

The Effect of a Three-Way Catalytic Converter on Particulate Matter from a Gasoline Direct-Injection Engine During Cold-Start

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ABSTRACT

This work investigates the effect of a three-way catalytic converter and sampling dilution ratio on nano-scale exhaust particulate matter emissions from a gasoline direct-injection engine during cold-start and warm-up transients. Experimental results are presented from a four cylinder in-line, four stroke, wall-guided direct-injection, turbo-charged and inter-cooled 1.6 litre gasoline engine. A fast-response particulate spectrometer for exhaust nano-particle measurement up to 1000 nm was utilised. It was observed that the three-way catalytic converter had a significant effect on particle number density, reducing the total particle number by up to 65 % over the duration of the cold-start test. The greatest change in particle number density occurred for particles less than 23 nm diameter, with reductions of up to 95 % being observed, whilst the number density for particles above 50 nm diameter exhibited a significant increase. The exhaust temperature plays a significant role on the influence of the catalytic converter on the nano-scale particulate matter. It is evident that the dilution ratio of the exhaust sample has a distinct effect on the particulate matter number and size distribution, influencing the engine-out PM more significantly than the tailpipe-out PM during cold-start engine operation. The catalytic converter also has a considerable effect on the estimated total particle mass.

CITATION: Whelan, I., Timoney, D., Smith, W. and Samuel, S., "The Effect of a Three-Way Catalytic Converter on Particulate Matter from a Gasoline Direct-Injection Engine During Cold-Start," *SAE Int. J. Engines* 6(2):2013, doi: 10.4271/2013-01-1305.

INTRODUCTION

Particulate matter (PM) can be very hazardous to human health. Adverse health effects seem to be linked to nucleation mode (NM) particles, which have equivalent diameters of less than 50 nm, and are the primary particles formed during combustion [1, 2]. These nano-scale particles dominate size distributions in terms of number concentrations and are able to penetrate farther than larger particles into the respiratory system [3, 4]. Recent biological studies suggest that particle surface area and chemistry are more important factors than particle mass [5]. According to Hall *et al.* [6], NM particles may be far more biologically active than accumulation mode (AM) particles of the same chemical composition. The AM is composed of particles which have equivalent diameters ranging from approximately 50 to 1000 nm, and are generally formed via agglomeration of primary NM particles [2]. This suggests that particle surface area or number may be more

relevant than particle mass for assessing critical PM levels. Therefore, the cumulative effect of small, nano-scale particles may result in greater toxicity to the lung than a similar mass of larger particles with correspondingly lower surface area [6].

Cold-start emissions are defined as the emissions produced by an engine during the initial warm-up period, after a sufficiently long period of non-use, and before the engine, catalytic converter or other emission reduction systems have reached their optimum operating conditions [7, 8]. Cold-start emissions are known to contribute significantly to emissions during vehicle drive-cycle testing [9, 10]. There is considerable evidence to support the hypothesis that many short journeys generate considerably more pollution than one journey of the same distance [7]. The short-trip is known to predominate in the driving patterns of a large percentage of the driving population, with a considerable percentage of this consisting of the 'school-trip' [7].



The purpose of a three-way catalytic converter (TWC) is to convert carbon monoxide (CO), hydrocarbon (HC), and oxides of nitrogen (NO_x) in the exhaust gas into carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2) so that tailpipe-out emissions are at an acceptable level [11]. In other words, the TWC is designed to complete the imperfect combustion process performed by the engine and to bring the exhaust gas mixture to equilibrium composition at relatively low temperatures [7]. However, until the TWC reaches its 'light-off' temperature, i.e. the temperature at which the conversion efficiency passes 50 %, it remains essentially ineffective [10]. Gasoline engines fitted with TWCs emit large quantities of CO and HC during the cold-start phase of engine operation as the conversion efficiency is low before the TWC has reached its light-off temperature [9, 12]. The light-off temperature is a key feature of TWC performance during cold-start, and it has been shown that the time taken to reach light-off temperature is strongly dependent on the rate of temperature increase [10]. The light-off temperature for CO conversion is $\sim 220^\circ\text{C}$, and the light-off temperature for HC conversion is $\sim 260^\circ\text{C}$ [13]. A TWC is effective at converting CO, HC and NO_x to CO_2 and H_2O at stoichiometric air-fuel ratios (AFR). At stoichiometric AFR, the exhaust gas should theoretically consist of nitrogen, water and CO_2 , with no unconsumed oxygen or fuel remaining [7, 14]. The optimal conversion efficiency for a TWC lies within a narrow band of AFRs around stoichiometry, known as the 'lambda window' [1]. TWCs are not specifically designed to have any effect on combustion generated PM from gasoline engines. Therefore, the effect of the TWC on nano-scale, PM emissions from gasoline engines during cold-start conditions is relatively unknown [12].

Several new technologies and approaches have been adopted to reduce the time for the TWC to reach light-off temperature during cold-start. These include two-stage combustion, use of electrically-powered engine block heaters, close-coupling of the TWC to the engine, thermal energy storage devices and secondary injection of air into the exhaust to combat scarcity of oxygen [7, 14, 15]. Close-coupling of the TWC to the engine is the most common approach employed to reduce the time to light-off. However, close-coupling can introduce unwanted heat into the engine compartment and can have detrimental effects on the TWC, known as thermal aging [16, 17]. Thermal aging can induce other issues such as poisoning (chemical reactions with the catalyst), fouling (deposits blocking the accessibility of the exhaust gas to the catalyst), and loss of wash-coat and other components [17]. These effects can reduce the life of the TWC and increase the time to light-off. Considerable reductions in CO and HC emissions during cold-start have been achieved by using these various technologies to reduce the time for the TWC to reach its light-off temperature. However, the effect of the TWC on PM emissions during transient cold-start engine operation has received little attention.

The main objective of this work is to study the effect of a TWC on nano-scale PM from a gasoline direct-injection (GDI) engine operating under cold-start conditions. A direct comparison between pre-TWC (engine-out) and post-TWC (tailpipe-out) PM emissions, under the same operating conditions, will improve our understanding of the effect of a TWC on nano-scale PM, in terms of total particle number concentration, particle size distribution and estimated total particle mass.

EXPERIMENTAL SET-UP

Engine

An in-line four cylinder, four stroke, wall-guided direct-injection, turbo-charged and inter-cooled 1.6 l gasoline engine was used in this study. The engine tested in this work utilises two injection events to obtain a stoichiometric, weak stratified mixture in the combustion chamber during cold-start, known as homogeneous-stratified (HOS) mode operation. To achieve HOS mode, fuel is injected into the combustion chamber during the intake stroke (in order to form a homogeneous, premixed, lean mixture) and during the compression stroke (creating a slightly rich mixture near the spark plug) to form a weak stratification [18]. As a result of HOS mode, excessively lean regions, which can result in flame extinction, are avoided. The near-stoichiometric region at the spark gap, as a result of the second injection, promotes good early flame development, leading to more stable combustion [18]. By splitting the total amount of fuel into two separate pulses, both charge cooling and knock suppression can also be achieved. Charge cooling allows a higher compression ratio to be employed in relation to conventional gasoline engines as a result of a lower charge temperature, thus improving thermodynamic efficiency [19, 20]. Specifications of the engine are listed in Table 1. A schematic diagram depicting the experimental set-up is shown in Figure 1. The engine test bed utilises a Schenck W150 eddy current dynamometer with a CADET V12 engine dynamometer control system.

Table 1. GDI Test Engine Specifications

Bore (mm)	77.0
Stroke (mm)	85.8
Displacement (cm^3)	1598
Compression Ratio	10.5:1
Rated Power (kW)	130 @ 6000 rpm
Rated Torque (Nm)	240 @ 4000 rpm
BMEP (kPa)	1887

Fuel

To ensure repeatability of the engine testing, and to eliminate the batch-to-batch variability of pump-grade gasoline, a reference test gasoline was used throughout the test program. The fuel used was a Euro IV certified reference

test fuel. Some key specifications of the test fuel are shown in [Table 2](#).

Table 2. Reference Test Fuel Specifications

Density (kg/litre)	0.75
Research Octane Number	96.5
Volume of Aromatics (%)	31.8
Reid Vapour Pressure (kPa)	57.8
Carbon Content (% mass)	86.01
Hydrogen Content (% mass)	13.09
Oxygen Content (% mass)	0.90

Particulate measuring system

The engine test bed system was equipped with a Signal gaseous exhaust emission analyser system along with a Cambustion DMS-500 fast-response particulate spectrometer for exhaust nano-particle measurement. A heated Signal selector switch valve, maintained at 190 °C, allowed the user to sample either pre- or post-TWC exhaust (i.e. either engine-out or tailpipe-out exhaust samples). The Cambustion DMS-500 provides a number / size spectrum for solid and non-solid particles in the diameter range between 5-1000 nm [21]. For the purpose of this study the size spectrum was divided into the following five size ‘bins’: 5-23 nm, 23-50 nm, 50-100 nm, 100-300 nm and 300-1000 nm diameter. These bins were chosen to represent the two main modes of PM, NM (< 50 nm) and AM (> 50 nm). A sample of the engine exhaust gases is drawn into the DMS-500 through a 5 m heated line, maintained at 58 °C. A scroll-type vacuum pump draws the sample through an electrically conductive tube, within which the particles become ionised. A central, high-voltage rod within the classifier column deflects the charged particles toward 22 grounded electrometer rings via electrical repulsion [22]. Particle landing position is a function of its charge and aerodynamic drag, from which its size may be inferred [22]. The DMS output is a matrix of particle number concentration as a function of particle diameter and time. Due to the sensitivity of the instrument to noise and background particle levels, a bi-lognormal output is generated which separates the NM from the AM particles. The bi-lognormal fit eliminates noise at both the high and low ends of the measured raw particle spectrum. The particle number concentration matrix is averaged over the duration of the measurement to yield a plot of mean concentration versus particle diameter, which can then be integrated to obtain the total particle number concentration emitted by the engine [23]. Within the DMS-500 there are two dilution stages: primary and secondary dilution. The primary dilution ratio (DR) is kept constant at five and the secondary DR can be varied from 20 to 500, as shown in [Figure 2](#). The secondary dilution is performed at constant temperature. A secondary DR of one can also be employed. To prevent the condensation of water vapour in the exhaust sample, the DMS-500 applies dry, compressed air at the point of

sampling (1st dilution stage) to reduce the partial pressure of water in the exhaust [24]. The dilution air is first passed through a high efficiency particulate air (HEPA) filter to remove airborne particles. The secondary dilution stage utilises a rotating disk diluter. The rotating disk transfers particle laden gas from the exhaust stream to the inlet of the DMS-500 sample column. The frequency of this gas transfer determines the DR. The remaining exhaust gas that is not transferred passes through a HEPA filter and is mixed with the transferred particle laden exhaust gas, as shown in [Figure 2](#). This secondary dilution does not introduce fresh air so the composition of the exhaust gas does not change. The prevention of condensation of water vapour is further assisted by the sampling head and line operating at a constant sub-atmospheric pressure (250 mbar absolute pressure - alleviating the issue of pressure fluctuations), and elevated temperature (58 °C). Pre-heating of the primary dilution air to the temperature of the heated line means that the engine aerosol is rapidly ‘cooled’ to the temperature of the line, thus reducing thermophoresis [24]. The use of electrically conductive tubing in the sample line prevents problems caused by static electricity, and the rapid transit time in the sample line reduces the likelihood of particle agglomeration [24]. Dilution at the sampling point reduces particle concentration, hence reducing the chance of agglomeration.

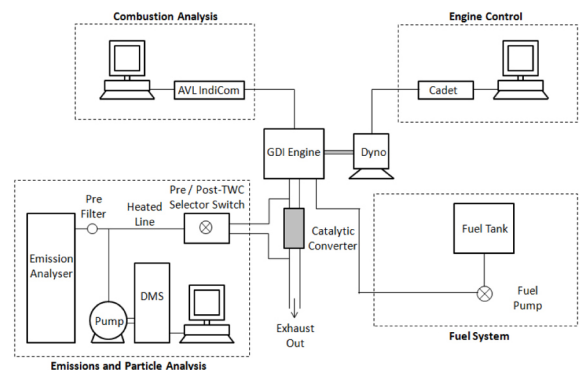


Figure 1. Test cell layout and control systems

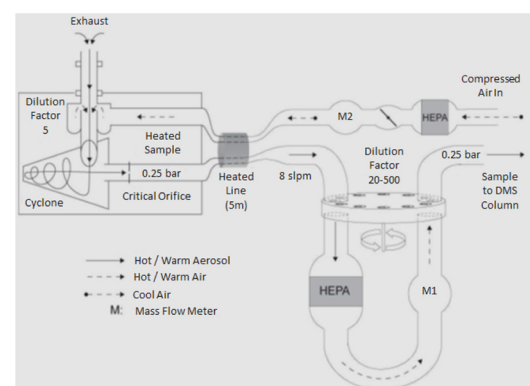


Figure 2. Cambustion DMS-500 dilution system [24]

Test method

All experiments were carried out under cold-start conditions. In this study, this involved engine coolant and oil temperatures of 20 °C prior to engine start-up. Exhaust temperature was measured post-TWC. The engine was allowed to warm-up at a constant engine speed of 900 rpm (representative of idle conditions after cold-start) and 10 Nm dynamometer load (0.79 bar BMEP, typical of auxiliary loads) to ensure stability and control of the engine operation. The engine warm-up characteristics were controlled by the engine control unit, i.e. double injection with standard spark advance. No catalyst heating strategy is employed. The cold-start test was carried out over a 15 min period, i.e. until the engine coolant temperature had reached ~75 °C. Pre- and post-TWC tests were performed on separate days to ensure the engine temperature had stabilised overnight to cold-start conditions. All instruments were set to log the data as soon as the engine started to ensure the initial PM emissions were recorded. The CADET V12 and dynamometer system could control the engine speed within ± 2 rpm and the load within ± 0.5 Nm. Three exhaust sample DRs were tested in this study, i.e. total DRs of 5, 100 and 150. The instrument was auto-zeroed before each test. During the auto-zero, the rotating disc diluter system is stopped so that all the air flow into the classifier is HEPA filtered [25]. The true instrument noise base is measured and recorded so it can be applied to the bi-lognormal fit.

A statistical analysis of the repeatability of the PM measurement system was performed over three separate days. Five consecutive tests, each of 3 min duration, were performed at fully warmed up conditions. Tests were performed pre- and post-TWC at a total DR of 100. The Coefficient of Variance (CoV) is used as a measure of repeatability. Table 3 shows the pre- and post-TWC CoV data of the repeatability study. It can be seen that the PM measurements are very repeatable, with a variation of no more than 8.70 % for pre-TWC particle number density measurements, and no more than 4.39 % for the post-TWC particle number density measurements. In terms of the size bins, the 23-50 nm, 50-100 nm and 100-300 nm size ranges had the lowest CoV; the 5-23 nm and 300-1000 nm had the highest CoV.

Table 3. Repeatability Test CoV Data

Test Description	Pre-TWC	Post-TWC
CoV – Day 1 (%)	8.70	3.84
CoV – Day 2 (%)	2.91	2.57
CoV – Day 3 (%)	2.70	4.39
Day-to-day CoV (%)	6.72	7.23

RESULTS AND DISCUSSIONS

To study the effect of a TWC on nano-scale PM from a GDI engine operating under cold-start conditions, and to gain an insight into TWC efficiency during cold-start, pre- and

post-TWC exhaust emissions were sampled and analysed in terms of particle number density, size distribution, and estimated total mass. Nano-scale PM, measured using the Cambustion DMS-500 fast-response particle spectrometer, in the range of 5-1000 nm equivalent diameter were grouped into five particle size ranges for this investigation: 5-23 nm, 23-50 nm, 50-100 nm, 100-300 nm and 300-1000 nm diameter. Plots showing particle number density use a logarithmic scale y-axis due to the large range of values covered by the five particle size ranges studied. Figure 3 shows post-processed, moving-average, data plots for a typical cold-start. The moving-average plots are based on ten-second time-interval-average data for the duration of the cold-start test, with the main reason for this type of plot being readability and clarity for the reader. All of the following figures show cold-start test results at a total DR of 100, except for Figures 13, 14, 15 which shows the effect of DR on pre- and post-TWC particle number density during a cold-start. A single DR was chosen for the comparison of pre- and post-TWC as the effect of the TWC on PM is the main focus of this study.

The effect of the TWC on nano-scale PM is characterised by the trapping efficiency (TE), which is defined as follows:

$$TE = \left(\frac{(Pre-TWC \text{ PM No.Density}) - (Post-TWC \text{ PM No.Density})}{Pre-TWC \text{ PM No.Density}} \right) \times 100 \% \quad (3.1)$$

For example, in terms of particle number density, positive TE indicates a decrease in particle number density after the TWC, i.e. the TWC either traps particles or causes particles to agglomerate, reducing the total number density. This agglomeration can also cause a negative TE for a given size range, i.e. there may be more particles of a particular size range after the TWC due to agglomeration

Particulate Matter Characteristics

Both pre- and post-TWC particle number density measured during a 15 min cold-start test are presented in Figure 3, which also plots exhaust gas temperature. It is clear from the two PM plots that there is a significant difference between the pre- and post-TWC PM emissions. The steady-state level of the pre-TWC particle number density is $\sim 1.2 \times 10^6$ N/cc (number/cc). It takes up to 450 s for this steady-state level to be reached. The post-TWC steady-state particle number density level is $\sim 3.2 \times 10^5$ N/cc, which is reached more rapidly, after ~ 120 s. From these two plots it can be concluded that, for identical cold-start engine operating conditions, the post-TWC particle number density is considerably lower than the pre-TWC particle number density. It is also clear that the steady-state level is reached significantly faster for the post-TWC PM than for the pre-TWC PM. This phenomenon holds true for all of the dilution ratios tested, signifying that the PM results are repeatable,