

Particle Filter Systems for High Sulfur Fuels

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Before 1990, HDV Diesel fuel in most countries contained 2000 ppm sulfur. DPF compatible with high sulfur content fuel were developed beginning 1980. These developments were documented at the annual SAE Sessions on "Diesel Particulate Emission Control" from 1982 onwards. Wall flow DPFs of this development period were already very effective but catalyst based regeneration methods, proposed by JM in 1988 with the so-called CRT-system using Pt could not be used because of the high Sulfur content of the fuel. The influence of the fuel sulfur on the Pt-based catalysts is well documented by JM: with the presence of sulfur and oxygen the catalytic converter favors the conversion of $\text{SO}_2 \rightarrow \text{SO}_3$. This tenaciously inhibits other oxidation reactions, especially the reaction $\text{NO} \rightarrow \text{NO}_2$, needed for the soot combustion - so that the CRT reaction finally ceases. On the other hand, when ULSD is used the reaction $\text{NO} \rightarrow \text{NO}_2$ is favored.

Low-sulfur fuels first became available from 1996 in Sweden. The main reason was the environmental impact of Sulfur on the Swedish lakes and forests due to SO_2 emission and sulfate formation, the so-called acid-rain formation. In other European countries and Switzerland the sulfur content also fell stepwise from 2000 ppm to 500 (1992), 350 (1996), 50 ppm (1998) and finally in 2002 to 10 ppm. CRT-DPF could be introduced stepwise and ULSD fuel also permitted the use of Diesel oxidation catalytic converters.

Introduction of low Sulfur fuel however, remained limited. Many developing and emerging countries still use fuels with > 1000 ppm S. Even most modern industrialized countries use this high-S cheaper fuel for construction machines, non-road and stationary engines, and locomotives. Fuels in ocean shipping have even higher S concentrations up to 4 %. Hence, emission control has been delayed in these sectors.

Particle filter technology for high polluting off-road engines, burning high sulfur fuels, was therefore studied to define best available retrofit-technology for these applications. Target areas of immediate interest are underground workplaces and construction machines in France, UK, Italy, China and other countries. As a result of these considerations all systems using precious metal catalysts and catalytic combustion had to be excluded from these high sulfur fuel applications. Burner systems, base metal coatings and fuel borne catalysts were selected as promising candidates. This study presents the investigation of two FBC systems, both based on iron.

TESTED FUELS

Type			Swiss market fuel	China market fuel	Test Fuel
Manufacturer			Shell	Sinopec	Shell
Property	Method	Unit	ULSD, SN 18 11 60-1-2009	HSD China Fuel	HSD Formulated
Density (at 15°C)	EN ISO 12185	kg/m ³	825.2	848.6	841.8
Viscosity (at 40°C)	EN ISO 3104	mm ² /s	2.199	2.733	2.083
Cetane number	ISO 5165	-	49.9	45.8	45.3
Cetane index	ISO 4264	-	51.8	ND	ND
Sulfur content	EN ISO 20846	mg/kg	7.7	1223	1369
Cloud point	ISO 3015	°C	-11	ND	ND
Pour point (CFPP)	EN 116	°C	-23	ND	ND
Flash point	EN ISO 2719	°C	56.0	ND	ND
Heating value		MJ/kg	min.42.5	ND	ND
Aromatic hydrocarbons	ISO 3837	Vol %	max. 2	ND	ND
Boiling analysis (340°C)	EN ISO 3405	Vol %	96.1	91.1	94.4
Ash	EN ISO 6245	mg/kg	< 0.001	< 0.001	< 0.001
Fe of additized fuel	SPO 631	mg/kg	18.7 / 18.1	ND	18.5 / 18.1

TESTED PARTICLE FILTERS

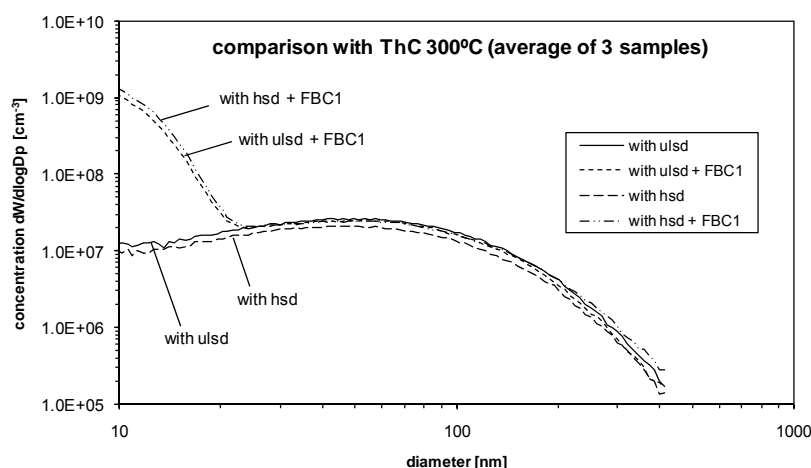
Manufacturer		Dinex A/S	Pirelli Eco Technology S.p.A.
Material		SiC	SiC
Porosity	[%]	45	42
Pore size	[μm]	15	20
Cell number	[CPSI]	150	180
Wall thickness	[mm]	0.7	0.43
Space velocity	[s^{-1}]	30.2	22.8
Regeneration		FBC passive	FBC active
Manufacturer of FBC		Innospec	Pirelli Eco Technology
Specification		Satacen [®] 4	CAM-FBC active
FBC content max.		20 mg Fe / kg fuel	20 mg Fe / kg fuel

LEGALLY LIMITED EMISSIONS

	CO	HC	NOx	Fuel Consumption	PM
	[g/kWh]	[g/kWh]	[g/kWh]	[g/kWh]	[g/ filter]
ULSD	0.62	0.25	6.79	227.4	2.2
HSD	0.69	0.24	7.49	227.9	2.17
ULSD + FBC	0.65	0.26	6.82	230.3	2.6
HSD + FBC	0.65	0.26	7.28	229.0	2.41

With the exception of PM, the emissions are measured steady state as legally prescribed. The data are reported, as usual, energy specific in [g/kWh] terms. PM [g/kWh] could not be determined in these tests, because particle samples had to be collected for subsequent TGA- and EC/OC-analysis. The reported PM [g/filter] data correspond to the loading cycle. There is no significant disparity in the gaseous emissions and in the fuel consumption. The particle mass PM is higher for the tests with iron additive, as expected.

PARTICLE SIZE ANALYSIS (without DPF)

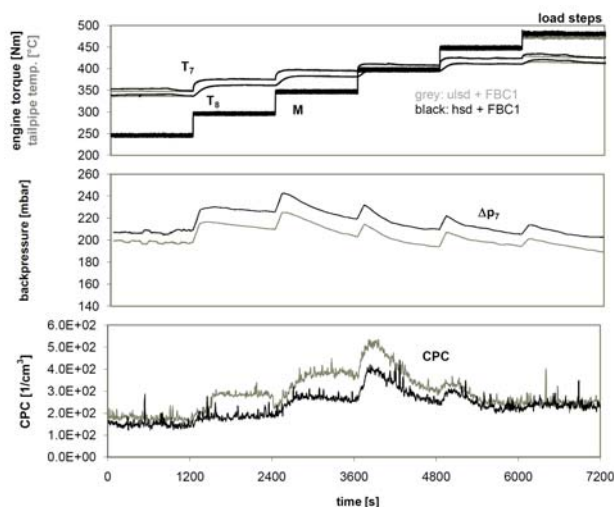


The size distribution reveals almost no difference for the 4 fuel variants. The iron additive causes the expected increase of particle count in the range 10 – 25 nm. These are ultra fine iron oxide clusters formed after combustion of the metal organic additive substances. These very fine particles result in a large specific surface that promotes catalytic effects during the filter regeneration. VERT certified DPF systems very efficiently intercept these fine FBC oxide particles as they remove all solid particles including metal oxide particles from engine wear and lubrication oil by over 99 % to an extent that they are usually not detectable in the size spectrum after the DPF. The filtration attributes of these two VERT-certified DPF are well documented. Hence, size measurements were not done after the DPF.

FILTER LOADING AND REGENERATION

The filters became soot-loaded in a dynamic cycle. Soot was generated in rapid acceleration cycles from idling until full load, thus avoiding the temperature rising to values at which the FBC doped fuel would trigger filter regeneration. The aim was to attain the highest possible filter loading to subsequently test the regeneration response. The filter loaded with soot in the described cycle, was regenerated according to the Swiss standard test protocol SN 277 206. The regeneration begins below 340°C exhaust-gas temperature. The load is increased every 20 minutes until full load. Plotted are the temperatures T7 before DPF and T8 after DPF, torque, pressure loss across the filter Δp_7 and the particle emission in the CPC count.

The results show that, already at the first operating point, the back-pressure decreased despite increasing soot load and increasing volume throughput. Already at this 340°C temperature, the balance-point is passed. Increasing the temperature steepens the regeneration gradient until termination of the test after running 20 minutes at full load. There is almost no evident difference between the two fuels.



Also thermo-gravimetric data, coupled with simultaneous MS-detection of volatile combustion products (H_2O , CO , CO_2 , SO , SO_2) did not show any influence of the S-content on the combustion characteristics of the soot collected from the engine when running with ULSC and HSD.

In conclusion this investigation, comparing 2 DPF-systems using iron based FBC-regeneration with European Diesel fuel (sulfur content < 10 ppm) and high sulfur test fuel (sulfur content 1369 ppm) as it is typically used in China did not show any significant differences with respect to the limited emissions CO , HC , NO_x and PM , nor to the EC/OC ratio of the soot, nor to the characteristics of residual soot combustion, nor to the regeneration response. Evidently, the FBC iron-oxide enables that the sulfur (both of the fuel and the lube oil) entering combustion subsequently exits as gaseous SO_2 . No sulfate is formed and thus the particle formation is unaffected. These conclusions are of course limited to short term effects and to the operation profiles used during this investigation. Further investigations will be required.

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- Song.J et al., Fuel Sulfur Effect on Membrane Coated Diesel Particulate Filter; SAE 2002-01-2788
- Allansson R. et al., Continuously Regenerating Trap (CRTTM);SAE 2002-01-1271
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Particle Filter Systems for High Sulfur Fuel

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Before 1990 Diesel fuel in most countries contained 2000 ppm sulfur, which was stepwise reduced to 500 and 350 ppm because of environmental effects like acid rain. Starting in Y 2000 a growing number of industrialized countries introduced ultra low sulfur (ULS)-fuel below 50 ppm to allow the use of precious metal catalysis for ICE emission control by DOC and DPF. This also triggered the introduction of the NO₂-regenerating particle filter concepts like the successful JM CRT – underestimating the problem of NO₂-emissions, which only now is addressed.

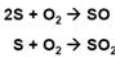
Many offroad markets however, and most developing countries still use fuels with > 1000 ppm S and therefore emission control does not penetrate as fast into these sectors. It has also to be emphasized that in most countries the offroad sector contributes nearly as much PM- emissions as the onroad sector. Particle filter technology for high polluting offroad engines burning high sulfur fuels was therefore studied in order to define best available technology for these applications. Target areas of immediate interest are working places worldwide, construction in France, UK, Italy and onroad as well as offroad in Chinese cities.

Sulfur and DPF History in Switzerland

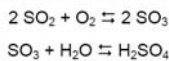
Year	Sulfur-Content mg/kg	DPF -Retrofits
1972	5000	-
1985	3000	-
1987	2000	-
1994	500	453
2000	350	2425
2005	50	11'365
2008	10	18'500

S-Reactions with and w/o PGM

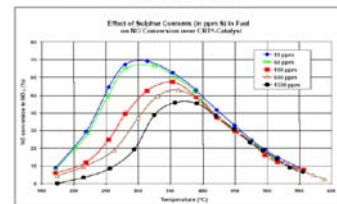
Reactions without PGM → exits as Gas



Reactions with PGM → exits as liquid Droplet

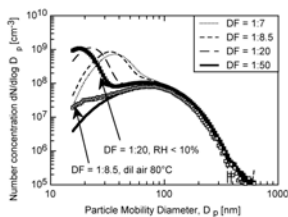


NO₂-Generation Characteristics



Before Y 2000 DPF had to cope with high sulfur fuels, which was no problem as long as no Pt-containing catalytic coatings were used. Pt-coatings, using the NO₂ regeneration route however, are inhibited by sulfur and could only be introduced in combination with ultralow sulfur Diesel fuels

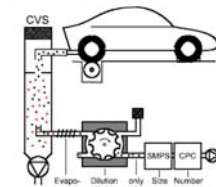
Condensation of Sulfate depending on Temperature and Dilution



Filter Efficiencies based on PN or PM after 2000 op.hours with CRT and < 50 ppm S

DPF	Operation Point	PM [%]	PN [%]
DPF7	2	-1581	99.86
	6	53	99.87
	5	70	99.86
	1	-189	99.95
	2	-784	99.95
	2	-62	99.92
	6	74	99.96
	5	88	99.96
1	38	99.96	
	88	99.84	

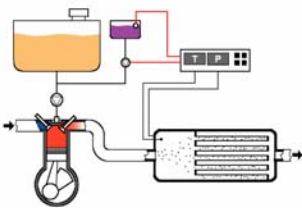
Measurement of Solid Particle Number acc. to EU-PMP (EURO VI)



Sulfate starts to condense when the exhaust gas cools down below 300 °C and forms ultrafine sulfuric acid droplets which seem to increase the overall number of particles downstream of a DPF if solid and volatile phase are not separated. Total particle mass PM can become very high since sulfate is binding up to 8 molecules of combustion water. Particle mass (PM) measurement is therefore strongly misleading.

While Pt-coated DPF systems must be excluded with high sulfur fuel many other DPF regeneration systems can still be used. In this research organometallic Fe was used, which is known as FBC (= fuel borne catalyst) to regenerate DPF at temperatures over 300 °C very fast and efficient. FBC systems are available as passive and active systems with ignition assist. Sulfur content of fuel during these tests was as high as 1360 ppm.

Passive Regeneration with Fuel Borne Catalyst is independent on Fuel Sulfur



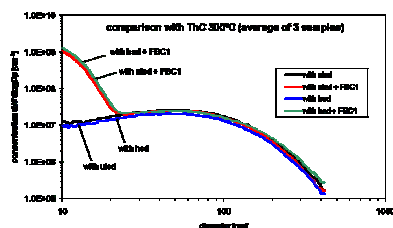
Active Regeneration with electric hot Spots is possible in Combination with SiC-Substrates



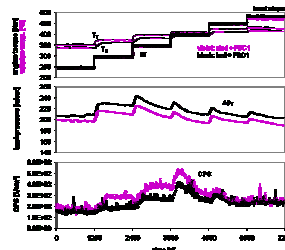
Analysis fo ULSF, Chines Fuel and Test Fuel

Type	Swiss market fuel	China market fuel	Test Fuel		
Manufacturer	Shell	Sinopec	Shell		
Property	Method	Unit	ULSF, SN 15 11 60-1-2009	HSD China Fuel Sample	HSD Formulated
Density (at 15°C)	EN ISO 13185	kg/m ³	807.2	808.6	811.8
Viscosity (at 40°C)	EN ISO 3104	Mm ² P	2.189	2.733	2.263
Calorific number	ISO 5165	-	45.9	45.9	45.3
Calorific index	ISO 4264	-	51.8	-	-
Sulfur content	EN ISO 20846	Mg/kg	7.7	1223	1369
Cloud point	EN ISO 3015	°C	-11	-	-
Pour point (CFFP)	EN 116	°C	-23	-	-
Flashpoint	EN ISO 2719	°C	56.6	-	-
Heating value	EN ISO 2719	MJ/kg	Min. 42.5	-	-
Aromatic hydrocarbons	ISO 3837	Vol.%	Max. 7	-	-
Testing analysis (340°C)	EN ISO 3405	Vol. %	98.7	91.1	94.4
ash	EN ISO 6245	Mg/kg	< 0.001	< 0.001	< 0.001
Fe of added fuel	SPO 631	Mg/kg	18.7 / 18.1	-	18.5 / 18.1

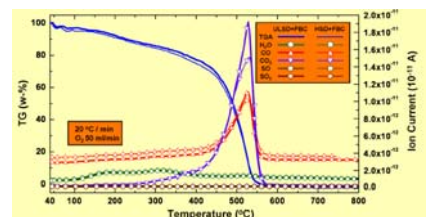
Particle Size and Number at PMP Sampling conditions: 300 °C ; DR 1:100 w/wo FBC



Regeneration comparing HSF and ULSF, both with FBC, shows no difference



Thermogravimetric Analysis



Formation of solid particles in the engine does not seem different whether the fuel contains sulfur or not. Regeneration also does not show any obvious difference and combustion behaviour, investigated by thermogravimetric analysis seems not influenced by the sulfur content at all. It can therefore be concluded that besides burners and electric heaters, FBC systems work successfully independent on sulfur level. The fact, that FBC-systems also suppress the formation of NO₂ becomes an important additional feature. Since regeneration with FBC systems however only starts above 300 °C, in many cases regeneration must be actively triggered. This DPF technology now opens very large markets for retrofit and may allow to tighten emission regulations in these market faster than expected.