

# Mobile Source Air Toxics (MSATs) from High Efficiency Clean Combustion: Catalytic Exhaust Treatment Effects

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## ABSTRACT

High Efficiency Clean Combustion (HECC) strategies such as homogenous charge compression ignition (HCCI) and pre-mixed charge compression ignition (PCCI) offer much promise for the reduction of NO<sub>x</sub> and PM from diesel engines. While delivering low PM and low NO<sub>x</sub>, these combustion modes often produce much higher levels of CO and HC than conventional diesel combustion modes. In addition, partially oxygenated species such as formaldehyde (an MSAT) and other aldehydes increase with HECC modes. The higher levels of CO and HCs have the potential to compromise the performance of the catalytic aftertreatment, specifically at low load operating points. As HECC strategies become incorporated into vehicle calibrations, manufacturers need to avoid producing MSATs in higher quantities than found in conventional combustion modes. This paper describes research on two different HECC strategies, HCCI and PCCI. Engine-out data for several MSAT species (formaldehyde, acetaldehyde, benzene, toluene, ethylbenzene, xylenes, naphthalene, PAHs, diesel PM) as well as other HC species are presented and compared when possible with conventional operation. In addition, catalyst-out values were measured to assess the destruction of individual MSATs over the catalyst. At low engine loads, MSATs were higher and catalyst performance was poorer. Particle sizing results identify large differences between PM from conventional and HECC operation.

## INTRODUCTION

Increasingly stringent emissions regulations for diesel engines and vehicles, as well as concern for fuel efficiency, have resulted in new developments in both emissions control technology and in-cylinder combustion strategies. Lowering engine-out NO<sub>x</sub> and PM reduces demands on the emissions control and potentially enables more durable catalyst formulations.

Conventional approaches to diesel combustion have been plagued by a trade-off between NO<sub>x</sub> and PM emissions. A strategy that reduced one pollutant

typically increased the other. Recent theoretical and experimental studies describe combustion regimes which exhibit simultaneous low NO<sub>x</sub> and PM emissions [1-10]. While the details of the various approaches to new combustion regimes vary somewhat, the approaches share the goal of burning the injected fuel charge in a lean pre-mixed combustion event. Formation of PM is reduced by the fuel-lean conditions in the premixed combustion. NO<sub>x</sub> formation is avoided by use of exhaust gas recirculation (EGR) to reduce the flame temperature. Previous papers from our group describe HECC operation, associated engine performance, and regulated emissions [6-8].

In vehicle applications, HECC strategies are most often incorporated into low-load operating points due to the rapid pressure rise typically associated with the premixed combustion. HECC strategies often increase CO and HC exhaust concentration as well, and we have previously reported large increases in aldehydes and other partially-oxygenated HC species not typically responsive to the total HC measurement [11, 12]. A major concern with HECC is the ability of a catalyst to remove MSATs at exhaust temperatures near the light-off temperature; if the catalyst function is overwhelmed with CO oxidation, for instance, MSAT species could slip through and be emitted at much higher levels than conventional diesel combustion.

## EXPERIMENTAL APPROACH

In this paper, we report on extensive HC speciation from the exhaust of two engines: one operating in PCCI and conventional mode, and the other operating in HCCI mode. In addition, each engine was equipped with catalytic emissions control, so the effectiveness of the aftertreatment for removing HC species will be assessed.

## ENGINE PLATFORMS

**HCCI** - A naturally aspirated, 4 stroke, Hatz DI diesel engine was modified from its original configuration for HCCI use by reducing the compression ratio from 20:1

to 10.5:1, and by removing of the diesel fuel injector. The engine specifications are given in Table 1.

Intake air temperature modification up to 290°C was used as the only method for controlling HCCI combustion. Fuel was delivered using a small laboratory metering pump and was fumigated into the intake manifold using air-assisted partial vaporization atomization. Full details of the engine modifications appeared earlier [12].

**Table 1. HCCI Engine Specifications**

|                                      |                  |
|--------------------------------------|------------------|
| Engine Displacement (cc)             | 517              |
| Bore (cm)                            | 9.7              |
| Stroke (cm)                          | 7.0              |
| Compression Ratio After Modification | 10.5             |
| Intake Valve Opening (CA deg)        | 710 <sup>1</sup> |
| Intake Valve Closing (CA deg)        | 218 <sup>1</sup> |
| Exhaust Valve Opening (CA deg)       | 499 <sup>1</sup> |
| Exhaust Valve Closing (CA deg)       | 20 <sup>1</sup>  |
| Intake Air Temperature (°C)          | 30-290           |

1. TDC of compression stroke is 360 CA deg, valve events measured at 0.01" lift

Experiments were conducted by performing sweeps of combustion phasing by sweeping the intake air temperature to identify the maximum efficiency condition at each fueling rate. A constant-speed induction motor, coupled to the engine with a timing belt, held the engine speed at 1800 rpm. A torque meter was not used in the experimental setup, so instead engine power output is reported as IMEP. High intake temperatures result in advanced combustion phasing, high NO<sub>x</sub> emissions, and high rates of cylinder pressure rise. Low intake temperatures resulted in instability, misfire, and low combustion efficiency. Peak efficiency occurs at an intermediate temperature as we have reported previously [12]. Fuel was fumigated into the intake manifold to initiate HCCI combustion at four different fueling rates: 6.8, 8.5, 10.5, and 12.5 ml/min. HC speciation was performed at the peak efficiency condition for each fueling rate, and details of each of the operating conditions can be seen in Table 2.

**Table 2. HCCI Engine Operating Conditions**

| Fuel Rate (ml/min) | Intake Temperature (C) | IMEP (bar) | $\Phi$ <sup>1</sup> | Combustion Efficiency (%) |
|--------------------|------------------------|------------|---------------------|---------------------------|
| 6.8                | 290                    | 1.6        | 0.32                | 81%                       |
| 8.5                | 240                    | 2.0        | 0.38                | 84%                       |
| 10.5               | 170                    | 2.7        | 0.41                | 95%                       |
| 12.5               | 160                    | 3.2        | 0.46                | 97%                       |

1. Fuel-air equivalence ratio

A low temperature diesel oxidation catalyst, typical of the state-of-the-art in 2005, was installed in the exhaust. The catalyst had a volume of 0.25 L which resulted in a space velocity of 52,000 – 61,000 hr<sup>-1</sup>. The catalyst temperatures were 198, 214, 226, 252 °C for IMEP

values of 1.6, 2.0, 2.7, and 3.2, respectively. Emissions and HC samples were taken upstream and downstream of the catalyst.

**PCCI Engine** – The same experimental setup and regeneration strategies used in this study have been described in previous work on the same platform [13-16]; brief details of the setup will be repeated here. A Mercedes OM668 4-cylinder, 1.7-liter common-rail diesel engine was coupled to a motoring DC dynamometer. The engine, which is a 1999 model used in the Mercedes A170 in Europe, has a bore and stroke of 80 mm and 84 mm respectively, and it has a rated power output of 66kW (89 hp) at 4200 rpm. Modifications to the engine included the addition of an electronic intake throttle, an electronically controlled high flow exhaust gas recirculation valve (in lieu of the stock vacuum-operated valve), and an EGR cooler. Additionally, the factory engine control module was replaced with a rapid development engine controller based on a dSpace® MicroAutoBox. This rapid development system (RDS) was developed in partnership with Ricardo, Inc., and provides complete control over all engine electronics, including timing, duration, number of fuel injection events, fuel rail pressure, intake throttle, EGR valve, and turbocharger wastegate.

For this research, the engine was equipped with a 2.47 L NO<sub>x</sub> storage and reduction catalyst. Details of the catalyst and catalyst performance on criteria emissions are in a research paper published at this conference [17]. For the MSAT study, we focused on Ad Hoc Modes 1, 2, and 3. Ad Hoc steady state modes have been used previously to simulate the light-duty Federal Test Procedure (FTP) using an engine dynamometer [18-20]. The speeds and loads are listed in Table 3. In addition to conventional combustion settings, typical of the original calibration for the base engine used in this study, two other settings were used. The first was the PCCI and the second was an alternating PCCI setting in which the engine was shifted at five minute intervals between the conventional point and the PCCI setting. Because the PM filter samples took upwards of 20 minutes to collect, the PCCI setting would result in a drift upwards of the HC emissions by as much as 50%. In contrast, the alternating PCCI setting, sampling was done only when in PCCI mode, and the HC emissions were steadier. Note that space velocity decreased in PCCI mode due to increased EGR flow.

## FUEL

Experiments were carried out using ultra-low sulfur certification diesel (Diesel 2007 ULS Fuel) sourced from Chevron-Phillips Specialty Chemical Company. Selected properties provided by the vendor are listed in Table 4.

## EMISSIONS SAMPLING AND COLLECTION

CO, CO<sub>2</sub>, O<sub>2</sub>, HC, NO<sub>x</sub> – Standard heated chemiluminescence and flame ionization instruments were utilized for measuring the NO<sub>x</sub> and unburned hydrocarbons, respectively. CO and CO<sub>2</sub> were measured using non-dispersive infrared (NDIR) instruments. Paramagnetic detection (PMD) was used to

**Table 3. Multi-Cylinder Engine Points (Ad Hoc)**

| Mode                        | Speed RPM | Load BMEP | Catalyst T (°C) <sup>1</sup> | Space Velocity(hr <sup>-1</sup> ) |
|-----------------------------|-----------|-----------|------------------------------|-----------------------------------|
| 1. Conv<br>PCCI<br>Alt PCCI | 1500      | 0.8       | 119                          | 19,000<br>12,000<br>12,000        |
| 2. Conv<br>PCCI<br>Alt PCCI | 1500      | 2.6       | 256                          | 21,000<br>9,000<br>9,000          |
| 3. Conv<br>PCCI<br>Alt PCCI | 2000      | 2.2       | 220                          | 26,000<br>16,000<br>16,000        |

1. The temperature of the catalyst is for the PCCI mode only. Catalyst out emissions are not reported in this work for the conventional (Conv.) and alternating PCCI modes (Alt PCCI).

**Table 4. Properties of 2007 Certification Fuel<sup>1</sup>**

| ASTM   | Description           | Value   |
|--------|-----------------------|---------|
| D-4052 | Specific Gravity      | 0.845   |
| D-445  | Viscosity             | 2.1 cSt |
| D-5453 | Sulfur                | 8.2 ppm |
| D-613  | Cetane number         | 44      |
| D-5186 | Polynuclear aromatics | 7%      |
| D-1319 | Aromatics             | 29.1%   |
| D-1319 | Olefins               | 1.6%    |
| D-1319 | Saturates             | 69.3%   |

1. From Certificate of Analysis, lot no. 71PUL701

measure O<sub>2</sub> concentration. The sample was chilled prior to measurement by PMD and NDIR instruments to achieve a non-condensing sample condition. These instruments sampled from the raw engine exhaust using a heated filter for removal of particulates. The sample stream was conveyed from the heated filter to the instruments through a heated transfer line maintained at 190 °C.

**Dilute Sampling Apparatus** – A micro-dilution device was configured to provide a dilute (non-condensing) exhaust stream for analyzing exhaust particulate and chemistry. The device was based on a design by Abdul-Khalek and Kittleson [21] The raw exhaust was routed to the microdiluter through a heated sampling line maintained at 190 °C. The microdiluter walls were heated so that

the gas temperature was held constant at 45 °C. The dilution ratio was determined at the start of each sample by measuring volumetric flow rates. Various samples were extracted from the dilute gas stream for subsequent analysis.

**Unregulated HC Species collection** – A Nicolet REGA 7000 Fourier-Transform Infrared (FTIR) Spectrometer equipped with a heated 10 m gas cell was utilized to measure a number of gas phase species. The species of principal interest were formaldehyde (H<sub>2</sub>CO), acetaldehyde (C<sub>2</sub>H<sub>4</sub>O), and 1,3 butadiene (C<sub>4</sub>H<sub>6</sub>). The FTIR sampled from the raw engine exhaust, using a heated filter for removal of particulates.

Volatile organic species were collected from the microdilution tunnel in pre-cleaned, evacuated stainless steel canisters (Entek). Semi-volatile organic compounds (SOC) were trapped from the dilute exhaust stream on an Empore™ SDB-XC resin impregnated membrane filter placed downstream of the filters used for PM samples [22]. PM was collected on Pallflex TX-40 Teflon™ coated quartz fiber filters. Aldehydes and ketones were collected on DNPH-coated solid phase extraction cartridges (Waters Corp.) from the dilute exhaust. Flow rate was maintained at 1 l/min through the cartridges.

**ORGANIC EMISSIONS SPECIATION** - A Hewlett-Packard gas chromatograph mass spectrometer (GC/MS) with Entek 7000 Preconcentrator was used for the identification and quantification of HC species from diluted samples collected in the stainless steel canisters. Canisters were analyzed within 30 minutes of collection. HC species were separated using a Supelco Equity™-1 column.

The Empore™ membranes were eluted with ethyl acetate and dichloromethane and the extracts analyzed by GC/MS using a Supelco Equity™-5 column for separation.

The filters were extracted in a laboratory microwave extractor (MARS from CEM Corp.). In this procedure, 20 ml of a mixture of 50:50 acetone:hexane is used in a quartz-lined microwave vessel. The temperature is ramped to 115 °C and held for 10 minutes. The method was adapted from an EPA method for solvent extraction of soils contaminated with fuel hydrocarbons. This method, recently pioneered in our laboratory, allows for simultaneous extraction of up to 13 PM filters and uses a minimum amount of solvent. More details appear in Lewis et al. [23].

The DNPH derivatives were extracted and then analyzed using a Hewlett-Packard 1100 HPLC with UV detection. The eluent from the HPLC unit was transferred directly to a Bruker Daltonics® Esquire mass spectrometer where the hydrazone derivatives were identified using a negative electrospray ionization mass spectrometer (ESI/MS). HPLC documents conducted using Restek A Linc C18 column.