

DIESEL EMULSION FUELS AND THEIR IMPACTS IN DIESEL ENGINES

A REVIEW AND COMMENTARY

Project Number	Q008689
Document Number	C008689-001
Updated issue	23rd May 2016
Client Confidential	SulNOx Research and Development Ltd.



Updated Issue May 2016

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DIESEL EMULSION FUELS AND THEIR IMPACTS IN DIESEL ENGINES – A REVIEW AND COMMENTARY

1 INTRODUCTION

SulNOx owns a number of proprietary technologies aimed at some of the current industry challenges, including: engine performance, fuel efficiency improvements and emissions reductions.

□ These technologies include:

- Novel chemical technologies capable of stably emulsifying fuels to a high level of water content (>25%)
- Advanced physical mixing technologies that, combined with the emulsification chemistry, are aimed at reducing the size of the micelles within the water-in-fuel emulsion, while employing less surfactant

Following discussions on March 25th at the Partridge Green offices of SulNOx, Ricardo issued a proposal document (B008689-001) which described a multi-stage scope of work to investigate the performance and capabilities of these technologies.

The first of these stages was to provide a literature review describing current understanding of the effects and capabilities of emulsions when combusted in diesel engines. This document represents that review.

2 OBJECTIVES

- To summarise the technology and impacts of water-in-diesel emulsified fuels combusted in diesel engines
- To review the impact of emulsion fuel additives on engine durability
- To investigate non-water emulsions
- To identify performance levels and competitors in the emulsions market
- To briefly consider possible opportunities for the exploitation of the emulsion technologies.

3 BACKGROUND

Interest in the use of water within diesel fuel as a water-in-diesel emulsion can be traced back many decades. It may appear, looking back, that interest in emulsions has followed a “sine wave” of activity. By this, it is meant that in the past the benefits of emulsions were pursued by a steadily increasing number of researchers until a peak of activity is reached. Engine technology changes due to legislation then limit the benefits of emulsions, and research activity declines. The last peak was between 2000 and 2003 following a great deal of research that commenced around 1995. For this reason many of the papers addressed in this review come from that period in time. In the past few years, there has been fresh interest in emulsions, particularly in South-Eastern and Sub-continental Asia.

Legislative pressures to reduce pollutant emissions from heavy-duty diesel engines have been the driving force behind the development of water-in-diesel emulsions. Highly respected companies in the oil and additive industries have experimented and commercialised fuel emulsion formulations, and robust claims for their influence on emissions have been published. These formulations enabled emulsions to gain a foothold as emissions remediation technologies predominantly targeting NOx and PM, though claims for fuel consumption benefits do appear. The major markets for these were in truck and bus fleets. However, as more stringent emissions legislation has been enacted in developed markets, catalytic solutions with very high efficiency for PM reduction (diesel particulate filters; DPF, >98% efficient) and NOx reduction (Selective Catalytic Reduction; SCR, >90% efficient) have been developed and these appear to have superseded emulsions as emissions control solutions, except in existing fleets.

There is currently some evidence that emulsions may be being considered once more to assist in the combustion of diesel fuels containing levels of Fatty Acid Methyl Ester (FAME) biofuels, oxygenated compounds and biogenic liquids. Emulsion use in developing markets is also seeing some activity.

4 COMPOSITION OF DIESEL/WATER EMULSION PRODUCTS

Water-in-diesel emulsions are fuel products in which an emulsification agent (surfactant) is employed to encapsulate and stabilize dispersed water droplets within diesel fuel. The surfactant has a lipophilic tail to interact with the bulk fuel and a hydrophilic head to interact with the water. Historically the mean water droplet size seems to have been towards the upper end of the range 100nm to 1 μ m, often around 700nm, but limited data exists on quantification of the micellar diameters. NanOil claims <100nm for its product on its website, but no further data are given¹.

Water-in-diesel emulsions are 2-phase dispersions, in that there is one carrier phase (diesel) and one dispersed phase (water) along with its surfactant. It is also possible to have 3-phase dispersions where the carrier phase and two distinct surfactants embody two dispersed chemistries. These 3-phase dispersions may enable advanced diesel emulsions to be created (Section 9.6).

The stability of a diesel emulsion appears to be related to several factors²:

- emulsification technique
- water content
- surfactant content
- mixing duration
- type and duration of agitation

Surfactants are the critical element of the emulsion: they enable encapsulation of the water, influence the long-term stability of the fuel; they must be compatible with the additives used both in the general diesel fuel and also provide for additional engine protection. According to one study³, it has been observed for diesel fuels that it is advantageous to use a mixture of surfactants comprising 60 to 95% sorbitan monoleate by weight and 5 to 40% polyethyleneglycol hydroxystearate by weight. This mixture, in addition to stabilizing the emulsions that are produced, also acts as a lubricant and antifreeze.

The amount of surfactant required is related to the water content and the time required for stability. In one study⁴, the presence of 0.2% surfactant and 2 minutes of mixing time at 15,000 rpm reported that both 10% and 20% water-in-diesel emulsions remained stable for ~5 weeks. In the same study it was noted that to gain similar stability with higher water levels required both increased surfactant levels and longer mixing times.

In Europe in 2003, the use of water-in-diesel emulsions was sufficiently widespread for there to be an industry association representing their interests. This was the 'European Emulsified Fuel Manufacturers' Association' or EEFMA. At this time there were four main products which were commercially available. Table 1 lists product and company names, markets and the percentage composition of each fuel.

Table 1: Composition of Commercial Diesel/ Water Products

COMPOSITION, %wt	DIESEL	WATER	SURFACTANT ADDITIVE	MAIN MARKETS
Aquazole™ (Elf Antar)	85± 3% (EN 590)	13± 3% (Domestic)	2% to 3%	France, Italy, US
PuriNOx™ (Lubrizol)	88% to 77% (UK ULSD)	10% to 20% (De-mineralised)	2% to 3%	Italy, UK, US
Gecam™ (Camtec, then Pirelli Ambiente)	88%	10.3% (De-mineralised)	1.7%	France, Italy, Switzerland
Aquadyn / Aquadisel (Clean Fuels Technology)	~85%	~13%	~2%	Italy, (US – California, Texas), later Australia

There is no evidence that the industry body is still in existence, but EEFMA achieved a CEN workshop agreement that defines the fuel specifications and quality for emulsions (CWA 15145: 2004)⁵.

4.1 Non-surfactant Emulsions

It is possible to create short-lived emulsions and introduce them into combustion almost immediately. Two such systems are the "Emulsion Engine Feeding System" (EEFS)^{6,7} and the "NoNox Emulsion Combustion System"⁸. These solely use physical mixing processes to generate the emulsions, and typically generate macro emulsions with dispersed phase droplets of $\geq 1\mu\text{m}$ in diameter. The EEFS system has been demonstrated with up to 20% water or ethanol in diesel, while the NoNOx website claims up to 30% water emulsions.

5 EMISSIONS BENEFITS

Injecting water into an internal combustion engine as part of an emulsion has been recognised for many years as a method of reducing NOx and particulate/smoke emissions.

The mechanisms by which water affects emissions of NOx and particulate/smoke may be described as follows:

5.1 NOx Emissions

The latent evaporation heat of water, combined with its high thermal capacity reduces peak combustion temperature and hence reduces nitrogen oxide formation. The reduction in NOx as a result of this mechanism can be considered in a semi quantitative way: roughly, 1% NOx reduction will occur for every 1% of water included in the fuel⁹.

5.2 Particulate Emissions

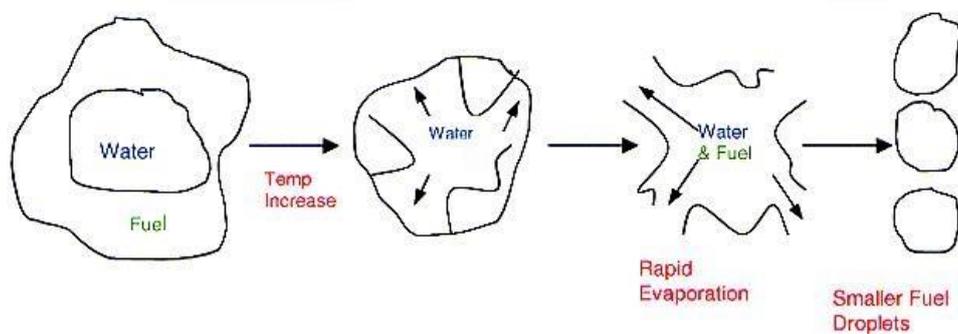
There are several possible mechanisms by which water-in-fuel could help reduce particulate formation

- Water will dilute key combustion intermediates that lead to particulate formation
- Oxidative species formed from oxygen in water by dissociation (specifically OH radicals¹⁰) will help suppress soot early in the nucleation process and inhibit its peak production
- Water could influence fuel spray characteristics through the “micro explosion” phenomenon. Fuel-air mixing is increased during both pre-mixed and controlled-mixing combustion phases¹¹.

It is likely that the micro explosion effect will be the main mechanism for reduced particulate formation. In water/ diesel emulsions, water droplets encased within a fuel droplet can instantaneously vaporise as the in-cylinder temperature increases during injection. The water quickly and violently evaporates, breaking the encapsulating oil layer¹² and fragmenting the fuel droplet into smaller droplets (Figure 1) resulting in more complete vaporisation and mixing of the fuel. Improving fuel distribution may help eliminate local rich zones where incomplete combustion can occur. Thus the action of the water results in a selective reduction in the insoluble carbon fraction of particulate. It is possible that this micro explosion phenomenon may only exist in droplets >250nm diameter¹³.

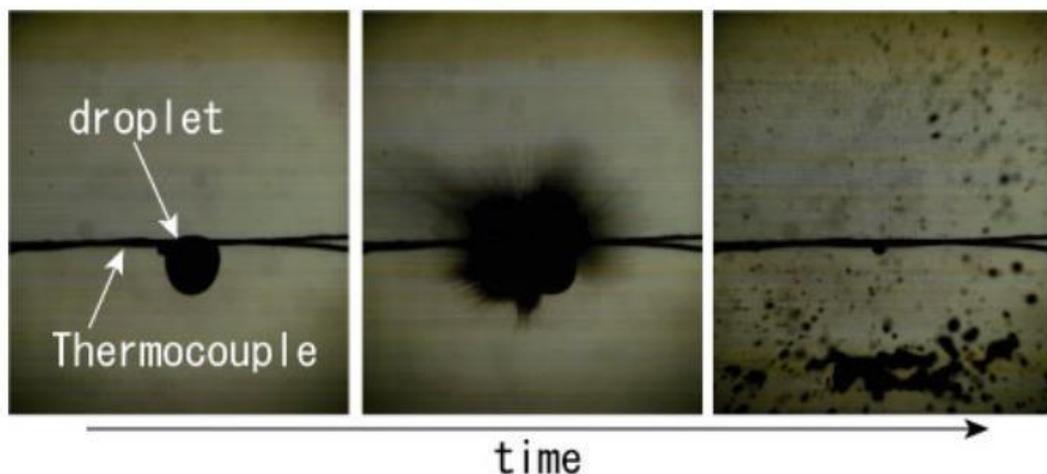
In addition, the surfactants themselves may moderate the micro-explosion; also the surfactant's combustion may possibly improve soot oxidation characteristics. No published work exploring these potential positive mechanisms has been identified.

Figure 1: Schematic of Microexplosion Effect



A micro-explosion effect has been photographed in larger droplets by the Kochi Technical University in Japan¹⁴ (Figure 2).

Figure 2: Thermal Explosion of Emulsion Droplet (Reference 14)



5.3 Published Emissions Data – Engine Tests

The absolute effect of a novel fuel formulation on emissions and engine characteristics will depend on both the engine type and on whether or not the engine has been optimised to run on that particular fuel formulation (Section 6).

Elf¹⁵ undertook European 13-mode test cycles on Euro I and Euro II level engines, and European Steady Cycle (ESC) test for Euro III level, on Renault VI 620-45 engines. Injection pump settings were modified to obtain torque characteristics as close as possible to those obtained on conventional diesel fuel. Full results on the Euro I engine are shown in Table 2:

Table 2: Renault VI 620-45 (Euro I) Engine test on Aquazole

Engine: RVI 620-45 Type: EURO I (g/kWh)	Diesel	Aquazole	Variation
Specific consumption	204.9	201.3	-1.8%
NOx	9.15	7.8	-14.8%
HC	0.60	0.56	-6.7%
HC+NOx	9.75	8.36	-14.3%
CO	0.58	0.72	+24.1%
PM	0.137	0.116	-15.3%
Mode 6-PM g/kWh	0.121	0.07	-42.1%
Mode 6-Smoke Bosch	0.58	0.27	-52.6%
Smoke opacity 1/m On accel. test	1.42	0.45	-68.3%

Elf noted the following general results when comparing Aquazole (~13% water) with diesel fuel on engine bench tests:

- Approximately 15% reduction (significant) in NOx emissions
- Variable and insignificant effect on CO and HC emissions, independent of test range and engine type
- 50% to 70% reduction in black smoke
- Reduction in particulate mass up to 40%

Lubrizol¹⁶ presented data from an 8 – mode test on an 8 cylinder, 34.5L engine. Using 20% diesel/ water emulsion with no engine recalibration caused power output to be reduced up to 15%, NOx emissions to be reduced by 15%, and particulates to be reduced by 50%.

Further work by Lubrizol¹⁷, using the AVL 8-Mode steady-state test method in a 1998calibrated Caterpillar 3176 engine, showed 19% and 16% NOx and PM reductions respectively.

Previously, on their website¹⁸, Camtec/Pirelli quoted the following emissions reductions with the use of their Gecam fuel compared to conventional diesel:

Table 3: Emissions Reductions with Gecam 'White Diesel' Fuel

10% Emulsion	PM	CO	NOx
Euro II bus, Milan bus cycle	56%	42%	5%
Euro III tractor, ESC	59%	32%	6%

Notes: (1) Pirelli made no claims for fuel consumption; (2) Pirelli no longer market the emulsion technology and the website¹⁸, though recorded in the Ricardo database, has been taken down.

5.4 Published Emissions Data – Fleet Trials

Elf have published data from the Paris Bus fleet (RATP)¹⁵, which has had some vehicles operating on Aquazole for a few years. Smoke opacity measurements were taken from buses of different engine technologies, ranging from Euro 0 to Euro II, during free acceleration. Smoke opacity reductions varied from 29% to 83% according to engine technology and operation, and results were significant across the range.

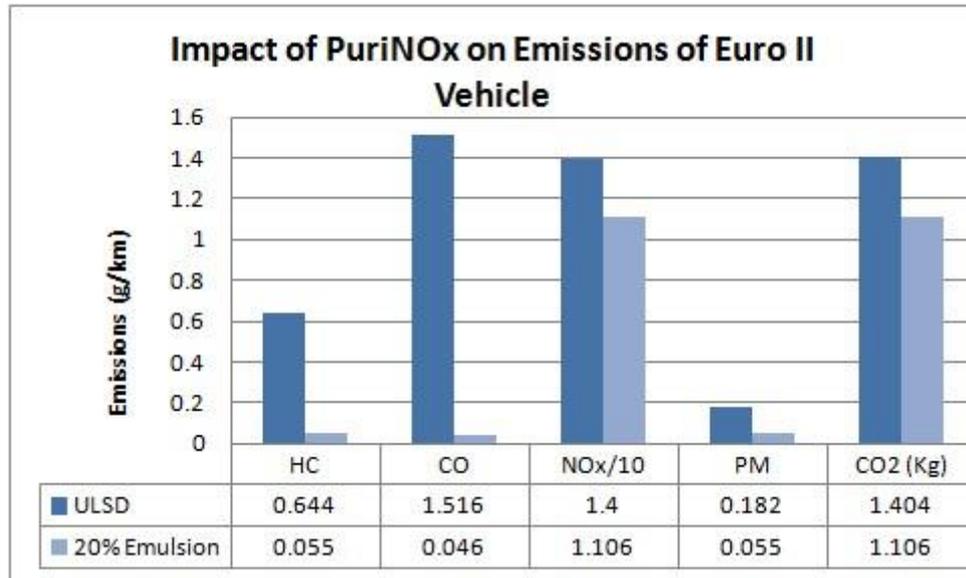
5.5 Published Emissions Data – Emulsion Fuels in Combination with Emissions Control Technology

There has been some concern that the reduction in exhaust gas temperature experienced when running on emulsion fuels may not allow effective operation of heavy-duty emissions control technology such as oxidation catalysts or diesel particulate filters (DPF).

Lubrizol¹⁶ investigated the emissions potential of their PuriNOx fuel in combination with heavy-duty catalyst technologies. Three buses (2 Euro 0 and 1 Euro II) were evaluated over the Millbrook London Transport Bus Cycle. The emissions effects of running these vehicles on a combination of PuriNOx fuel and an oxidation catalyst were compared with a baseline of ultra-low sulphur diesel (ULSD) only.

Figure 3 shows results obtained from the Euro II vehicle equipped with an oxidation catalyst.

Figure 3: Euro II Olympian Emissions (g/km)



The combined diesel oxidation catalyst (DOC) and PuriNOx reduced total particulate by 70% compared to the baseline, and reduced NOx by 21%. Lubrizol have also stated that running the fuel in conjunction with a DPF “did not adversely affect [engine or emissions] performance”. This suggests that any reductions in combustion temperatures are not adversely impacting DOC function.

Elf¹⁵ has also evaluated their fuel in conjunction with a DPF, in this case a Continuously Regenerating Trap (CRT). A Volvo bus was tested with a low sulphur (30ppm) quality Aquazole, with no modification of injection pump setting. The combination of emulsified fuel and CRT gave a particle reduction of >90%.

The above results suggest that the reduction in exhaust gas temperature due to emulsion use does not adversely affect catalyst and particulate filter performance over the test conditions.

There is scant data that evaluates NOx reductions achieved through combining water in-diesel emulsions with EGR, though one study¹⁹ on a 1.5 litre HSDI diesel indicates that NOx and PM emissions reductions (of $\leq 50\%$ and $\leq 94\%$ respectively) still occur: emissions benefits were achieved through improving the NOx–PM trade-off at various EGR rates. This indicates that, in principle at least, emulsified fuels and EGR could be considered complementary technologies. It should be noted that this study did not consider any possible durability or long term fuel-compatibility issues.

It is possible that the use of a water-in-diesel emulsion may have benefits when combined with modern catalytic emissions control systems²⁰. Emissions requirements for the next stage of European legislation (Euro VI) are highly demanding and will require the fitment of both DPFs and highly-efficient SCR systems and, in some cases, both these combined with Exhaust Gas Recirculation (EGR).

The use of a 20% water in diesel emulsion, that results in ~20% reduction in engine out NOx and 40 – 50% reduction in PM would potentially enable engine manufacturers to optimise emissions control strategies by a number of routes:

- reducing the EGR rate
- eliminating the EGR cooler
- enabling complete removal of EGR circuit
- reducing the efficiency required of the SCR system and hence the urea consumption
- decreasing the regeneration frequency of the DPF

These would enable potential reductions in after treatment costs including precious metal loading and could also have a positive impact on net fuel consumption.

Actual benefits realised would be dependent on the engine hardware's ability to tolerate the potential issues described in Section 6, appropriate engine calibration for the fuel and the user impact of more frequent refuelling.

6 EFFECTS ON ENGINE PERFORMANCE

Manufacturers of emulsions normally market their products as a straight replacement for standard diesel fuel, as they claim that no optimisation of the engine is required. In almost all cases the fuels are intended for heavy-duty engine use.

Diesel engine fuel injection equipment (FIE) normally operates on a volumetric basis and therefore the most immediate influence will be that the water will displace fuel by whatever percentage it is incorporated. At part load conditions, the operator or driver will compensate for this by increasing the fuelling in order to obtain the required power output. However, at maximum load conditions it will not be possible to achieve the designed maximum power if the percentage of water is above a few percent. Operators may make their own decision to compensate for power loss by adjusting the fuelling. Normally this means extending the injection period to achieve the same energy input per stroke as with standard diesel. However, extending the injection period means that fuel is injected later in the cycle which may increase soot emissions. The best method is to increase the injection rate such that the same energy is injected per degree crank angle for the emulsion as with straight diesel.

For example, if with straight diesel the injection period at full load is 20° crank angle and the injected quantity is 200mm³ - then with a diesel emulsion the injection rate should be increased to inject 200mm³ of diesel in the same injection period of 20°. This, of course, can only be done with an advanced injection system, or if the engine/FIE is being developed to run on a specific emulsion.

The most positive influences on diesel combustion are seen at high load operation. At high load useful reductions in NOx and smoke/particulate emissions are achievable with optimised levels of the “right” emulsion; also a slight improvement in combustion efficiency is possible. This improvement can be reflected in a reduction in specific fuel consumption of the order of 2%. At light load operation, a common influence of an emulsion is to cause an increase in HC emissions and maybe also CO. It is possible that this is due to the water component causing “quenching” at the boundary areas of the combustion chamber and hence the emission of unburned or partially burnt products could be increased for this reason.

6.1 Performance Improvements

The potential for improving thermal efficiency by a few per cent has been demonstrated by many researchers and it therefore follows that power output increases by a similar amount. However, claims are often made for emulsions that no real power loss occurs even for emulsions containing more than a few per cent water. A summary of literature findings on brake thermal efficiency are given below:

- In a study on a 1400cc DI Diesel engine with a 30% water in diesel emulsion, an average increase of 5% in brake thermal efficiency was observed over several steady state operating conditions²⁴
- The use of a 20% emulsion in a single cylinder DI engine led to a 3.5% increase in brake thermal efficiency²¹.
- Elf¹⁵ reported some results equating to increased brake thermal efficiency of ~ 3%
- A programme reported by the US EPA, which included a detailed emissions assessment of PuriNOx²², concluded that power losses with emulsions were usually proportional to the fuel displaced by the water. However some claims, including those of Lubrizol, for smaller reductions may have some credence - indicating possible power gains.
- Brake thermal efficiency was shown to increase with increasing water-in-diesel content from 0% to 10% to 20% on a single cylinder DI diesel²³. This is attributed to the expansion of water providing additional force to the piston and increasing torque. The increase in work done and reduction in diesel burned increases brake thermal efficiency.
- A Greaves single cylinder engine was used to explore combustion and emissions effects of 0, 5, 10, 15, 20% water-in-diesel emulsions. Brake Thermal Efficiency was shown to increase with percentage of water present²⁴.

6.2 Fuel Economy Impacts

When considering fuel economy impacts with emulsified fuels, the one indisputable fact is that when switching from an entirely mineral-based fuel to an emulsion the vehicle range per tank is reduced and so the need for more frequent stops to refill arises. This issue may be highly significant for the commercial operator.

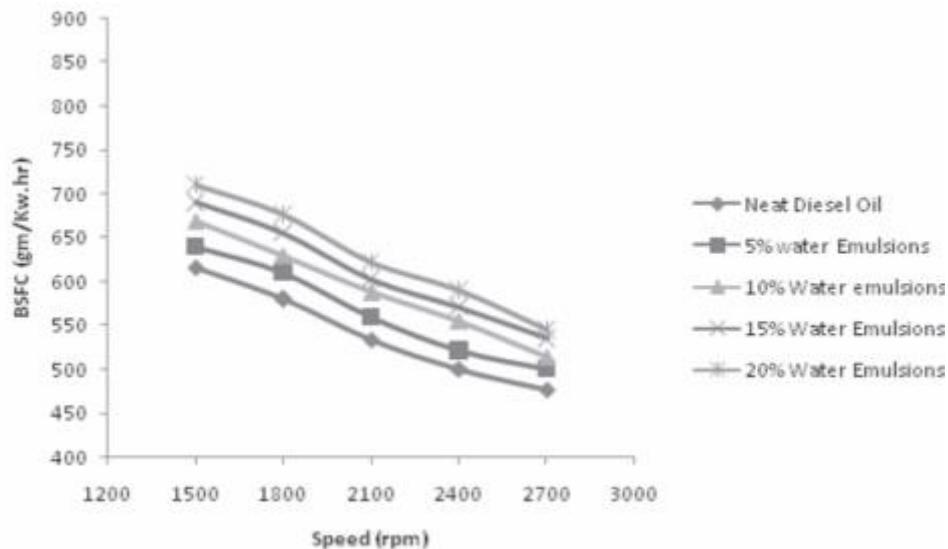
When considering potential fuel consumption 'benefits' of an emulsion these need to be assessed as the difference between the expected reduction in fuel (or energy) consumption from the water that displaces the fuel and the actual observed reduction in fuel (or energy) consumption observed. A summary of literature findings on fuel economy are given below:

- On a 1998-calibrated Caterpillar 3176 engine, and with the same start of injection timing, the brake specific energy consumption was reduced by 0.7% with a 20% emulsion¹⁷.
- In study comparing baseline diesel with a 20% PuriNOx emulsion²⁵, results showed increased fuel consumption levels that ranged from 11.7% to 27.2% depending on engine type. The mean reduction was 16.9%. In general the fuel efficiency penalty was lower from electronically controlled on-road engines (~15%) than mechanically controlled on-road engines (~19%).

There are indications here that small fuel consumption benefits may be present.

- A study on a water-cooled DI diesel engine concluded that there was no negative impact on BSFC of a 20% water-in-diesel emulsion that delivered NOx reductions of ~30% relative to the baseline diesel. Optimising the injection timing enabled a ~3% BSFC improvement at constant NOx²⁶.
- In a fleet trial Shell Australia's Aquadiesel²⁷ reportedly showed an 11.8% fuel consumption increase with a 13% emulsion blend, compared with an expected fuel consumption increase of 16.8% (if fuel consumption is proportional to calorific value).
- In an engine dynamometer study that employed 6% water in an emulsion with 20% FAME-based biodiesel²⁸ the measured fuel consumption, after correction for energy content, was the same as that seen for both the non-emulsified energy-corrected B20 and for the baseline diesel. The engine was a 1997 12.7 litres Detroit diesel series 60.
- BSFC was shown to reduce with increasing water-in-diesel content on a single cylinder DI diesel²³. The reduction in BSFC was greatest at high load but was in the range 0-10% for both 10% and 20% emulsions.
- A Greaves single cylinder engine was used to explore combustion and emissions effects of 0, 5, 10, 15, 20% water-in-diesel emulsions²⁴. BSFC increased with increasing water content (considering total water plus diesel volume consumed) but visual inspection (Figure 4) of results suggests minimal impact of the emulsion on the consumption of the diesel fraction of fuel across the speed range 1500rpm to 2700 rpm.

Figure 4: Minimal Impact of Emulsions on BSFC



- Tests²⁹ on a 2.5 litre 4-cylinder Ford diesel engine showed fractionally higher fuel BSFC figures (mg/KJ) from a 20% emulsion compared with baseline diesel.
- In a study of 4 Euro II buses, the fuel economy was compared between baseline diesel and a 13% water-in-diesel emulsion³⁰ provided by BP Hellas*. Each bus ran a similar duty-cycle on ULSD and then on the emulsion. Results

* (Believed to be PuriNOx)

From the pairs showed a 2% FE gain from bus#1, a 26% FC penalty from bus#2, a 9.8% FC penalty from bus#3 and a 7.1% gain from bus#4. Overall on a fuel consumption basis (L/km) the penalty with the emulsion was ~2%, which compares very favourably with the 13% water content. However, the wide scatter of effects, and inconsistency of bus duty-cycle within pairs, leads to low confidence in these findings.

- A fleet trial of 121 buses conducted by Arriva in the UK examined the fuel consumption impacts of running a 10% PuriNOx water-in-diesel emulsion³¹. The study concluded that increases in fuel consumption ranged from 0% to 9% but were always less than 10%. This implies a net increase in fuel efficiency from the remaining diesel fraction.

7 POSSIBLE ISSUES WITH EMULSION FUELS

There is limited mention of potential engine hardware issues in the literature as the majority of studies are presented by organisations looking to either sell or validate the emissions control capabilities of the fuels. Commentary below by internal Ricardo experts accompanies published data.

7.1 Lubricity

Lubricity properties of diesel fuel may be affected by the diluent effect of the water. Elf¹⁵ have shown high frequency reciprocating rig (HFRR) lubricity data on two diesel fuels, one higher sulphur (<500ppm) and one lower sulphur (30ppm), and two emulsions formulated from these fuels, shown in the table below:

Table 4: Lubricity Data for Emulsified Fuels with Two Sulphur Levels

	Fuel 1	Aquazole + Fuel 1	Fuel 2	Aquazole + Fuel 2
Sulphur, ppm	<500	<450	30	26
Wear Scar Diameter, 1.4(µm)	369	274	347	269

It is known that ELF¹⁵ included lubricity improver additives to ensure this was not an issue with Aquazole, and it is anticipated that all emulsions fuels would contain additives with similar functionality.

7.2 Corrosion

Introducing a water component into the fuel may increase the potential for corrosion and wear of fuel injection equipment. Lubrizol, Elf and Camtec stated that their emulsions offer corrosion protection properties, via additisation, which are analogous to conventional diesel. They argue that, because the water droplets are encapsulated within fuel droplets, the FIE will recognise the fuel as diesel and not water.

Not all engine manufacturers and the manufacturers of fuel injection equipment (FIE) will maintain the same level of warranty if the customer uses an emulsion as fuel, though some did validate emulsions in Euro III vehicles (Section 7.7).

Initially, the major FIE manufacturers (Bosch, Delphi & Stanadyne) issued a joint statement effectively withdrawing warranty cover if alternative fuels (including emulsions) were used, with the main focus being on corrosion and lubricity challenges. It is understood that this statement was later withdrawn.

Fleet trials covering some 15 million km were undertaken by the Iveco group in Italy running on Gecam fuel. Parameters such as lubricity, corrosion, analysis of injectors, FIE pump and engine oil degradation was investigated. From the favourable results of these analyses, Iveco offered extended warranty cover to the use of Gecam fuel (Section 7.7).

7.3 Emulsion Stability

The commercial emulsion fuels described in this report are water-in-diesel fuel micro emulsion type, where the water droplets in the emulsion are less than 1 micron in size. Current manufacturers of emulsions claim “shelf life” stability of at least three months and there is no real reason to doubt this claim. Achieving good stability from manufacture has been a critical part of emulsion development. Indeed it has been observed by Ricardo that some coupling agents (surfactants) are perhaps “too good”, such that the emulsion becomes immiscible with ordinary diesel giving the potential for flushing/cleaning issues. For this reason, some manufacturers insisted that vehicle operating on emulsions should be ‘firewalled’ from the possibility of being filled with straight diesel (Section 7.7).

The stability of emulsion products in service is an area that may require further research. This is highlighted because there is a strong trend toward very high pressure FIE, now reaching towards 3000 bar, with high re-circulation rates at fuel temperatures in excess of 100°C. This trend will make in-service stability more difficult to maintain.

7.4 Low Temperature Operability

Good cold-weather performance is ensured by separately addressing the diesel and water components of the emulsion. The diesel portion is treated with conventional wax modifier additives and the water portion by the addition of mono ethylene glycol or similar “anti-freezes” such as methanol. Optimisation of the additive package ensures good low temperature operability.

7.5 Deposit Build-Up

If the water used in the emulsion is from domestic supplies, there is a possibility of deposits resulting from minerals in the water (calcium and magnesium) if engines are running for extended periods at a constant load regime. However, emulsified fuels are mainly targeted at urban vehicle use where the use is highly transient.

7.6 Incompatibility with EGR

Engines with high levels of EGR may experience combustion instability with the use of emulsion fuels; this may impact the emissions benefits and fuel consumption. However, a Euro VI engine designed to run on emulsions might be able to avoid the use of high levels of EGR or, in some cases, be of a design to avoid EGR use entirely.

7.7 Manufacturer’s Warranties for Operating on Emulsions

As presented in Table 1, by 2003 water-in-diesel emulsions were in use in several European countries³² and as a consequence a number of OEMs had studied and validated products (Table 5).

Table 5: OEM Warranted Emulsion Use

Company	Product	Distributor	OEM
Pirelli	Gecam	AGIP, Petrofuel, RA.M.Oil, ERG, SARAS	IVECO, MAN, Deutz
Clean Fuels Technology (now Alternative Petroleum Technologies)	Aquadiesel	IPLOM, Shell (in Australia)	N/A
Lubrizol	PuriNOx	BP, Q8, Blanco Petroli, Green oils	Mack, Caterpillar, MAN
Total (ELF)	Aquazole	Total network	Irisbus, IVECO, Scania, RVI

It is anticipated that these warranties would apply to vehicles sold after 2003 but not to the later generations of vehicles (Euro IV+) so, in effect, Euro III vehicles.

Certain strictures were applied relevant to these warranties, for example in Italy:

- Diesel fuel used for emulsions must be current pump grade EN590
- The emulsion must not be used if > 4 months following delivery
- No mixing of emulsions produced by different technologies
- No mixing of emulsions with diesel fuel
- Emulsions must be prepared in good quality de-ionized water with maximum conductivity of 30 $\mu\text{S}/\text{cm}$
- Additives and emulsifiers containing halogens or heavy metals are not permitted

The Air Resources Board has approved several emulsions for use in California. These approvals include evaluations of potential engine damage, but focus on the ability to reduce NOx and PM. For example: the ARB has verified Lubrizol's PuriNOx for achieving at least 50 percent reduction in PM and 15 percent reduction of NOx in 1988 through 2003 model year diesel engines used in on-road applications³³.

8 MODERN STUDIES

There are a number of recent publications that address diesel fuel emulsions, some are refocused with alternative fuels, or alternative fuel blends as the carrier phase; others replacing water as the dispersed phase. These include:

- Using alcohols or alcohol water blends in place of the aqueous phase in the emulsion.
 - Ethanol-ethylacetate-diesel micro emulsions have been employed as potential replacements for neat mineral diesel³⁴. NOx and PM reductions were realised and normal engine operation was achieved, but no claims were made for fuel economy benefits. In another study, brake specific energy consumption was shown to reduce with the combination of water, ethyl acetate and increased injection pressure³⁵. 2% EZEE surfactant (Godrej) was employed. Reductions in NOx, Soot, CO and HC were observed, with NOx reductions of ~1% per 1% of water + ethyl acetate in the fuel.
 - The combustion of an ethanol-diesel emulsion was shown to reduce PM but lead to an increase in NO_x.³⁶ This was attributed to the low cetane number of the ethanol retarding the ignition timing. This NOx increase was countered by the further addition of dimethylether (DME) which acts as a cetane improver. No claims were made for fuel economy benefits.
 - Bioethanol and diesel emulsions with and without a high cetane (~125) ignition improver (diethylether; DEE) were tested in a single cylinder DI diesel engine³⁷. At full load, smoke emissions were observed to reduce by ~23% with a 15% emulsion, while NOx was reduced by less than 1% in total. In this work, brake thermal efficiency at full load was observed to reduce by ~1% with the 15% emulsion, with greater reductions seen when DEE was added.
- Using water with biofuels in order to neutralise NOx penalties
 - APT (formerly Clean Fuels Technologies, Table 1) found that adding 6.5% water as an emulsion to B20 biodiesel effectively neutralised the increases in NOx introduced by adding the FAME to the baseline diesel³⁸. Testing was performed in top-handler units at the Port of Los Angeles. Claims are made for well-to-wheels CO₂ reductions, NO_x neutrality and reduced PM, but not for fuel economy benefits

- Emulsification of high levels of FAME (a straight FAME + water emulsion) indicated similar NO_x and PM reduction trends as seen with mineral diesel emulsions³⁹. No claims were made for fuel economy benefits.
- The Karlsruhe Institute of Technology tested macro emulsions of ethanol diesel and ethanol-water-diesel emulsions in a Stage IIIA common rail DI diesel engine (1600bar) with external EGR⁴⁰. The macro emulsions were mechanically prepared on-line without use of surfactant. In general, Soot and NO_x emissions were slightly lower with a 5% ethanol, 5% water emulsion than with a 10% ethanol emulsion. The addition of the ethanol and water was shown to reduce soot emissions, so increase the engine's tolerance to EGR (higher rates are possible). It therefore proved possible to optimise injection timing and EGR rates to achieve Stage IIIB soot and NO_x emissions with the Stage IIIA engine running on a 10% ethanol, 10% water in diesel emulsion.
- Creating emulsions of biofuels and other non-water components to create energetic diesel fuels
 - Wood pyrolysis oil (WPO) was dispersed in jatropha methyl ester (JME) using Span 80 surfactant at ~2% addition⁴¹. 5%, 10% and 15% blends of WPO were tested. WPO contains fatty acids, aromatics and phenols, plus some water. Tests in a single cylinder 4-stroke diesel generator indicated increased thermal efficiencies of ~3%, 6% and 11% relative to baseline diesel. Reductions in NO_x (~3%) and smoke (~6%) with the 15% blend relative to diesel, were lower than typically seen with water-diesel emulsions.
 - Emulsions of a bio-oil generated from corn stalks by a pyrolysis process were tested in a single cylinder naturally aspirated DI diesel engine⁴². The bio-oil is primarily comprised of oxygenated organics and water, so is immiscible with diesel. This oil has low cetane number, high density and high oxygen content. 10% (BO10) and 20% (BO20) blends were prepared using a surfactant mix (Span 80, Tween 20 and polyisobutylene succinimide) of about 1% by volume. Brake thermal efficiency of BO20 was lower than that of baseline diesel, while NO_x reductions increased with BO content, reaching ~20% at BO20. HC emissions reductions with BO level were inconsistent, while CO and smoke levels increased with raised BO levels.

One recent study was identified that tested conventional water-in-diesel emulsions in a 661cm³, single cylinder variable compression ratio, DI diesel engine⁴³. Surfactants SPAN80 and TWEEN80 were used in approximately equal proportions, comprising a total of ~2% of the fuel volume. Diesel fuel, 5%, 10%, 15%, 20% and 25% emulsions were tested at 17:1 and 18:1 compression ratios across several operating conditions, including full load. Brake thermal efficiency was seen to increase with water content. This effect was greatest at higher compression ratios. CO, HC and NOx (up to 32% at full load with 25% emulsion) reduced with increasing water content, but effects were greatest at the higher compression ratio. At both compression ratios, smoke levels were observed to progressively reduce with increased water content, except at 25% where an increase in smoke was observed.

Only one study has been identified that evaluates the performance of water-in-diesel emulsions in a truly modern engine. Straight diesel fuel plus 13% and 26% water-in-diesel emulsions were tested on a single cylinder, four stroke, DI diesel engine with common rail FIE, supercharging and cooled EGR⁴⁴. The emulsions were provided by Nanomizer Inc⁴⁵, with 2% surfactant used at 13% water and 4% surfactant used at 26% water. The effect of pilot injection quantity was also studied as part of the project. The following conclusions were made: since the emulsion fuel has poorer ignition quality, a larger pilot injection and smaller main injection can be employed, with larger heat release at piston top-dead centre and a shorter burn-out phase than seen with mineral diesel fuel; optimised pilot injection quantity and EGR enable low NOx and low smoke at operating conditions that traditionally give high smoke with mineral diesel; NOx emissions at full load were reduced by just over 1% for each % of water in the fuel.

9 REVIEW CONCLUSIONS

9.1 References

There has been limited activity in developed markets regarding investigations into water-in-diesel emulsions in the last 8 to 10 years, as this technology seems to have been shelved by the oil-industry majors. This is likely due to the wide adoption of diesel particulate filters, and their greater efficiency at reducing PM. As a consequence, this review largely contains references to the last peak of investigative activity, between 1995 and 2003 but with some renewed interest in the past 5 years. The majority of this activity is taking place in India, China and South-East Asia.

Several hundred scientific papers and thousands of internet articles exist that address emulsified fuels. However, very few make any claims for fuel consumption benefits. Those that were identified have been included in this review. NOx and PM advantages of water-in-diesel emulsions dominate the publications.

Some limited investigations into 2-phase emulsions using oxygenates other than water, and using diesel/FAME blends or pure FAME as the carrier phase, have been identified. However, these studies appear to be predominantly research-based rather than aimed at applications in production engines.

9.2 Fuel Specification for Emulsions

A specification for water-in-diesel emulsified fuels has been developed and is officially classified by CEN as CWA 15145:2004.

9.3 Users of Emulsions and Their Main Objectives

The predominant theme in the literature, and clear objective of emulsified diesel fuels, is the simultaneous reduction in NOx and PM. When applied to engine technologies of Euro III and earlier, with typical water content in the range 10-20%, there is abundant data to demonstrate NOx reductions of at least 0.5% to 1% for each 1% of water in the fuel and PM reductions of perhaps 1 to 3% for each 1% of water in the fuel. The percentage impact of low levels of water ($\leq 2\%$) on emissions may be greater (but this effect may be through some synergistic influence of the surfactant).

Tests on non-water emulsions tend to show reduced benefits on NOx and smoke relative to water, while water-ethanol emulsions may have a similar effect. Impacts on CO and HC may be engine dependent. It should be noted that these results may not be representative of what is possible in an optimised engine.

The main drawback of emulsions, aside from potential incompatibilities arising from the water in the fuel, is the decrease of range achieved. This arises through the loss of energy from the fuel displaced by water. For this reason emulsions tend to be avoided by users of light-duty vehicles and the long-distance trucking industry. Usage therefore focuses on 'captive' fleets, such as buses and delivery contractors.

Emulsion fuels have historically been targeted at fleet owners who are attempting to meet emissions requirements in low emissions zones, or who desire a cost-effective approach for reducing fleet emissions without costly engineering changes. There is no immediate evidence of OEMs either having calibrated their Euro III engines to run on emulsions or offering services to do so. This is perhaps not unexpected when many of the fleets and vehicles studied are comprised of aged technology vehicles with mechanical fuel injection systems.

9.4 Potential Fuel and Performance Benefits

Opportunities may exist in exploiting NOx and PM reductions in modern vehicles using electronically controlled FIE. When engines have been recalibrated to exploit NOx reductions from emulsions and rematch base fuel NOx levels, improvements in fuel economy have been realised.

Nevertheless, it is hard to categorically determine whether water in diesel emulsions have any fuel consumption benefit or penalty. Many studies do not appear to offer this information and it is perhaps significant that none of the major oil and additive industry companies (Lubrizol, BP, Shell, ELF), and latterly other players (Pirelli) have made marketing claims for fuel consumption benefits from their emulsions.

Many studies lack statistical robustness and also employ, perhaps, unrepresentative engines. However, compiling the results of the current review (Table 6) indicates that the majority of results with the most commonly used emulsion level (20%) are in the range 0% to 3% benefit.

These results might indicate that there is a small fuel consumption benefit to be exploited; potentially deriving from lower heat losses with the emulsion, but in most cases the studies referenced lacked statistical rigour.

Across all studies though, there is a consistent trend that improvements in thermal efficiency are present with the use of emulsions.

Table 6: Compiled Results of Fuel Economy Impacts

Percentage Emulsion	Approximate FE benefit (%)	Notes	Reference
13	-26	Worst	28
20	-0.5	approx	27
5	0	approx	22
6	0	approx	26
10	0	approx	22
15	0	approx	22
20	0	approx	24
20	0	approx	22
20	0.7	approx	16
10	1	worst case	29
20	3	approx	23
20	3	approx; at constant NOx	24
13	5	approx	25
13	7.1	best case	28
10	10	less than	21
10	10	best case	29
20	10	less than	21

9.5 Potential Issues

Several potential issues with emulsion fuels were identified by Ricardo and described in the review, though these were scarcely mentioned in the literature:

- Lubricity, mainly impacting the FIE
- Corrosivity, mainly impacting the FIE and ferrous components
- Emulsion stability, resulting in the potential separation of dispersed (water) and carrier (diesel fuel) phases, mainly impacting the FIE
- Low temperature operation, impacting the fuel system and startability
- Deposit build-up from minerals in the water

In general it appears that these issues could be largely solved by using fuel and emulsion additives and deionised water when preparing the emulsion. Guidelines for emulsion use were also identified, and as a result a number of OEMs warranted one or more emulsions for use with their engines.

9.6 Potential Opportunities

1. The immediate potential for emulsion fuels appears to be in cities within developing nations where visible smoke and NOx pollution may be an issue and where engine technologies are currently at Euro III or earlier. This is reflected in the predominant Indian authorship of recent papers on emulsions. The nature of water-in-diesel emulsions is such that their combustion may serve to impact the ignition delay, and increase combustion duration, of engines with mechanical fuel injection equipment, leading to reduced PM and some small fuel economy benefits, accompanied by reductions in NOx. For the same reasons, these fuels would deliver visible smoke benefits and possibly increase fuel economy in stationary diesel generator sets of older technologies. These 'immobile' engines would not be subject to the reduced range limitations that hinder the use of emulsions in mobile applications. Thermal efficiency improvements would be best exploited in large power generation plants.

There is potential for future exploitation of fuel emulsions in several new areas:

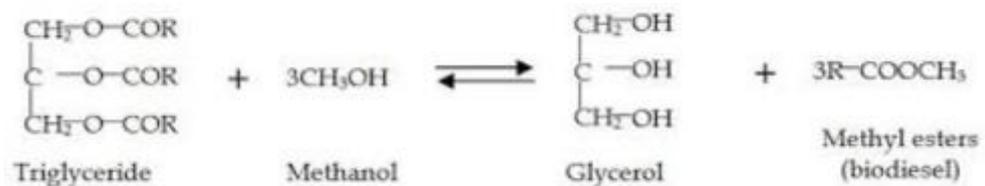
2. Optimising injection timing and other calibration parameters to exploit reductions in NOx and PM emissions to improve fuel consumption in the legacy fleet. Many captive fleets of Euro III and IV buses are now equipped with retrofit DPF and SCR systems. Without making any hardware changes, operating these buses on emulsion fuels would reduce engine-out levels of both NOx and PM. This would enable calibration changes to be made such that tailpipe emissions remain constant, but fuel economy is improved.
3. To use reductions in NOx and PM for cost savings on Euro VI technology engines. For example, reductions in both NOx and PM from a water-in-diesel fuel would enable the engine timing to be retarded, giving further reductions in NOx for the same PM. These reductions in NOx would reduce urea consumption leading to a direct cost-saving and a reduction in engine-out carbon dioxide (urea decomposition produces CO₂ as well as ammonia)

In these cases OEMS would need to lead the development by designing and calibrating fully compatible engines. This would be a substantial challenge.

4. 'Biofuel' emulsions combining biofuels with mineral fuels and water to moderate negative impacts on emissions. FAME and straight vegetable oil fuel components tend to be low volatility and poorly vaporised in combustion, so may preferentially survive combustion. A blend of a FAME-water emulsion, or vegetable oil –water emulsion with mineral diesel may enhance combustion of the biogenic part of the fuel, reducing emissions of HC, CO and the non-carbon fraction of PM.

5. The potential exists for using novel surfactants to generate emulsions from readily available oxygenated components. Compounds containing hydroxyl groups may be similarly encapsulated to water. An obvious candidate is glycerol. Glycerol is a by-product of the production of fatty acid methyl esters (FAME) from triglycerides and methanol⁴⁶.

Figure 5: Production of FAME by Transesterification (Adapted from Reference 31)



Glycerol is also fully miscible with water. A {glycerol-water} or straight glycerol emulsion in a FAME-mineral diesel blend would substantially improve the well to-wheels CO₂ credibility of the fuel, by adding the biogenic glycerol to the biogenic FAME. It would also have increased calorific value compared to a conventional water-diesel emulsion, so could increase operational range of vehicles using this fuel compared to a conventional water-in-diesel emulsion.

There may be many other suitable compounds that are waste products of industrial processes that could be considered for this approach.

6. It may be possible to develop 3-phase emulsions that combine baseline mineral diesel (or diesel-FAME) with two biogenic or waste products. These may have both emissions benefits and excellent well-to-wheels CO₂ characteristics.

9.7 Gap Analysis

9.7.1 Emulsions

There are many open questions associated with the production and usage of diesel emulsions. The most relevant of these are listed below:

- Surfactants
 - which chemistries are the most effective?
 - Is their optimum function influenced by the baseline chemistry of the diesel fuel?
 - How much influence do they have on the results observed: do they have high cetane numbers; does their presence impact emissions observed with low water blends?
 - How is the optimum stability achieved for any given surfactant?
- Mixing
 - How does the mixing approach, energy, duration relate to long-term stability, micelle size and in-cylinder behaviour?
 - What is the maximum diesel-water blend that will reliably run in a diesel engine? How would the minimum diesel content be impacted by introducing an additional oxygenated hydrocarbon component?
- Performance and emissions
 - Are impacts on performance and emissions linear with fuel water (and surfactant) content?
 - Are changes in fuel energy with added water and surfactant exactly equal to changes in engine performance?
 - What benefits are possible with emulsion fuels that contain 2 emulsified components in addition to diesel? Does one component have to be water to ensure micro explosions?
 - Are there other benefits of using emulsions, such as in-cylinder and FIE clean-up effects?
 - How can the combustion properties of emulsions be exploited in a synergistic way with modern after treatment systems?
- Fundamentals
 - Does the micro explosion effect exist? If so, which factors impact its appearance and magnitude?
 - How is the fuel spray impacted by the encapsulated water, and how does this evolve with time and temperature?

9.7.2 Modern Technology Engines

During the literature review, few evaluations on engines of post-Euro III technologies were identified. As a consequence, the compatibility of modern FIE and other engine hardware with emulsified fuels does not appear to have been robustly tested.

Since Euro III, EGR has been widely introduced and EGR rates have steadily risen to around 25% in some specialised applications at Euro V (for example, Scania). While EGR rates appear to be reducing at Euro VI, the compatibility of the legacy fleet's EGR systems is virtually untested.

Similarly, fuel injection pressures have increased dramatically from Euro III (~1200bar), reaching 2400 bar at Euro V and potentially climbing to >3000bar in Euro VI applications. Higher fuel temperatures may degrade surfactants and lead to water vaporisation in the fuel lines.

Any widespread application of emulsion fuels into modern vehicle fleets would need to consider these vehicle parc issues.

In the few studies located that consider emulsions in modern engines, there is certainly no evidence that the NOx and PM reduction capabilities are diminished. In fact, it may be that calibration approaches could enable the maximisation of simultaneous engine-out emissions reductions. No studies seeking to optimise emissions, including after-treatment, were located.

9.8 Active Players in the Emulsions Market

NanOil (Denmark; <http://nanoilemulsion.com/>) and Alternative Petroleum Technologies (US; <http://www.altpetrol.com/PDF/>) appear to be the main organisations currently working on water-in-diesel emulsion fuels for high speed internal combustion engines. Nanomizer Inc⁴⁵ appears to have a mechanical technology for creating micro emulsions with very small micelles, but the emulsions business appears to be just one strand of exploitation of their 'pulverisation' technology.

- NanOil prefers macro emulsions for HSDI diesel applications, the larger ~1µm droplets giving a characteristic milky-white appearance, and they also work in fuel/water emulsions for large engines. Water levels of 2% to 30% are discussed but data validating performance is not provided on their website.

They claim their surfactant has been proven with a number of mixing technologies. The last updates to the website appear to have been in mid-2013.

- Altpetrol does not describe the typical micelle size of their emulsion, but they appear to consistently employ 13-15% emulsions in their validation studies on IC engines (<http://www.altpetrol.com/en/4c-tech-third.html>) while using up to 2% surfactant. Their website contains the results of several studies looking at emissions, performance and efficiency comparisons with baseline fuels. It's worth noting that the website does not indicate any new activity or publications since 2011.

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