Effect of Fuel and Lube Oil Sulfur on the Performance of a Diesel Exhaust Gas Continuously Regenerating Trap

David Kittelson Center for Diesel Research University of Minnesota

11th ETH-Conference on Combustion Generated Nanoparticles August 13th –15th 2007

This work was supported by generous donations from BP, Castrol, Corning, Johnson-Matthey, TSI, and Volvo

Particle removal by exhaust filters



Figures courtesy Corning and Johnson-Matthey



- Most PM filtration systems being considered for 2007 are the wall flow type shown on the left. Without regeneration to oxidize soot these devices quickly plug.
- Catalyzed filtration systems like the J-M CRT® shown on the right reduce regeneration temperature by producing NO₂ from exhaust NO in an oxidizing catalyst upstream of filter
- The catalyst also converts SO_2 to SO_3 at higher temperatures
- The J-M CCRT® has a catalyzed washcoat on the filter as well to further reduce regeneration temperature
- A CRT followed by a sulfur trap was also tested

Summary

- Analysis of 5 years of on-road particle measurements to determine influence of fuel, lubricating oil, trap type and trap age on nanoparticle emissions measured downstream of a heavy-duty vehicle operated under real-world highway cruise conditions**
- Under on-road cruise conditions, the only particles found downstream of a CRT are mainly sulfuric acid nucleation mode particles*
 - Strong dependence on exhaust temperature
 - These particles constitute little particle mass
 - Storage and release of sulfates on catalyst substrate appears to play an important role

*Grose, M., et al., "Chemical and Physical Properties of Ultrafine Diesel Exhaust Particles Sampled Downstream of a Catalytic Trap," Environ. Sci. Technol.; 2006; 40(17) pp 5502 – 5507.

**Kittelson, D., et al., Effect of Fuel and Lube Oil Sulfur on the Performance of a Diesel Exhaust Gas Continuously Regenerating Trap, to be submitted to JAS.

UMN Mobile Emissions Laboratory (MEL)



How We Sample



July 15, 2005 - CRT, BP-6, ZSO, I-35

Test conditions for on-road filter evaluations

- Tests run with J-M CRT, CCRT, and CRTS
 - CRT consist of oxidizing catalyst plus wall flow filter
 - CCRT consist of oxidizing catalyst plus catalyzed wall flow filter
 - The CRTS consists of a CRT plus a sulfur trap
- 105 kph cruise on Minnesota rural freeway
 - Load and exhaust temperature varied with grade, headwind, tailwind
 - Exhaust T 240 to 380 C

Test Condition – 105 + 8 km/hr

Trial	Fuel	Oil Aftertreatment Dilution ratio			Season		Trial Fuel		1	Fuel S, ppm	Oil	OilS,%		
Destin	DD 15	1.00	NT	Avg	g Std		Fall 02		-5	BP-1:	5	15	HSO	0.261
Trial 01	BP-15 BD 50	L20 H20	CPT	4/	7 91 81 74		Fall 02		-4	BP-50	0	45	HSO	0.261
Trial 02	BI - 30 BP-15	LSO	CCRT	42	29 56		Summer 03		-3	BP-1	5	15	HSO	0.261
Trial 02	BP-15	LSO	CRT + S-Trap	34	40 33		Summer ()3	-2	BP-1	5	15		0.126
Trial 04	BP-15	LSO	CRT	50	07 69	69)3	1	DI I.	15	15		0.126
Trial 05	BP-15	LSO	CRT + S-Trap	40	06 24		Summer	$\frac{1}{2}$	-1 1		5	15		0.120
Trial 06	BP-15	LSO	CCRT CRT		00 48		Summer 03			DT - 30		43	150	0.201
Trial 07	BP-6	ZSO			60		Summer ()4	4	BP-1:	2	15		0.126
Trial 08	ECD	ZSO	CRT	47	73 75		Summer ()5 7		BP-6		4	ZSO	0.042
Trial 09	BP-6	HSO	CRT	37	79 39		Summer 05		8	ECD 6		6	ZSO	0.042
Trial 10	BP-50	ZSO	CRT + S-Trap	41	6 52		Summer ()5	9	BP-6	5	4	HSO	0.261
Trial 11	BP-50	O HSO CRT + S-Trap		30	52 40 55 21		Summer 06		12	BP-50		45	HSO	0.261
Trial 12	BP-50 ECD 1	NHSO	CRI	41	$\frac{55}{21}$		Summer ()6	13	ECD-	-1	6	VHSO	0.619
Trial 13	4 BP-6 LSO CRT			51	516 89		Summer 06		14	BP-6		4	LSO	0.142
	51 0	200				1								
Trial	Fuel	Oil	Aftertreatmen	it	Number of	Num	ber of plume	1	Number	of	Nu	mber of SMPS	Nuimber o	f plume
<u> </u>	DD 44				repetitions		samples	backg	ground sa	amples	bac	kground scans	SMPS s	cans
Baseline	BP-15	5 LSO	None		26		7877			14974		146		74
Trial 01	BP-50) HSO	CRT		28		8622			17896		160		80
Trial 02	BP-15	5 LSO	CCRT		72		22453			47314		433		214
Trial 03	BP-15	P-15 LSO CRT + S-Trap		р	33		10361			20490 192		98		
Trial 04	BP-15	5 LSO	CRT		57		17215			35184		350		169
Trial 05	BP-15	5 LSO	CRT + S-Trap	р	45		14436			30823		277		135
Trial 06	BP-15	5 LSO	CCRT		37		11615			23124		217		111
Trial 07	BP-6	ZSO	CRT		66		20943			44492		406		197
Trial 08	ECD	ECD ZSO CRT			38		12163	3		24831 229		113		
Trial 09	BP-6	5 HSO CRT		43		13882		26373			239		128	
Trial 10	BP-50) ZSO	CRT + S-Trap	р	41		13168	28891		28891		264		121
Trial 11	BP-50) HSO	CRT + S-Trap	р	60		18910		39326			358		178
Trial 12	BP-50) HSO	CRT		39		14456		29056			221	114	
Trial 13	ECD-	1 VHS	HSO CRT 40			14833		30386			239	119		
Trial 14	BP-6	BP-6 LSO CRT		37		13091			26498		210		105	

SMPS and EEPS Size Distributions - CRT



Note the much greater response of the EEPS to small particles under these transient conditions. The EEPS tracks well with the CPC on total number

Relationship Between Particle Concentration And Exhaust Temperature – CRT, CCRT, CRT + S-trap



- Averaging all tests shows the differences between the CRT and CCRT and CRT + S-trap.
- Data shown are for all runs regardless of fuel and lube

Correlate number emissions with age, fuel S, and oil S at constant binned T



Conclusions - 1

- Nucleation mode particle formation by the CRT is strongly temperature dependent, but neither the CCRT nor the CRT plus S trap form particles detectable above background at any temperature in the range examined
- The formation of nucleation mode particles by the CRT is proportional to fuel S, oil S, but decreases with catalyst age.
 - For the conditions tested a 10 ppm S fuel would be expected to produce from 4 to 7 x 10^8 particles/cm³
 - Particle formation per unit sulfur in the lube oil ranges from 0.15 0.45% of that per unit sulfur in the fuel.
 - For the conditions tested, the oil consumption of the Volvo is in the 0.05 0.15% of fuel consumption range. This suggest that S in the lube oil that is consumed is more effective at producing nuclei mode particles than the S in the fuel
 - For the conditions tested a 3000 ppm S lube oil would be expected to form as many particles as 4.5 to 13.5 ppm S fuel
- Other oil components may play a role, this is being examined by BP/Castrol

Storage and release effects

Nearly all particles downstream of CRT were in nucleation mode and strongly temperature dependent



Dp, nm

Here nucleation mode measurements have been converted to sulfur mass (as sulfate) and compared to compared to sulfur available in exhaust



Storage and release experiments

- On-road test indicate that stored sulfate is released at higher exhaust temperatures
- Lab tests done to confirm this
 - New CRTs tested in lab with zero S fuel and ultra low S lube oil – no nucleation mode formation at any temperature
 - Used CRTs from on-road tests installed on lab engine and tests with zero S fuel and ultra low S lube oil repeated
 - 1600 rpm
 - Vary load to vary exhaust T
 - Significant nucleation mode formation as temperature approaches 400 C

Sulfate release experiment – number measurements



Sulfate release – mass emission rates



Size distribution observed near peak temperature



Conclusions 2

- Zero S fuel eliminates nucleation mode formation with clean CRT
- It appears that in normal operation with ULSD sulfate is stored in the CRT catalyst at temperatures below about 350 C
- This material is released at higher exhaust temperatures
- This could lead to unexpected emissions for some operating cycles in passive systems
- It is likely that active regeneration would remove stored material

Contributors

- W. F. Watts, J. P. Johnson, J. Swanson, U of M
- C. Thorne, C. McCann, M. Payne, S. Goodier, C. Warrens, H. Preston, BP / Castrol
- U. Zink, D. Pickles, Corning
- C. Goersmann, M. V. Twigg, A. P. Walker, Johnson-Matthey
- R. Boddy, BP consultant

Summary SMPS Statistics

Trial	Fuel	Oil	Aftertreatment	Dilution ratio		CPC, pa	rt/cm ³	SMPS,	part/cm ³	NV	CPC/SMPS
				Avg	Std	Avg	Std	Avg	Std		
Baseline	BP-15	LSO	None	477	91	2.06E+07	1.20E+07	1.86E+07	6.21E+06	3.5E+03	1.10
Trial 01	BP-50	HSO	CRT	431	74	2.68E+09	5.02E+08	4.32E+08	2.79E+08	1.8E+06	6.20
Trial 02	BP-15	LSO	CCRT	429	56	-5.79E+06	1.43E+07	-2.11E+05	1.42E+05	-1.7E+04	27.46
Trial 03	BP-15	LSO	CRT + S-Trap	340	33	1.33E+07	4.17E+07	-9.32E+05	1.35E+06	7.1E+03	-14.31
Trial 04	BP-15	LSO	CRT	507	69	5.43E+08	1.85E+08	3.75E+07	1.62E+08	-1.4E+05	14.48
Trial 05	BP-15	LSO	CRT + S-Trap	406	24	-7.02E+07	1.13E+08	-7.65E+05	6.04E+05	7.5E+04	91.79
Trial 06	BP-15	LSO	CCRT	400	48	-8.22E+06	1.62E+07	-1.25E+06	2.71E+06	7.3E+03	6.58
Trial 07	BP-6	ZSO	CRT	381	60	3.88E+08	1.75E+08	2.88E+07	3.57E+07	-2.3E+05	13.50
Trial 08	ECD	ZSO	CRT	473	75	1.31E+08	1.25E+08	4.75E+06	9.55E+06	-3.3E+04	27.65
Trial 09	BP-6	HSO	CRT	379	39	1.04E+08	6.06E+07	2.75E+06	8.78E+06	-1.8E+04	37.72
Trial 10	BP-50	ZSO	CRT + S-Trap	416	52	-1.08E+07	6.53E+07	-1.12E+06	1.39E+06	6.0E+03	9.63
Trial 11	BP-50	HSO	CRT + S-Trap	362	40	-1.55E+07	1.87E+07	-1.62E+06	2.11E+06	9.5E+03	9.58
Trial 12	BP-50	HSO	CRT	385	21	2.17E+09	3.14E+08	3.16E+08	1.47E+08	4.2E+05	6.87
Trial 13	ECD-1	VHSO	CRT	413	41	1.23E+09	2.80E+08	7.97E+07	7.03E+09	1.8E+06	15.50
Trial 14	BP-6	LSO	CRT	516	89	1.55E+08	7.28E+07	1.16E+06	5.95E+05	-4.7E+03	134.08