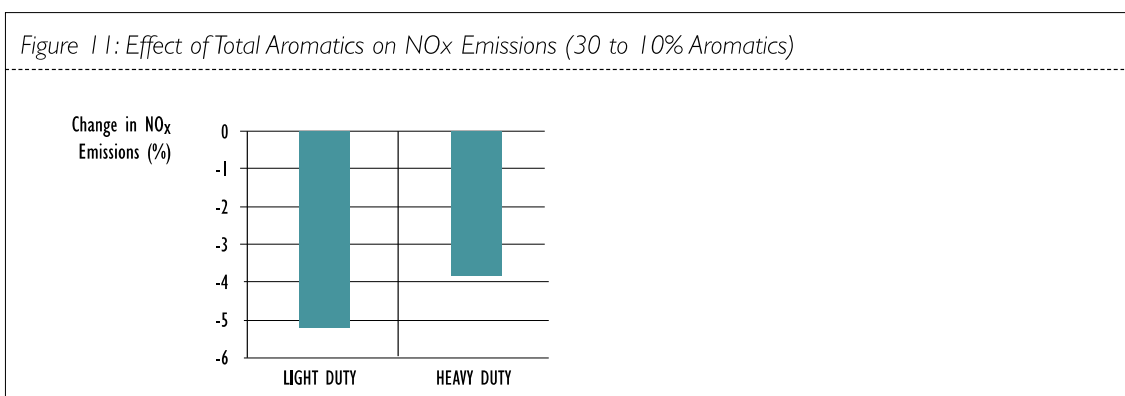
AROMATICS

Aromatics are molecules that contain at least one benzene ring. The fuel aromatic content will affect combustion and the formation of particulate and polycyclic aromatic hydrocarbons (PAH) emissions.

The diesel fuel aromatics content influences flame temperature, and therefore, NO_x emissions during the combustion. PAH in the fuel affect the formation of particulates and PAH emissions from a diesel engine.

Influence of Total Aromatics Content on NO_x Emissions

A higher aromatic content in the fuel will increase the flame temperature during combustion, which results in increased NO_x emissions. Testing in Europe (ACEA follow-up programme to EPEFE) demonstrated that a reduction of the total aromatic content from 30 to 10% yields significantly lower NO_x emissions as shown in Figure 11.



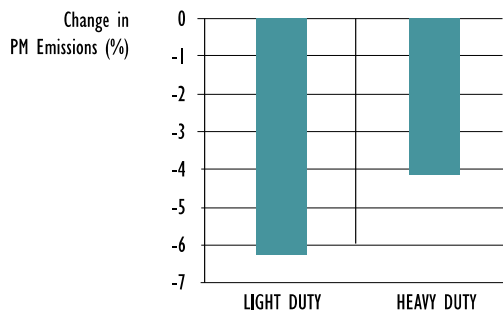
The light-duty data are based on the combined ECE/EUDC cycle, the heavy-duty on the 88/77/EEC 13-mode cycle.

Influence of Polyaromatic Content on Particulate Emissions

The influence of polyaromatic (di+, tri+) content on PM emissions was also investigated in

the EPEFE programme. Figure 12 shows the reductions of PM emissions that were measured when the polyaromatic content was reduced from 9 to 1 %.

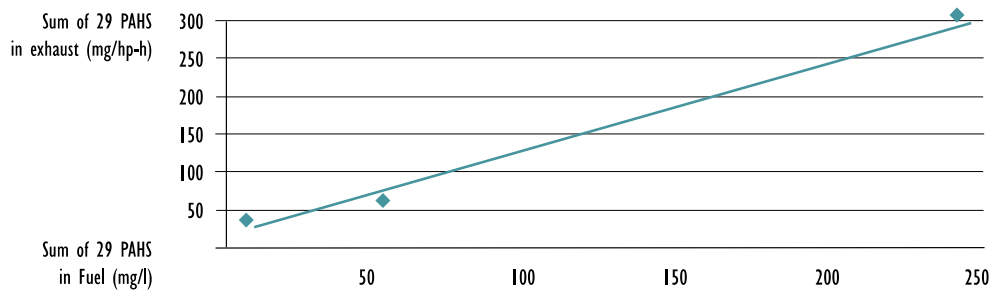
Figure 12: Effect of Polyaromatics on PM Emissions (from 9 to 1% di+ Polyaromatics)



Influence of PAH Content on PAH Emissions

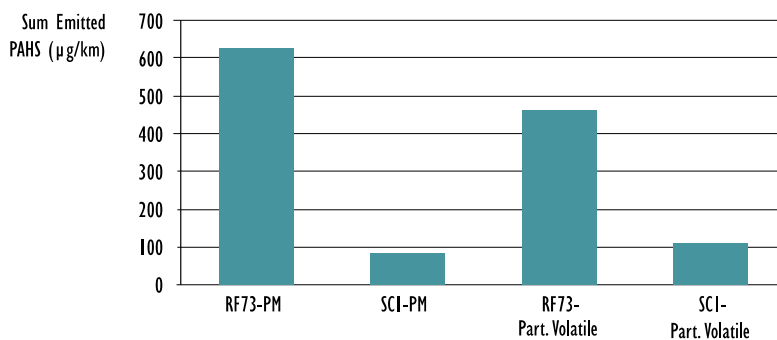
PAH (tri+) content in diesel fuel has been shown to directly correlate to PAH emissions in diesel engine exhaust. The PAH emissions of a truck diesel engine on the US transient cycle using fuels with different PAH contents were measured in a Swedish study. The results shown in Figure 13 demonstrate this direct correlation.

Figure 13: Effect of Fuel PAH on Emissions of PAH



The Swedish EPA also tested a Euro 2 diesel engine on the 88/77/EEC and the transient 'Braunschweig' cycle on Sweden Class 1 fuel (SC1, PAH =24 mg/l) and European reference fuel (RF73; PAH=2100 mg/l). Figure 14 shows the sum of emitted PAH's collected on the filter (PM) and the emissions of partly volatile PAH's (average of four cycles).

Figure 14: Effect of Fuel PAH on Emissions of PAH



DISTILLATION CHARACTERISTICS

The distillation curve of diesel fuel indicates the amount of fuel that will boil off at a given temperature. The curve can be divided into three parts:

- The light end, which affects startability;
- The region around the 50% evaporated point, which is linked to other fuel parameters such as viscosity and density; and,
- The heavy end, characterised by the T90, T95 and final boiling points. The heavy end has been the most thoroughly studied with respect to its effect on tailpipe emissions.

Influence of Heavy End on PM Emissions

In most new studies, only the influence of the upper boiling range has been investigated with respect to exhaust gas emissions, whereas the lower boiling range varied widely. Conclusions concerning the whole boiling range and distillation influence are therefore not possible. However, it is clear that too much fuel in the heavy end will result in coking and increased tailpipe emissions of soot/smoke/particulate matter.

Influence of T95 on Tailpipe Emissions

The effect of T95 on vehicle emissions was examined in the European EPEFE programme. The testing indicated that exhaust gas emissions from heavy-duty diesel engines were not significantly influenced by T95-variations between 375°C and 320°C. However, a tendency for lower NO_x and higher HC with lower T95 was observed.

In the case of light-duty diesel engines, the same reduction in T95 resulted in a 7% reduction in PM and 4.6% increase in NO_x emissions.

COLD FLOW

Diesel fuel can have a high content (up to 20%) of paraffinic hydrocarbons which have a limited solubility in the fuel and, if cooled sufficiently, will come out of solution as wax. Adequate cold flow performance, therefore, is one of the most fundamental quality criteria for diesel fuels. The cold flow characteristics are primarily dictated by:

- Fuel distillation range, mainly the back-end volatility;
- Hydrocarbon composition: content of paraffins, naphthenes, aromatics;
- Use of cold flow additives.

Measures of Cold Flow Performance

Diesel cold flow properties must be specified according to the seasonal and climatic needs in the region where the fuel is to be used. Wax in vehicle fuel systems is a potential source of operating problems; the low temperature properties of diesel fuels are therefore defined by wax-related tests:

- **Cloud Point, CP (ISO 3015, ASTM D2500):** The temperature at which the heaviest paraffins start to precipitate and form wax crystals; the fuel becomes 'cloudy'.
- **Cold Filter Plugging Point, CFPP (EN116):** The lowest temperature at which the fuel can pass through the filter in a standardised filtration test. The CFPP test was developed from vehicle operability data and demonstrates an acceptable correlation for fuels and vehicles in the market. For North American fuels however, CFPP is not a good predictor of cold flow operability. CFPP can be influenced by cold flow additives.
- **Low Temperature Flow Test, LTFT (ASTM D4539):** The LTFT was developed to

predict how diesel fuels in the United States and Canada will perform at low temperatures, in the diesel vehicles present in these markets. LTFT is a slow cooling test and therefore more severe than CFPP. LTFT temperature can be influenced by cold flow additives.

Cold Flow Limits

The diesel fuel cold flow performance can be specified by Cloud Point, by CFPP (with maximum delta between CFPP and Cloud Point), or by LTFT (in USA and Canada).

- If Cloud Point (only) or LTFT is used, the maximum allowed temperature should be set no higher than the lowest expected ambient temperature.
- If CFPP is used to predict cold flow, the maximum allowed CFPP temperature should be set equal to, or lower than, the lowest expected ambient temperature. In this case, the Cloud Point should be no more than 10°C above the CFPP specified.

Example:

- Lowest expected ambient temperature (statistical): -32°C.
- Maximum allowed CFPP temperature: -32°C.
- Maximum allowed Cloud Point: -22°C.

FOAM

Diesel fuel has a tendency to generate foam during tank filling, which slows the process and risks an overflow. Anti-foamants are sometimes added to diesel fuel, often as a component of a multifunctional additive package, to help speed up or to allow more complete filling of vehicle tanks. Their use also minimises the likelihood of fuel splashing on the ground, which, in turn, reduces the risk of spills polluting the ground, the atmosphere and the consumer.

Foam Control

Silicon surfactant additives are effective in suppressing the foaming tendency of diesel fuels, the choice of silicon and co-solvent depending on the characteristics of the fuel to be treated. Selection of a diesel anti-foamant is generally decided by the speed at which the foam collapses after vigorous manual agitation to simulate the effect of air entrainment during tank filling. It is important that the eventual additive chosen should not pose any problems for the long-term durability of the emission post-treatment control systems.

BIOFUELS and ALTERNATIVE SYNTHETIC FUEL COMPONENTS

Fatty Acid Methyl Esters

Fatty Acid Methyl Esters (FAME), also known as biodiesel, increasingly are being used to extend or replace diesel fuel. Such use has been driven largely by efforts in many nations to exploit agricultural produce and/or to reduce dependency on petroleum-based products.

Several different oils may be used to make biodiesel, for example, rapeseed, sunflower, palm, soy, cooking oils, animal fats and others. These oils must be reacted with an alcohol to form ester compounds before they can be used as biodiesel fuel. Unprocessed vegetable oils, animal fats and non-esterified fatty acids are not acceptable as transportation fuels due to their very low cetane, inappropriate cold flow properties, high injector fouling tendency and high kinematics viscosity level. Historically, methanol has been the alcohol most used to esterify the fatty acids, and the resultant product is called fatty acid methyl ester (FAME). Research is underway to enable use of ethanol as the

reactant alcohol, in which case the product is called fatty acid ethyl ester (FAEE).

The European standards organization, CEN, has published a FAME standard (EN 14214) that establishes specifications for biodiesel use as either: (i) a final fuel in engines designed or adapted for biodiesel use; or (ii) a blendstock for conventional diesel fuel. Similarly, ASTM International has established specifications for neat biodiesel (ASTM D 6751) but only for use as a blending component, not as a final fuel.

Generally, biodiesel is believed to enhance the lubricity of conventional diesel fuel and reduce exhaust gas particulate matter. Also, the production and use of biodiesel fuel is reported to lower carbon dioxide emissions on a source to wheel basis, compared to conventional diesel fuel.

At the same time, engine and vehicle manufacturers have concerns about introducing biodiesel into the marketplace, especially at higher levels. Specifically:

- Biodiesel may be less stable than conventional diesel fuel, so precautions are needed to avoid problems linked to the presence of oxidation products in the fuel. Some fuel injection equipment data suggest such problems may be exacerbated when biodiesel is blended with ultra-low sulphur diesel fuels.
- Biodiesel requires special care at low temperatures to avoid an excessive rise in viscosity and loss of fluidity. Additives may be required to alleviate these problems.
- Being hygroscopic, biodiesel fuels require special handling to prevent high water content and the consequent risk of corrosion and microbial growth.
- Deposit formation in the fuel injection system may be higher with biodiesel blends than with conventional diesel fuel, so detergent additive treatments are advised.
- At low ambient temperatures, FAME may produce precipitated solids above the cloud point, which can cause filterability problems.
- Biodiesel may negatively impact natural and nitrile rubber seals in fuel systems. Also, metals such as brass, bronze, copper, lead and zinc may oxidize from contact with biodiesel, thereby creating sediments. Transitioning from conventional diesel fuel to biodiesel blends may significantly increase tank sediments due to biodiesel's higher polarity, and these sediments may plug fuel filters. Thus, fuel system parts must be specially chosen for their compatibility with biodiesel.
- Neat (100%) biodiesel fuel and high concentration biodiesel blends have demonstrated an increase in NO_x exhaust emission levels.
- Biodiesel fuel that comes into contact with the vehicle's shell may be able to dissolve the paint coatings used to protect external surfaces.

In view of the high level of interest in this fuel, including among vehicle and engine manufacturers, biodiesel specifications and test methods will continue to be investigated.

Biodiesel (FAME) inherently has poor oxidation stability due to the nature of its chemical composition. Most FAME contains carbon-to-carbon double bonds in its chemical construction that are easily oxidized after production and during the storage and use of the fuel. Such oxidation reactions are why precautions must be taken, such as the use of oxidation stability enhancing additives like BHT, when blending and distributing biodiesel fuels.

To secure the quality of biodiesel blended fuel, additional oxidation stability criteria are being introduced into finished fuel specifications in some regions. The European standard for B7 requires a 20 hour minimum induction period by the modified Rancimat method (See EN 590). As part of a compulsory standard for B5, Japan requires either a delta TAN

maximum of 0.12 mg KOH/g or a minimum 65 minutes by the PetroOXY method. (The delta TAN method measures acid value before and after aging per ASTM D2274 (@ 115°C)); the growth in acid value is reported as delta TAN. The current European limit is believed to be inadequate to prevent corrosion in metal parts such as vehicle fuel tanks, however. Given on-going questions about the adequacy of various methods and limits, Europe and Japan are working to harmonize the oxidation stability test method by introducing the PetroOXY method. The goal of the investigation is to shorten the test duration and improve repeatability of the results. This research may lead to future revisions in the oxidation criterion and test method for biodiesel blended fuels. Figure 15a shows that a 35 hour minimum induction period by the modified Rancimat method is comparable to a delta TAN maximum of 0.12 mg KOH/g. Figure 15b shows the correlation between the PetroOxy and Delta TAN test methods for different FAME feedstocks and levels of antioxidant additive in B5 blends. Figure 15c shows the correlation between the PetroOxy and Rancimat methods for different diesel fuels, FAMEs and blend rates. It should be noted that the Rancimat and Delta TAN methods must be used with fuels containing FAME. All three of the correlations are based on fuels containing FAME.

Figure 15a : Correlation between Modified Rancimat Method and Delta TAN Method

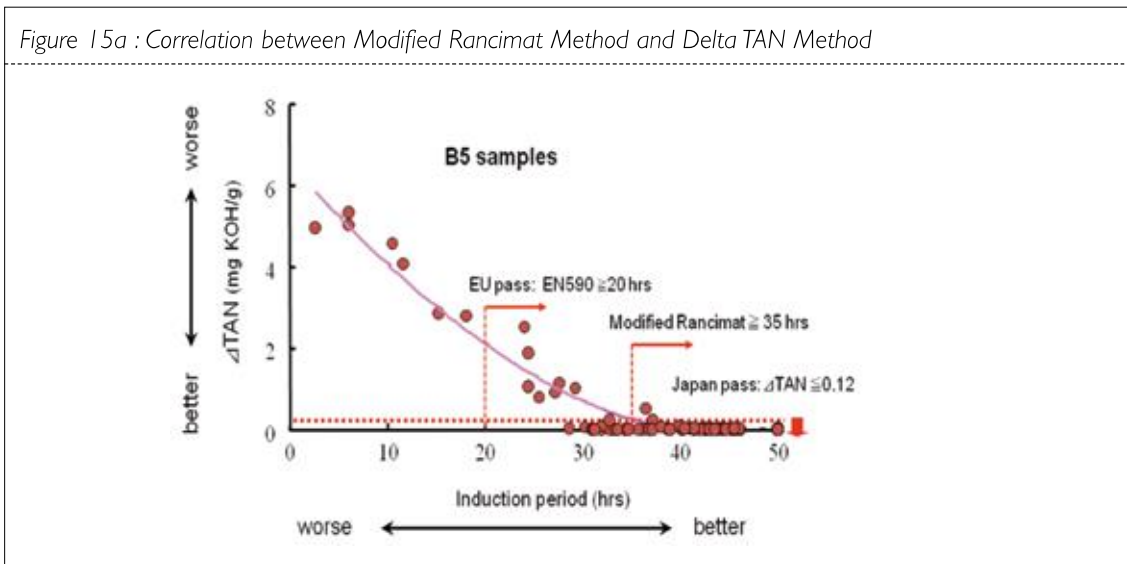


Figure 15b: Correlation between PetroOxy and Delta TAN Methods

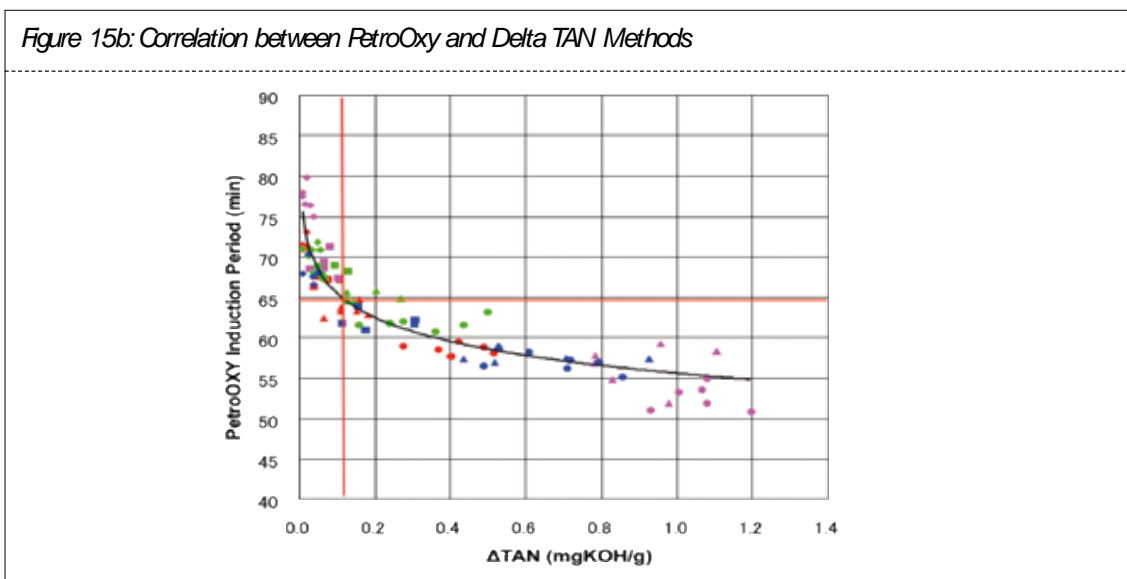
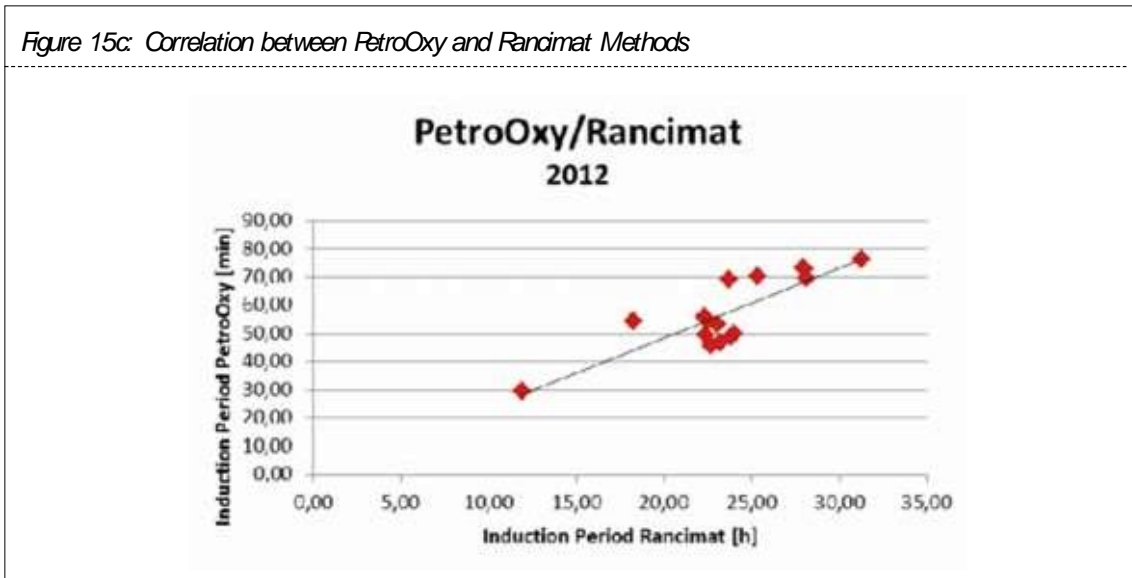


Figure 15c: Correlation between PetroOxy and Rancimat Methods



Synthetic Fuels

In recent years, various types of alternative and renewable diesel fuels have emerged that also can help extend or replace diesel fuel. The Fischer-Tropsch process, which was invented in the 1920s but today represents a variety of similar processes, converts feedstocks of biomass, methane (natural gas) or coal into paraffinic diesel fuels, commonly referred to as BTL ('biomass-to-liquid'), GTL ('gas-to-liquid') or CTL ('coal-to-liquid'), as the case may be. Regardless of feedstock, the process requires gasification and then synthesis to a liquid with the desired properties. BTL should not be confused with biodiesel (FAME), which is fundamentally a different fuel. Some of these blendstocks, particularly BTL, have relatively low well-to-wheel GHG emissions, and these are preferred over other synthetic fuels that are not considered to be low carbon fuels. CEN TS15940 may be used as a production guideline for GTL and HVO quality; additional engine validation may be needed to ensure the fuel ultimately works well in vehicles and engines.

These fuels are usable in any diesel engine either in pure form or blended with conventional diesel fuel, although they generally have poor lubricity, which requires the addition of appropriate additives to enable the fuel to meet or exceed requirements. The fuels are very clean-burning because they have virtually no sulphur or aromatics. They also have very high cetane levels, which enable more efficient engine operation. Their distillation profile differs from petroleum diesel fuel, and they have a lower density than the Charter's diesel fuel specification, however, and these factors may reduce fuel economy, compared to an equivalent volume of diesel fuel meeting the Charter's specification. CEN TS15940 may be used as a production guideline for GTL and HVO quality; additional engine validation may be needed to ensure the fuel ultimately works well in vehicles and engines.

Hydrotreated Vegetable Oils

Renewable feedstocks such as vegetable oils may be processed by variations of conventional petroleum refining, including hydrotreatment. These refining methods produce saturated paraffinic hydrocarbon molecules with extremely low aromatic levels and a very narrow distillation range, and properly processed, they can provide the required cold flow properties. Some HVO production processes may, however, yield non-paraffinic hydrocarbons in addition to paraffins, so additional controls may be needed to ensure acceptable quality fuel. CEN TS15940 may be used as a production guideline for GTL and HVO quality; additional engine validation may be needed to ensure the fuel ultimately works well in vehicles and engines.

Unlike FAME, the paraffinic middle distillate fuel oils produced by these methods are indistinguishable from conventional paraffinic fuel oils derived from petroleum and lack the residual process elements typical of biodiesel. Thus, they are highly suited as a blendstock for diesel fuel. Engine and vehicle manufacturers widely support the development of HVO fuels as a way to increase diesel fuel's renewable, low carbon content without the concerns associated with methyl ester fuels.

E-Diesel

Adding ethanol to diesel fuel (E-diesel) has been considered as a way to extend the volume of diesel fuel, reduce dependency on imported oil products or exploit agricultural produce and waste. E-diesel fuel typically has an extremely low flashpoint of about 13°C (55°F), which is well below the minimum limit set by various organisations: ASTM D975 standard of 52°C (126°F), EN590 standard of 55°C min (131°F), JIS K2204 standard of 45°C (113°F). Such flashpoint levels raise serious safety concerns (such as explosions), for fuel handling, storage and use. Vehicle and engine manufacturers are concerned that e-diesel may damage vehicle parts, especially fuel injectors, and cause other types of vehicle failure due to low lubricity. The fuel's compatibility with the vehicle in other ways, its impact on vehicle emissions and its health effects remain unknown. Since ethanol has lower energy content than diesel fuel, its presence in the fuel will reduce fuel economy. Therefore, until the many safety, performance and health concerns are resolved and sufficient peer-reviewed research is conducted in these important areas, manufacturers do not support adding ethanol to any category of diesel fuel.

INJECTOR CLEANLINESS

The fuel injector, which is designed to meter fuel to a high degree of accuracy, is a component of very high precision. The correct behaviour of the engine depends on the injector doing its job properly; otherwise there will be repercussions in terms of noise, smoke and emissions.

Effect of Injector Fouling

The tip of the injector is subject to a very harsh environment as it is in direct contact with the combustion process, both in pre-chamber and in direct injection engines. The solid matter products of combustion are deposited on the tip and can result either in partial or complete hole blockage, with partial blockage the more common effect. Either effect will alter significantly the operation of the injector by reducing fuel flow and affecting power and emissions.. For pre-chamber engines, the combustion products partially block the progressive delivery of the fuel at part load, and the combustion can become violent and disorganised. Likewise in direct injection engines, a partial or complete blockage of one of the fine spray holes will perturb the atomisation of the fuel jet, and the engine no longer functions as designed. Where pre-chamber engines are concerned, some coking is inevitable due to the type of injector used, and the choice of injector takes this into account. However, the coking level depends on the quality of the fuel, and excessive coking cannot be tolerated. The injectors of direct injection engines are initially more resistant to coking, but poor fuel quality can eventually block a spray hole.

Internal Diesel Injector Deposits

Engine and vehicle manufacturers recently have detected a new type of injector deposit that has been labelled Internal Diesel Injector Deposits (IDID). These deposits differ from injector nozzle (tip) coking deposits both in their location and their effects. The engine impacts range from increased noise and rough running to power loss and inability to start. Associated impacts include oil dilution, EGR line fouling, increased emissions and reductions in the efficiency and durability of emission control systems.

IDID have been found in several regions across a broad range of engine technologies, including both light and heavy duty vehicles, as well as non-road equipment. The rate of incidents has increased with the growth of common rail engines and their increasingly high fuel injection pressures, which are thought to be a contributing factor. Sub-ppm levels of metallic contaminants in the fuel, primarily Na and Zn, have been associated with IDID problems.

Two main types of IDID have been observed:

1. Lacquer or amide type deposits. Amine fuel constituents are thought to play a role, but the underlying mechanism, the types of constituents involved and the possibility of other co-contributors are open questions.
2. Carboxylate salt deposits. These deposits are thought to derive from reactions of sodium with organic acids present in FAME or in corrosion inhibitors used for pipeline protection.

Engineering solutions are unavailable to fully protect injectors from IDID risk. Some diesel fuel deposit control additives may mitigate the effects.

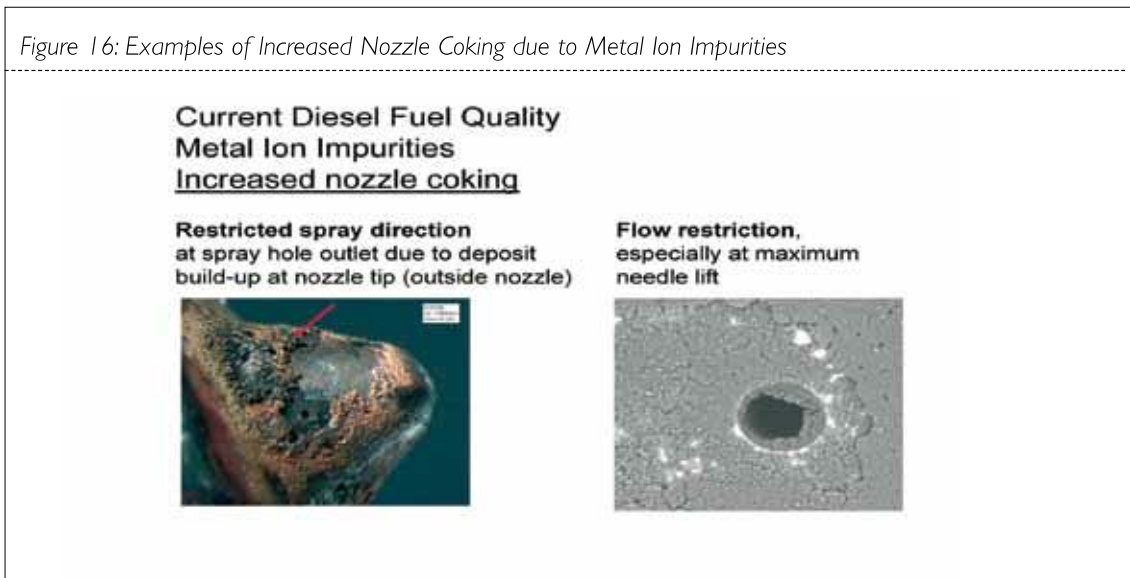
Currently, no standardized test is available to identify a fuel's risk of causing IDID. To improve this situation, CEC has initiated test development work to evaluate the IDID performance of fuels.

Influence of Detergent Additives

Detergent additives can remedy many of the concerns associated with injector cleanliness. High doses of these additives can partially clean an already heavily coked injector, while smaller doses can maintain injectors at an acceptably clean state, which ensures correct operation. Additive producers and fuel suppliers should check through field trials the extent to which their formulations may contribute to undesirable internal deposit formation at various treat rates. Many fuel distributors include these additives in commercial diesel fuels as quality features to obtain a 'keep clean' effect.

Cleanliness of the injectors has become an even higher priority at present as high-pressure injection systems are increasingly used on both heavy-duty and light-duty direct injection engines. The conformity of modern engines with their specified performance in terms of power, fuel consumption and emissions over time will depend largely on the cleanliness of their injectors. It has been observed in service and by many laboratories, both in manufacturing facilities and independently, that small quantities of metals such as zinc, copper, lead, sodium and potassium in diesel fuel can lead to significant injector fouling with subsequent engine power loss and increased exhaust gas PM. Figure 16 shows pictures of a nozzle with coking caused by metallic impurities.

Figure 16: Examples of Increased Nozzle Coking due to Metal Ion Impurities



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Metals can pollute the fuel during the distribution process, even if the fuel is clear when leaving the refinery. Ideally, a standardized engine test on a direct injection diesel engine would permit the setting of an acceptable limit value for injector fouling due either to metals being present in the fuel or to the fuel composition. At present, such a standardized test procedure has not been established, but candidate procedures are being considered. Until an engine performance test is established, therefore, it is prudent to require diesel fuel delivered at the filling station to respect the specific limits for each metal in the fuel, to reduce the risk of severe injector fouling in modern direct injection diesel engines. The technique for measuring the metals should be by inductively coupled plasma, such as with the ASTM D 5185 method (direct measurement improves the detection limit).

LUBRICITY

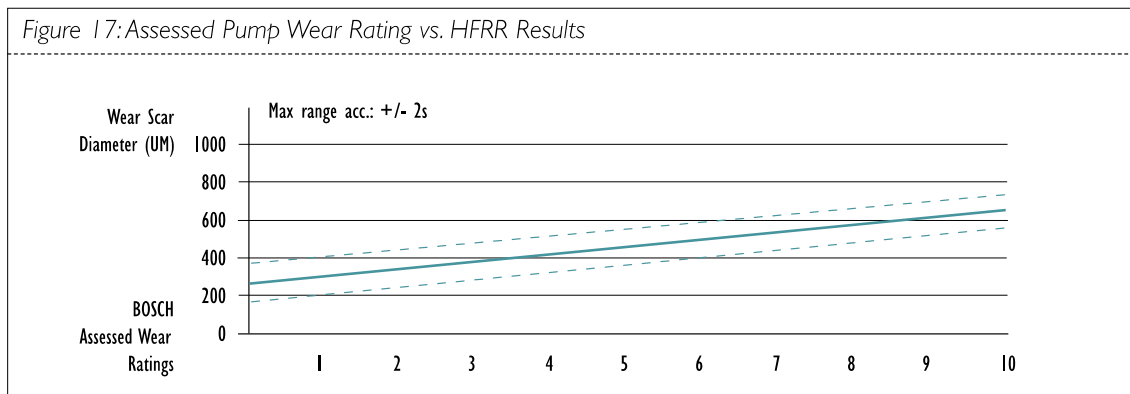
Lubrication at component boundaries is critical for protecting engines and fuel handling systems. The components of the diesel fuel that provide boundary lubrication are believed to be the heavier hydrocarbons and polar fuel compounds. Diesel fuel pumps without an external lubrication system rely on the lubricating properties of diesel fuel to ensure proper operation.

Refining processes to remove sulphur tend to simultaneously reduce diesel fuel components that provide natural lubricity. As diesel fuel sulphur levels decrease, the risk of inadequate lubricity also increases; however, poor lubricity has been observed even in diesel fuels with very high sulphur levels. Inexpensive additives can be used instead of changing the refining process to achieve the desired lubricity level.

Influence of Lubricity on Pump Wear

Inadequate lubricity can result in increased tailpipe emissions, excessive pump wear and, in some cases, catastrophic failure. Concerns over problems experienced with fuels with poor lubricity led to a significant international collaboration between oil companies, OEMs, additive companies and pump manufacturers to develop a test method and performance limit for fuel lubricity. The resultant method, the High Frequency Reciprocating Rig (HFRR) procedure, is a bench test that provides good correlation to measured pump effects.

Figure 17 shows the correlation between actual pump wear (measured by Bosch) and HFRR measured wear scar diameter. Bosch's rating scale describes 'normal wear' as less than 3.5 (which corresponds to a nominal HFRR Wear Scar Diameter of 400 μm). With a Bosch wear rating of 4, the pump will have decreased endurance, and ratings above 7 indicate potential fatal breakdown.



PARTICULATE CONTAMINATION

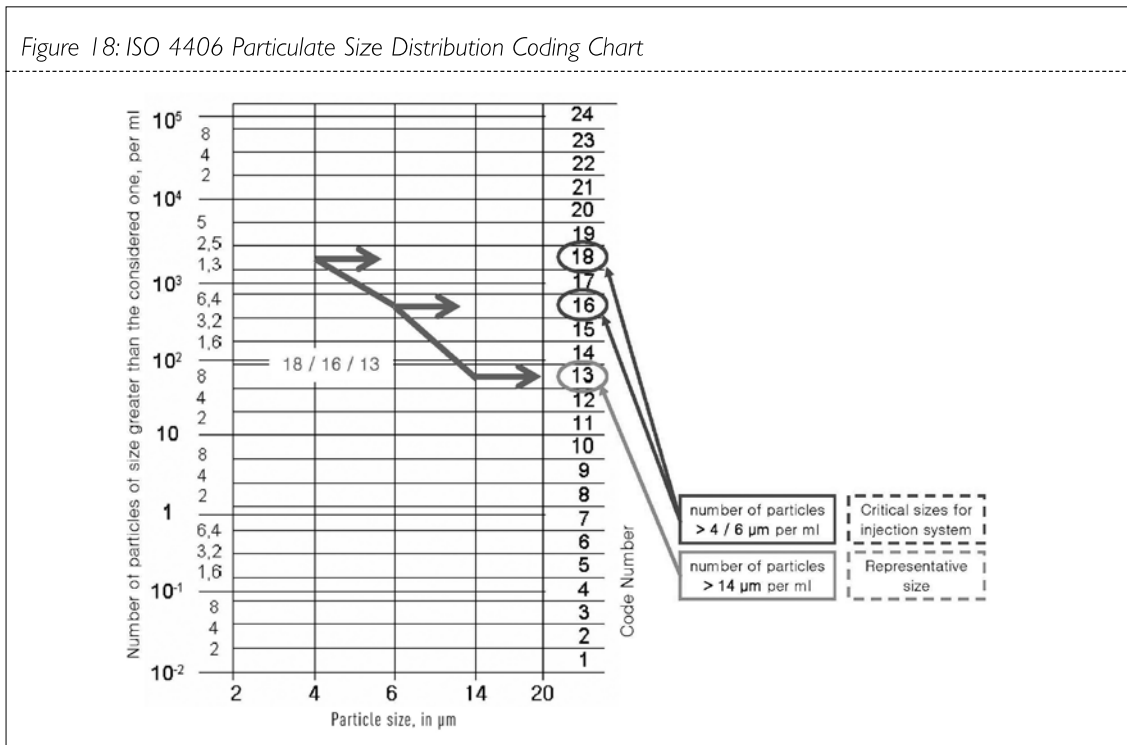
Fuel injection equipment manufacturers continue to develop fuel injection systems to reduce emissions and fuel consumption and to improve performance. Injection pressures have been increasing; currently, they have reached more than 2000 bars. Such levels of injection pressure demand reduced orifice sizes and component clearances, typically from 2 to 5 μm in injectors. Small, hard particles, which may be carried into these engine parts, are potential sources of engine failure.

Excessive diesel fuel contamination can cause premature clogging of diesel fuel filters, depending on the level of both hard and organic particles, and premature wear of modern fuel injection system parts. These impacts, depending on the size and the nature of the particles, will lead to:

- Reduced part lifetimes;
- Part malfunction;
- Engine failure; and
- Increased exhaust emissions.

Measuring fuel particle contamination necessarily considers both the size and number of particles per size class contained in the fuel, i.e. the particle size distribution. The ISO 4406 protocol provides a means of expressing the level of contamination by coding the size distribution. Three code numbers, corresponding to the numbers of particles of size greater than 4, 6 and 14 μm per millilitre, respectively, are reported. Figure 18 shows how to use the ISO 4406 coding method.

Figure 18: ISO 4406 Particulate Size Distribution Coding Chart



Engine and vehicle manufacturers recommend applying the Worldwide Fuel Charter's particulate contamination specification at the fuel station nozzle to prevent particles originating from fuel transport, storage and logistics from reaching the engine.

CONTAMINANTS

Contaminants, including some from additives, whether intentionally or inadvertently added during fuel production or distribution, also can cause significant harm to the powertrain, fuel, exhaust or emission control systems. Good housekeeping practices can help minimize or prevent inadvertent contamination. No detectable levels of the elements listed below should exist in diesel fuel, nor should they be used as components of any fuel additive package intended to improve diesel fuel and engine performance. These elements should be strictly controlled, and it may prove necessary to check and control the fuel quality at the pump.

- Calcium, copper, sodium, manganese, potassium, phosphorus and zinc, even at levels as low as 0.1ppm, can contribute to the formation of deposits in fuel injector internal surfaces and nozzles. Injector deposits reduce combustion efficiency and increase emissions. Concern about injector deposits is increasing as the latest nozzle technology with tighter clearances and higher pressures becomes more widely used in the marketplace.
- Chlorine, which is not naturally contained in petroleum, has been found in diesel fuel in both inorganic and organic forms. Inorganic chlorine usually enters the fuel as a result of contamination by sea water ballast during shipping or from the use of salt dryers during refining. Organic chlorine may enter the fuel through adulteration with chemical or waste solvents. Chlorine forms highly corrosive acids during combustion, which can reduce significantly the durability of the engine, fuel system and emission control system. In the worst case, the presence of chlorine may lead to catastrophic engine failure as injectors fail to operate or operate improperly after various periods and levels of exposure.

ANNEX F - House Keeping

The problems encountered by vehicles from poor quality fuel often are caused by adulteration that occurs in the fuel distribution system, after the fuel has left the refinery gate. Failure to invest in adequate pipeline and storage facilities and failure to maintain the equipment can lead to volatility losses, fuel leakage and contamination by particulates and water that, in turn, can lead to a host of vehicle problems.

Excess levels of water, for example, will lead to corrosion, as shown in Figure 19. Poor operating practices at the service station, such as too infrequent replacement of fuel dispenser filters or 'dipping' of tanks to check for water, can magnify these problems. Adding used engine oil to fuel is unacceptable unless expressly allowed by the manufacturer. Appropriate steps should be taken to minimize contamination by harmful elements such as copper, zinc and sodium. Helpful guidance to good housekeeping practices may be found in CEN/TR 15367-2, Petroleum Products.



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