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Effects of high octane additivated gasoline fuel on Three Way Catalysts performance under an accelerated catalyst ageing procedure

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Abstract

The adoption of high octane rating fuels in Gasoline Direct Injection (GDI) engines helps to improve fuel economy and thus reduce CO_2 emission. However, there is scarce literature regarding the impact of additives used in high octane rating fuels on the performance and durability of the exhaust aftertreatment components. This work investigates the effects of using an aniline (aromatic amine) octane enhancer added to a commercial gasoline fuel on the activity of a commercial Three Way Catalytic Converter (TWC) coupled to a GDI engine. TWC's capability in abating gaseous and particle emissions is studied for both the additivated and the baseline fuel during and after a fuel-induced accelerated catalyst ageing procedure. The accelerated catalyst ageing procedure is developed aiming to identify the impact of the engine fuel on the catalyst poisoning, while limiting catalyst thermal deactivation.

CO and NO conversion efficiencies in the TWC were close to 100% under the steady-state and transient stoichiometric engine operation for both fuels during and after the catalyst ageing procedure. There was a minor decrease (generally <10%) in the catalytic conversion efficiency of total HC for the additivated fuel, but not being significant to reflect any TWC chemical deactivation. The aniline type octane enhancer additive did not produce any detrimental effect on the TWC efficiency/performance. This investigation demonstrates that fuels being designed to promote a more efficient GDI engine operation can also enable the reduction of vehicle tailpipe CO_2 and pollutant emissions through synergies with the TWC for cleaner road vehicles.

Keywords: fuel; three way catalyst; catalyst ageing; gaseous emissions; particulate matter; aromatic amines

Nomenclature

aTWC: after Three Way Catalyst

BEVs: Battery Electric Vehicles

bTWC: before Three Way Catalyst

CAD: Crank Angle Degrees

CO: Carbon Monoxide

COV: Coefficient Of Variation

DVPE: Vapour pressure

E: Evaporated

EC: EU Commission Regulation

ECU: Engine Control Unit

ETBE: Ethyl Tertiary-Butyl Ether

EU: European Union

FTIR: Fourier Transform Infrared Spectroscopy

Fuel A: Additivated Fuel

Fuel B: Reference Fuel

GDI: Gasoline Direct Injection

GHG: Greenhouse Gases

GHSV: Gas Hourly Space Velocity

ICE: Internal Combustion Engines

IMEP: Indicated mean effective pressure

MON: Motor Octane Number

MTBE: Methyl Tertiary-Butyl Ether

NO_X: Nitrogen oxides

R: Constant catalyst thermal reactivity

RON: Research Octane Number

SMPS: Scanning Mobility Particle Sizer

t_e: number of equivalent hours

t_h: number of hours to complete a fixed distance

THC: Total Hydrocarbons

T_v: pre-TWC temperature

TWC: Three Way Catalyst

1. Introduction

A European Union (EU) long-term goal is the ambition of climate neutrality by 2050 (e.g. EU Energy Roadmap 2050) which motivates decarbonisation of the transport sector [1]. Passenger cars are forecasted to evolve towards battery electric vehicles (BEVs). However, a scenario where the utilisation

of ICE, as part of hybrid electric vehicles, in half of the vehicle fleet is predicted to lead to the same reduction in greenhouse gases (GHG) as converting the whole fleet to BEVs [2]. It is expected that ICE, and particularly efficient Gasoline Direct Injection (GDI) engines [3][4], to remain dominant [3] to fulfil the global transport demand in the foreseeable future. The use of more efficient and cleaner fuels, fuel blend components and fuel additives can contribute to the engine fuel economy improvement as well as GHG and pollutant emissions reduction. Octane rating is a key fuel property to enable utilising high compression ratio engines in order to improve performance and efficiency [5]. Octane improvers (antiknock agents) are classified into fuel components (e.g. isoparaffins [6], olefins [7], alcohols [8], ethers [9][10][11], esters [12], ketones [13], carbonates [14]) when the compound is generally present in more than 2% vol., and fuel additives (e.g. anilines [15] [16], amines [17], N-nitrosamines [18], phenols [19]). The use of fuel additives, being effective when used in lower amounts compared to fuel components, is considered a practical and economic approach. Therefore, investigating combinations of the most promising octane booster additives with high-octane components is recommended to obtain high-octane gasoline that is technically, economically, and environmentally viable [20].

The first antiknock agents were tetraalkylated lead compounds, but both health and environmental toxicity and the deteriorating impact on vehicle catalyst led to their usage prohibition [21][22]. Metallic anti-knock agents, such as methylcyclopentadienyl manganese tricarbonyl and ferrocene can be used at lower concentrations compared to lead compounds, but they tend to result in ash deposits in engine components after their combustion. Aniline-like compounds (aromatic amines) are known by their antiknock activity related to the abstraction of the amino hydrogen atom by reactive radical species and being ash-less [23][24][25]; while their application has been often limited by their potential toxicity. A recent study has classified anilines as one of the most promising fuel additives to be incorporated in future gasoline formulations, accounting for their antiknock effectiveness, side effects on the engine, possible effects on human health and the environment, and compatibility with existing infrastructure [20]. N-methyl-p-anisidine, N',N'-diethyl-2-methyl-p-phenylenediamine and N-nitroso-diphenylamine have been identified between more than 8 million aniline-like compounds considering reactivity as well as environmental and toxicological risks [26]. It has been also recently demonstrated that the

95 incorporation of aniline as an octane enhancer to a modern gasoline fuel leads to an increase in vehicle
96 power, a decrease in the time required for acceleration, and a reduction in fuel consumption [27].

97 Catalytic components have been used in exhaust aftertreatment systems for around five decades to abate
98 vehicular emissions, and prevent them to be released to the atmosphere such as the Three Way Catalyst
99 (TWC) [28]. Maintaining the aftertreatment system's designed performance during its whole
100 operational life is a key to fulfil emissions regulations and reach the targeted positive impact on air
101 quality and climate change. In GDI engines the TWC durability in abating emissions depends on the
102 level and nature of engine-out species (including inhibitors/promoters [29][30], poisons, and
103 impurities), the exhaust gas/catalyst temperatures, the species' residence time within the aftertreatment
104 system, and the fluctuations in temperature, gas phase composition and flow rates. The TWC's
105 deactivation/ageing is linked to changes in the catalyst structure and state leading to the
106 deactivation/loss of active sites from the monolith surface and consequently to the deterioration of the
107 catalyst performance. A long-term exposure to high temperatures, high temperature gradients, and rich
108 and lean air-fuel ratio variations within the catalysts are the main factors leading to the substrate and
109 washcoat damages (thermal ageing) [33][34], and thus a loss in the catalytic activity. The major thermal
110 ageing mechanisms include thermal degradation (at around 800-900 °C) and sintering of the catalytic
111 active centres (at above 600 °C). Chemical ageing of the catalyst is generally caused by the
112 accumulation of non-desirable species, derived from fuels, lubricants and additives, on the catalytic
113 surfaces, and/or the suppression of its oxygen storage capacity. Sulphur in the fuel and/or lubricants has
114 been commonly identified as a non-desirable specie reducing the performance of the exhaust
115 aftertreatment components, e.g. NO_x adsorbers for lean GDI engines [35]. There are also other fuel
116 additives (e.g. lead and manganese), and wear inhibitor oil additives (e.g. Zinc dialkyldithiophosphates
117 [36]) considered as strong catalyst deactivators. However, the impact of advanced octane enhancement
118 additive compounds used in modern fuels on the performance and durability of the exhaust
119 aftertreatment components has not been extensively studied.

120 Legislators, researchers, and original equipment manufacturers have been working on developing
121 procedures to shorten the catalyst durability testing time by implementing alternative methods for

accelerated aging of catalysts [32]. The developed methodologies as well as most of the studies on aftertreatment durability have been mainly focused on high temperature (thermal) ageing, as it is being considered the dominant ageing mechanism. However, with the exhaust gas temperature being progressively reduced over the years due to the development of the more efficient GDI engine technology, it is of interest to separately investigate an accelerated chemical ageing procedure focused on the effects of compounds that the catalyst is exposed to.

This work investigates the impact of using small concentrations of an advanced aniline derivative octane enhancer additive in a modern gasoline fuel on the GDI engine combustion and emissions characteristics, as well as the performance of a commercial TWC. A newly designed accelerated catalyst ageing procedure with the main focus on chemical ageing is utilised to study the potential synergies/interactions between the additivated high octane fuel and the TWC at different ageing stages. Moreover, the transient response of the TWC to changes in its inlet gas coming from the engine during the ageing procedure is examined. Additional objectives are to evaluate the size-resolved removal efficiency of exhaust particle emissions by the TWC and the impact of the fuel on light-off characteristics of the scaled-down TWC at the initial (fresh) and final stages (aged) of the ageing procedure. All of the results are compared to those obtained when running on a baseline gasoline fuel.

2. Material and Methods

2.1 Gasoline Direct Injection Engine

The engine was a 2-L four-cylinder turbocharged GDI engine. The main engine specifications and a schematic of the experimental setup are shown in Table 1 and Figure 1, respectively.

2.2 Fuels and Catalysts

The two fuels used in this study were provided by Repsol, both meeting the specifications for winter gasoline EN-228. Fuel B (baseline) is a commercial type gasoline representing the grades distributed in Spain (98 RON). Fuel A (additivated) is a modification of the 98 RON commercial gasoline (Fuel B) by only adding an aniline derivative octane additive (< 0.7% v/v), with a target of 100 RON. It has to be noted that the octane booster is added to a base fuel which already contained a high octane rating

148 component, i.e. ethyl tertiary-butyl ether (ETBE). The additive has a high efficiency to increase RON,
149 while it does not considerably change any other key fuel properties/characteristics as it can be seen in
150 Table 2. Two commercial full scale and two scaled-down TWCs were used for this study (Table 3).
151 Details about how these catalysts were tested are provided in sub-section 2.4.

152 *2.3 Instrumentation*

153 Engine speed and torque, critical fluid temperatures and data acquisition for a variety of analogue
154 signals were managed by the CADET control software from Sierra CP Engineering. The engine
155 manufacturer provided a development engine control unit (ECU), which enables access to the engine
156 calibration settings and sensors reading via Accurate technologies vision software. To acquire data from
157 the ECU, a controller area network hub was used. For this work the engine was operated with the
158 standard ECU calibration settings for both fuels (e.g. same injection, spark and valve timings).

159 Fuel consumption was measured with Rheonik RM015 Coriolis fuel flow meter (±0.12% accuracy).
160 The fuel temperature was controlled by a Sierra CP Engineering fuel conditioning unit, and was
161 maintained at 28 °C for all the tests. An AVL piezo-electric pressure transducer and an AVL charge
162 amplifier were employed to measure in-cylinder pressure for fuel combustion analysis. In-cylinder
163 pressure values were referenced to each 0.5 crank angle degrees (CAD) using a crankshaft encoder. The
164 in-cylinder pressure was referenced to the intake manifold pressure at the intake bottom dead centre
165 using an absolute pressure transducer located in the intake runner close to the port entry. In-cylinder
166 pressure, real time indicated mean effective pressure (IMEP), coefficient of variation (COV) of IMEP,
167 peak pressure and position of peak pressure were acquired through in-house LabVIEW. Mass fraction
168 burnt was obtained using a custom Matlab post-processing script.

169 A 2030 MKS Fourier Transform Infrared Spectroscopy (FTIR) was used to measure the gaseous
170 exhaust species emitted from the engine (engine output or before the TWC, bTWC) as well as after the
171 TWC (aTWC) to calculate TWC conversion efficiency. The gaseous species included, but not limited
172 to, CO, NO_x, NH_3, CH_4 and total hydrocarbons (THCs). The gas sample was heated and maintained at
173 191 °C to prevent any water and HC condensation. A TSI Scanning Mobility Particle Sizer (SMPS)

was employed to measure particle size distributions before and after the TWC. The SMPS is composed of a series 3080 electrostatic classifier, a 3081 Differential Mobility Analyser and a 3775 Condensation Particle Counter. An ejector diluter was employed to dilute the exhaust gas by air before entering into the SMPS. The dilution air temperature was kept constant at 150 °C in order to avoid hydrocarbon condensation and nucleation.

2.4 TWC ageing procedure

The fuel effects on the TWC performance was evaluated under an accelerated ageing procedure. The procedure was designed based on the TWC durability tests established by the EU Commission Regulation (EC) No 692/2008 implementing and amending Regulation (EC) No 715/2007 of the European Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles [37][38]. The cycle is shown in Figure 2 and further details can be found in Table 4.

The standard cycle estimates the number of equivalent hours (t_e) to carry out the accelerated ageing tests based on the number of hours to complete a fixed distance, that in this case has been selected as 160,000 km (t_h); a pre-TWC temperature, in this case 500 °C (T_v); and a constant catalyst thermal reactivity of 17,500 (R) as specified in the standard (see Equation 1). The number of hours was calculated assuming a vehicle speed of 80 km/h. According to Equation 1, the duration of the ageing test can be reduced by increasing the catalyst inlet temperature. However, as the aim of the present work is to study the potential catalyst chemical ageing effect of the high octane rating additive, very high catalyst inlet temperatures were avoided as this can result in catalyst thermal ageing, hindering the effects of the fuel properties on TWC durability. A T_r pre-TWC temperature of 650 °C was chosen resulting in a value of 50 h (t_e) of engine running to perform the accelerated ageing tests. Rapid pre-catalyst rich and lean air/fuel changes by the combination of rich engine operation and external air addition were implemented as suggested in the standard, Figure 2. The cycle was repeated for the total duration of 50 hours.

$$t_e = t_h exp\left[R \cdot \left(\frac{1}{T_r} - \frac{1}{T_v}\right)\right] \quad \text{Equation 1}$$

The engine condition selected for applying the standard cycle was 60 Nm, approximately 3.8 bar brake mean effective pressure, and 2100 rpm, at which engine operation stability and the pre-TWC target temperature were achieved. The internal exhaust gas recirculation technique was applied using the methods developed by the original equipment manufacturer. The engine intake air temperature was maintained at 45 ℃ while the coolant and oil temperatures were 95±0.5 °C and 99±2 °C, respectively for both fuels.

In order to achieve the target timings in the ageing procedure, an in-house Matlab script was developed and was linked to the ATI Vision to ensure that the automated sequence is repeated accurately (see Table 4). An Arduino microcontroller was used for accurate timing of the air injection in both main exhaust and reactor fitted in the furnace (Figure 1).

To carry out the tests for the two fuels, two full scale TWC were used (one per fuel) and fitted in a customised stainless steel canning (Figure 1). The exhaust gas temperatures before and after the TWCs were monitored using k-type thermocouples. The gaseous emissions measurements before and after the TWCs were recorded every hour during the ageing procedure. The conversion efficiency of various species in the TWC was assessed at steady state conditions every 5 hours of ageing.

The two scaled-down TWCs were used in parallel to investigate the ageing effects on the TWC light-off activity. They were placed in a stainless-steel reactor inside a furnace to control temperature and flow rate as shown in the experimental setup schematic (Figure 1). To mimic the operating conditions of the full scale TWCs and obtain comparable ageing effect for scaled-down cores, the gas temperatures at the inlet of the scaled-down TWCs and gas hourly space velocity (GHSV) for the cores were controlled during the tests. A small portion of engine-out exhaust gas was passed through the cores to maintain the GHSV at 40000 h^{-1}. The calculation of the GHSV is based on Equation 2:

$$\text{GHSV}\ (\text{h}^{-1}) = \frac{1}{\text{Contact time (h)}} = \frac{\text{Feed rate}\ (\text{m}^3\text{h}^{-1})}{\text{Catalyst bed volume}\ (\text{m}^3)} \quad \text{Equation 2}$$

The light-off activity of the scaled-down TWC was investigated at the beginning (0 hour) and at the end (50 hour) of the ageing process. The procedure to study the light-off activity was as follows: i) the gas temperature at the inlet of the cores was initially maintained at 100°C, ii) once the engine reached a steady-state condition, part of the exhaust stream was directed through the cores, iii) the gas temperature was then increased with a ramp-up of 10 °C/min until 300 °C, at which CO and NO conversion efficiencies were approximately 100%.

3. Results and Discussion

3.1 Combustion analysis

Combustion characteristics of the two fuels were studied through in-cylinder pressure and mass fraction burnt traces (see Figure 3 left and right, respectively) at stoichiometric steady state engine condition (2100 rpm, 60 Nm). There were no significant differences in the fuel combustion process under the engine operating condition at which the ageing cycle was implemented. Therefore, it is believed that any possible differences in emissions and TWC performance when using fuel A, compared to fuel B, were not due to the combustion process, as their combustion characteristics were similar.

3.2 Gaseous emissions: TWC performance at the steady-state stoichiometric condition

Regulated gaseous emissions such as carbon monoxide (CO), nitrogen oxides (NO_x) and total hydrocarbons (THC) have been analysed (Figure 4). These results are obtained by specifically operating the engine at stoichiometric steady state engine operation (2100 rpm, 60 Nm) for the purpose of the analysis. In addition, methane (CH_4) as one of the most challenging hydrocarbon species to be catalytically oxidised [39][40], with a global warming potential of >20 times higher than CO_2 (over a 100 years period) [41], has been discussed. Stoichiometric engine-out emissions results, particularly for CO and NO_x, showed small variations during the 50 hours of the ageing tests for each fuel, which supports the repeatability of the experimental conditions (within 5-10%). Engine-out carbonaceous emissions of CO, CH_4, and THC for fuel A (high octane rating fuel) were slightly lower (approximately 5%) than those for fuel B, while there were no significant differences in engine-out NO emissions. These gaseous emissions results show a positive impact of the additive on the completion of the fuel

oxidation process. This positive impact is thought to be mainly induced by the chemical effect of the additive as in-cylinder pressure and rate of heat released traces were not significantly different compared to those of fuel B.

Gaseous emissions aTWC are shown in Figure 5. It has to be noted that the emissions levels for both fuels remained at very low levels (under 80 ppm for CO and THC and below 10 ppm for NO emissions) during the entire 50 hours duration of the ageing procedure. The results also show a slightly increasing trend with time in aTWC THC gaseous emissions for fuel A, while there is not a clear trend in the case of emissions for fuel B. The combination of the results shown in Figure 4 and Figure 5 evidence CO and NO TWC conversion efficiencies close to 100% for both fuels during the whole accelerated catalyst ageing procedure. There was a small decrease in catalyst conversion efficiency for THC for Fuel A and for CH_4 emissions for both fuels with the ageing time of the catalyst. It is thought that this small decrease in TWC conversion efficiency of unburnt HC is related to the TWC's oxygen storage capacity and not to any additive-induced catalyst deactivation which would have resulted in much larger losses in TWC activity. This is further explained in section 3.4 (TWC performance during the ageing cycle). In any case, THC conversion efficiency was kept approximately 90% for both fuels after the representative number of equivalent hours estimated from the standard cycle to study any potential chemical deactivation. Therefore, there is no evidence of TWC deactivation during the developed accelerated catalyst ageing procedure.

3.3 Particle emissions: TWC performance at the steady-state stoichiometric condition

Figure 6 illustrates the particle size distributions measured before and after the TWC at stoichiometric steady state engine condition (2100 rpm, 60 Nm). The relative difference between them is also calculated and denoted as particle reduction (removal) efficiency (Fuel A in blue and Fuel B in red colour). Results show that particle concentration levels for fuels A and B were similar, while being slightly lower (approximately 3% in terms of total particle concentration) for the case of the higher octane rating fuel (Fuel A). This lower particle emissions is consistent with the slightly lower levels of engine-out gaseous carbonaceous emissions discussed in section 3.2. The abatement of the number of particles along the TWC was larger for small particle sizes (approximately 50% for particle sizes below

10nm), while it was in average approximately 10% across larger particle sizes. A similar trend was observed for both fuels, though the TWC particle abatement efficiency for the additivated fuel was slightly larger than for the baseline fuel. Similar TWC particle abatement efficiencies have been reported [42], being attributed to the removal of some hydrocarbon species which can nucleate and form small particles as well as some particle losses (mainly particle diffusion losses) along the TWCs, especially noticeable for smaller particles [43].

Figure 7 shows the particle emissions measured before and after the TWC and their reduction efficiency after applying the ageing procedure for both fuels (50 hours). Similar to the particle emissions levels at the start of the tests and carbonaceous emission results, the engine-out particle emissions level for Fuel A was slightly lower than the case of the base fuel. The effect of the aged TWC on particle levels was similar to that of the TWC before applying the ageing procedure, as it can be seen from the same particle reduction efficiencies in terms of pattern and values. Therefore, it can be concluded that the ageing procedure has not affected the ability of the TWC in removing particles.

The comparison of the results shown in Figure 6 and Figure 7 indicates that particle removal efficiency has not been affected by the ageing procedure. Particle removal efficiency over the TWC for small particles (smaller than 10nm) was higher than that of larger particles for both fuels, which is a characteristic of diffusion particle losses [44][45]. In addition, particle reduction efficiency for smaller particles showed a larger dispersion than in the case of larger particles. This is believed to be due to the lower particle concentrations and greater variability of nucleation mode particles (both bTWC and aTWC).

3.4 Gaseous emissions: TWC performance during the ageing cycle

Gaseous emissions bTWC and aTWC were measured every hour during the catalyst ageing procedure shown in Figure 2 (engine operation at stoichiometric 0-40 s, rich 41-45 s, rich with air injection in the exhaust 46-55 s, and stoichiometric with air injection 56-60 s) for both fuels. This allows to assess the fuel effects on emissions formation and catalyst performance under non-conventional (large variations in lean and rich pre-catalyst conditions) and transient catalyst operating conditions at different stages of the ageing procedure.

A representative example of bTWC and aTWC gaseous emissions corresponding to the catalyst ageing cycle are shown in Figure 8 and Figure 9, respectively. In this particular case, emissions values were recorded after 10 hours of the catalyst ageing procedure. During the cycle, at the engine stoichiometric condition (from 0 to 40 s) engine-out CO, THC and NO emissions (Figure 8) were at similar levels to those emitted at the steady-state engine condition used to evaluate the catalyst activity at every 5 hours as shown in Figure 4. Engine-out CO and THC emissions for the higher octane rating fuel were slightly lower than those for Fuel B, while there were no significant differences in engine-out NO emissions. Moreover, similar to results in section 3.2, aTWC emissions were very low (Figure 9) for both fuels indicating that the catalyst was working very efficiently at the stoichiometric condition (from 0 to 40 s).

As expected, when the GDI engine condition was changed to rich operation (from 41 to 45 s), engine-out CO and THC emissions significantly increased (doubled up and 50% increase, respectively), while engine-out NO and oxygen (not shown here) levels decreased (Figure 8). These changes in the pre-TWC emissions produce an unbalanced level of reactants, which affects the TWC performance. The aTWC CO and THC levels (Figure 9), significantly increased due to their inefficient oxidation in the TWC as a result of the decreased levels of NO_x and oxygen. NO emissions remained at very low levels (below 10 ppm, Figure 9) as there was an increased level of CO and THC that catalytically reduced NO_x emissions.

Then, the air injection in the exhaust bTWC was activated (from 46 to 55 s). Engine-out emissions did not change as the engine was kept under the same rich operation (Figure 8). The injection of air bTWC led to a significant increase in aTWC NO emissions (Figure 9) due to the competition between NO and oxygen to react with CO and THC within the TWC. Finally, the engine operation was changed to the stoichiometric condition while maintaining the pre-TWC air injection, which significantly reduced engine-out and aTWC CO and THC emissions.

Figure 10 shows the evolution of the conversion efficiency of gaseous emissions over the TWC during the whole ageing experiments, when the engine was running under the stoichiometric condition with no pre-TWC air injection. This engine and catalyst condition is comparable to the steady-state condition

328 analysed in section 3.2. However, in this case the data was taken from the transient ageing cycle (the
329 stoichiometric part) and thus is subject to the quick variations of the engine and catalyst conditions (e.g.
330 rich, lean and stoichiometric operation) which might affect the state of the TWC active sites. CO
331 (approximately 97%) and NO (approximately 99%) conversion efficiencies were very high for both
332 fuels for the entire duration of the ageing procedure. A slight reduction in THC, and CH_4, conversion
333 efficiency was observed for both fuels while the conversion efficiency for Fuel A (approximately 92%)
334 was generally lower than that for Fuel B (approximately 96%). The results and findings are comparable
335 to those obtained when the steady-state stoichiometric operating condition was evaluated (section 3.2),
336 indicating that the small reductions in conversion efficiency during the ageing procedure are not
337 significant to demonstrate any catalyst poisoning or deactivation.

338 TWC conversion efficiency has also been evaluated under the rich engine operation stage of the ageing
339 cycles (Figure 11). NO conversion efficiency was always 100% (not shown), while lower values of
340 conversion efficiency were recorded for CO and THC. There seemed to be a decrease in CO and THC
341 conversion efficiency along the ageing cycle performed on the same day (see Figure 11). It is thought
342 that the rich operation during the ageing cycle decreased the catalyst oxygen storage capacity and as a
343 result it reduced the catalyst performance under the rich condition at the later hours on the same day. In
344 the following day and at the start of the tests the catalyst conversion efficiency levels were partially
345 restored. The decrease in rich-phase catalyst performance was observed for both fuels reassuring that
346 such deterioration in TWC performance was not due to the fuels (additive package), but because of the
347 challenging catalyst conditions imposed by the ageing cycle.

348 *3.5 Light-off studies of the scaled-down TWCs*

349 Results presented in the previous sections were used to evaluate the catalyst performance at a
350 temperature (approximately 650 °C) beyond the catalyst light-off temperature. This section provides
351 the TWC performance results (in terms of CO conversion efficiency as a representative example) over
352 a wider and lower temperature range enabling to understand the fuel impact and TWC ageing effects
353 on the catalyst light-off performance. These conditions are relevant to the cold start engine operation.

Figure 12 shows similar CO TWC light-off activity for both fuels before the ageing procedure. These results support that the differences in the emissions levels for Fuel A and B do not significantly affect TWC light-off and conversion efficiency. Figure 12 also enables the comparison of the light-off characteristics of the two TWCs (for fuel A and B) at the end of the accelerated ageing procedure. Consistent with the full-scale catalyst study, no sign of deactivation was observed, given the similarity in CO light-off temperatures for the two TWCs. These results support the non-significant catalyst deterioration during the ageing procedure for both fuels as well as the absence of any potential TWC poisoning induced by the additive.

4. Conclusions

An accelerated catalyst ageing method on a GDI engine has been designed aiming to investigate the effects of an advanced aniline octane booster additive incorporated to a gasoline fuel on the TWC performance. The ageing method has been designed with the focus to study TWC chemical ageing while preventing thermal deactivation.

CO and NO TWC conversion efficiencies remained at ~99% over the duration of the accelerated ageing procedure under steady-state and transient stoichiometric engine operation for both fuels. There was a small decrease in the steady-state and transient stoichiometric TWC THC conversion efficiency; however, such decrease was not significant to evidence TWC chemical deactivation as a result of using the additivated fuel. The TWC light-off performance was also studied before and after the ageing procedure. No sign of deactivation was observed supporting the non-significant catalyst performance deterioration during the ageing procedure for both fuels.

This investigation demonstrates that fuels being designed to promote a more efficient/flexible GDI engine operation can also enable the reduction of vehicle carbon footprint (CO_2 emissions) and tailpipe pollutant emissions (through synergies with the aftertreatment) for cleaner road vehicles. The newly designed high octane rating fuel, containing the aromatic amines, has demonstrated no detrimental effects on the TWC performance over the accelerated catalyst ageing tests. This has been corroborated at a large scale with the successful conclusion of commercial pilot phase of the fuel at three petrol stations and its usage in various vehicles over the years with no reports of deteriorating effects.

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498 **List of Figures**

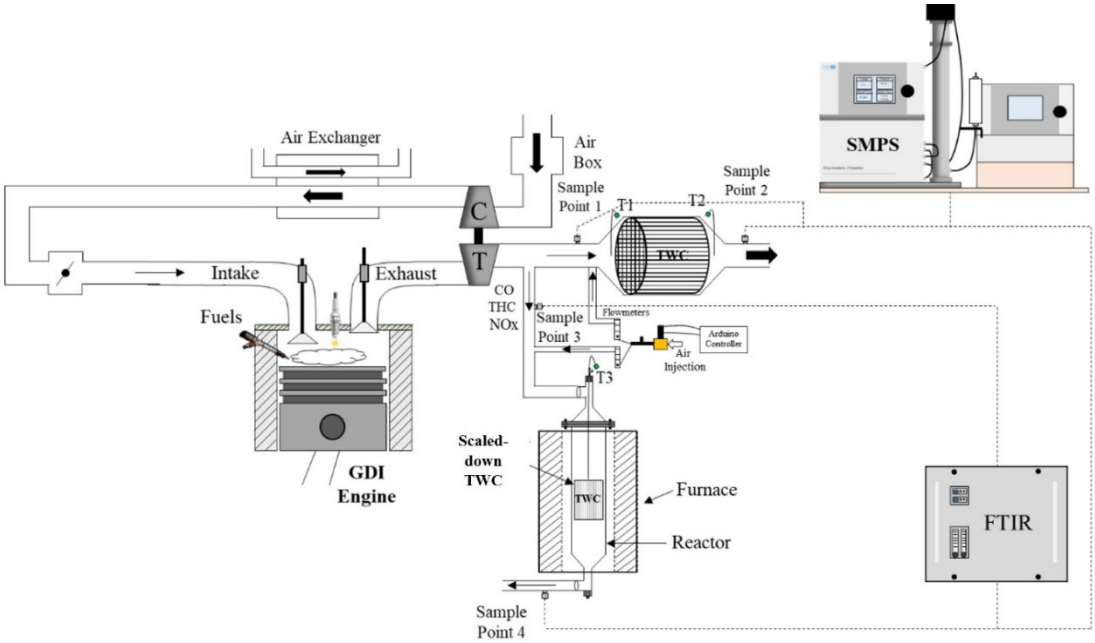
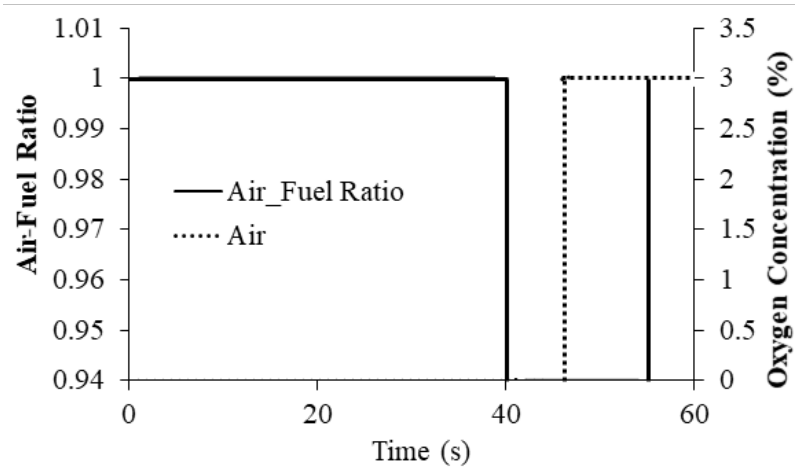


Figure 1



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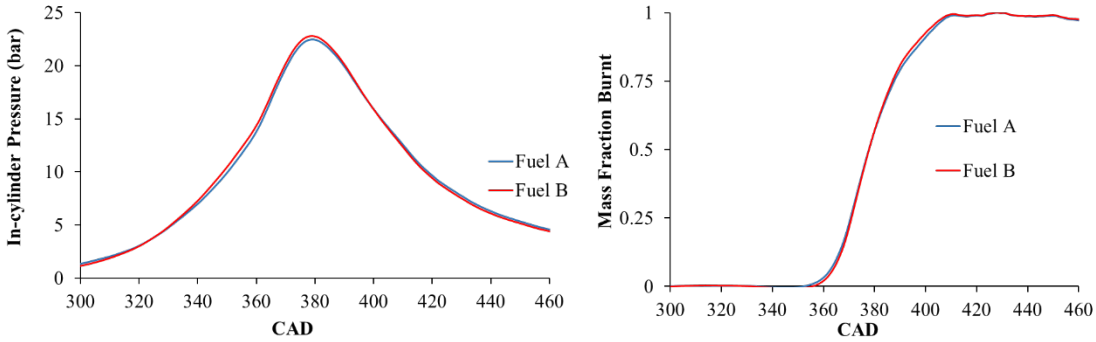

Figure 3

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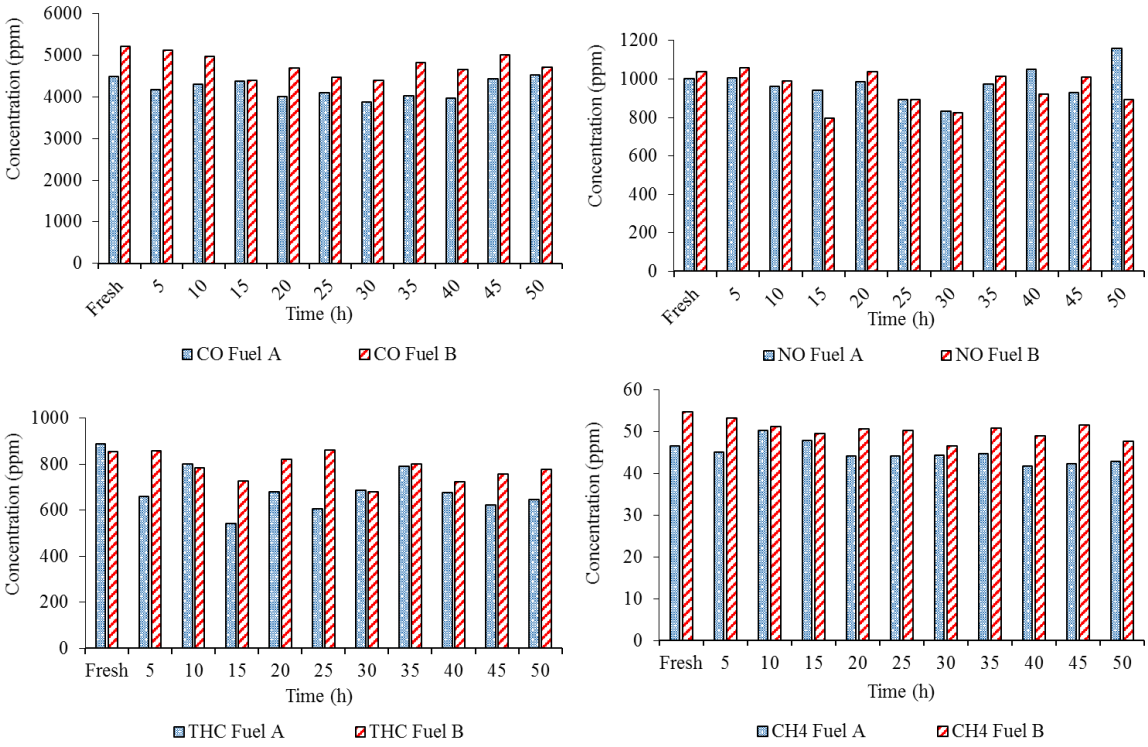

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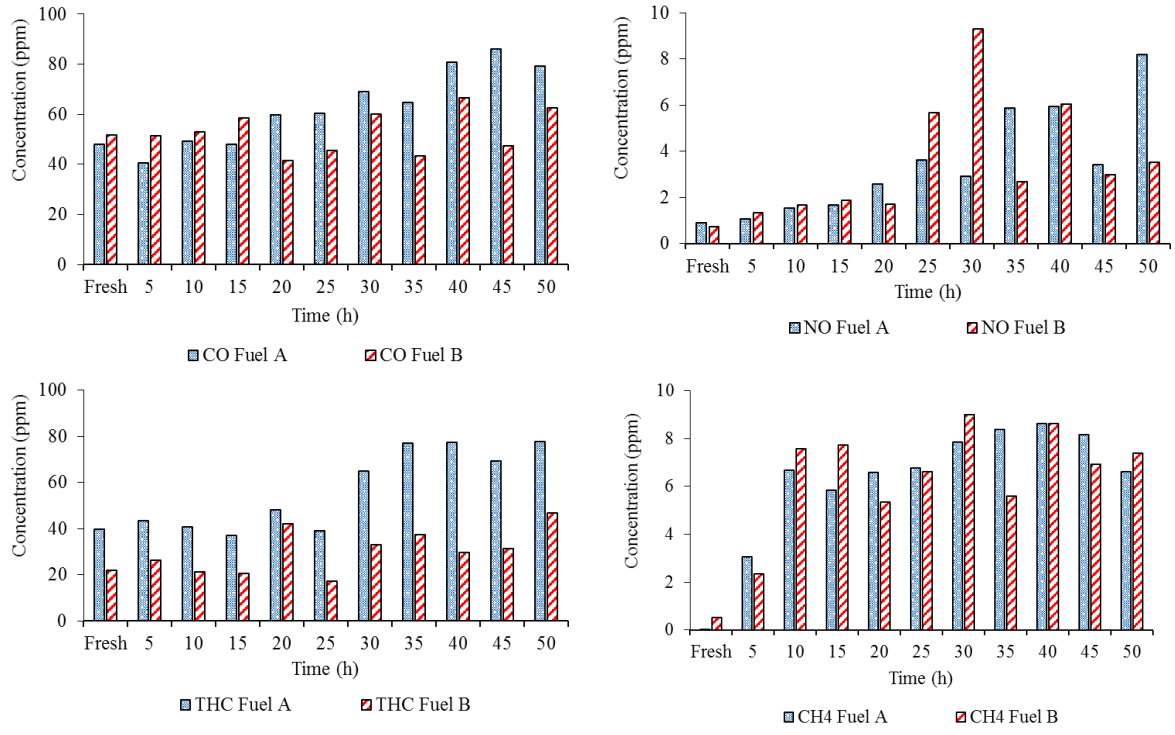

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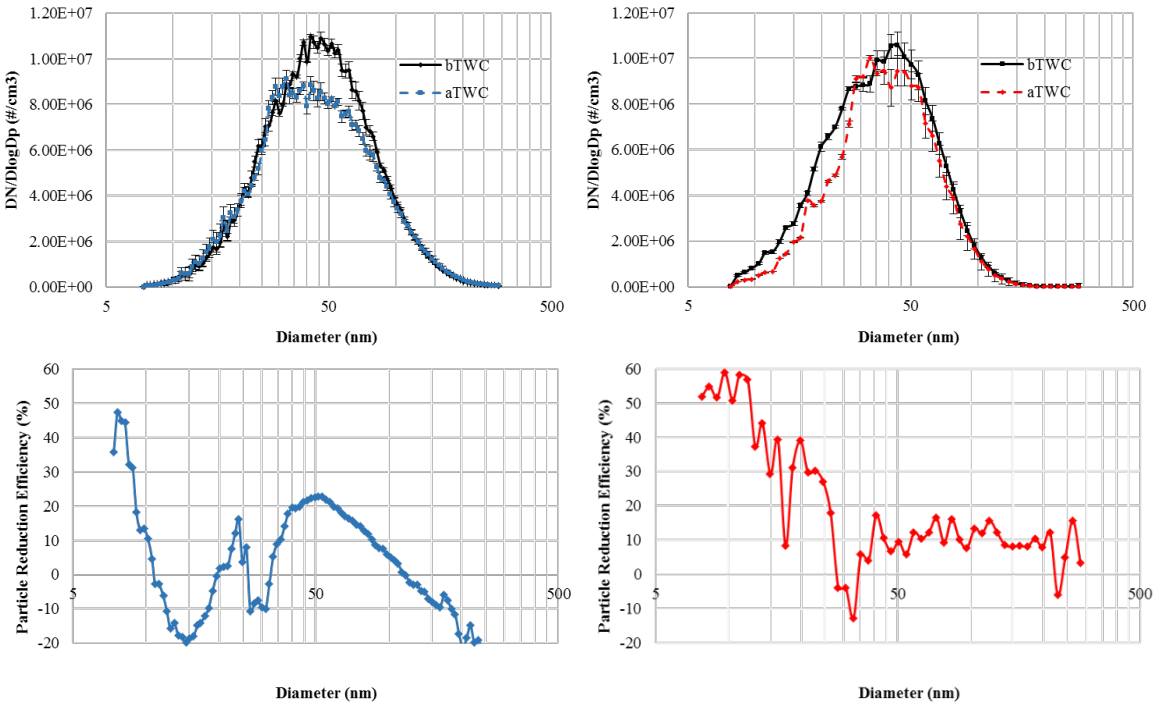

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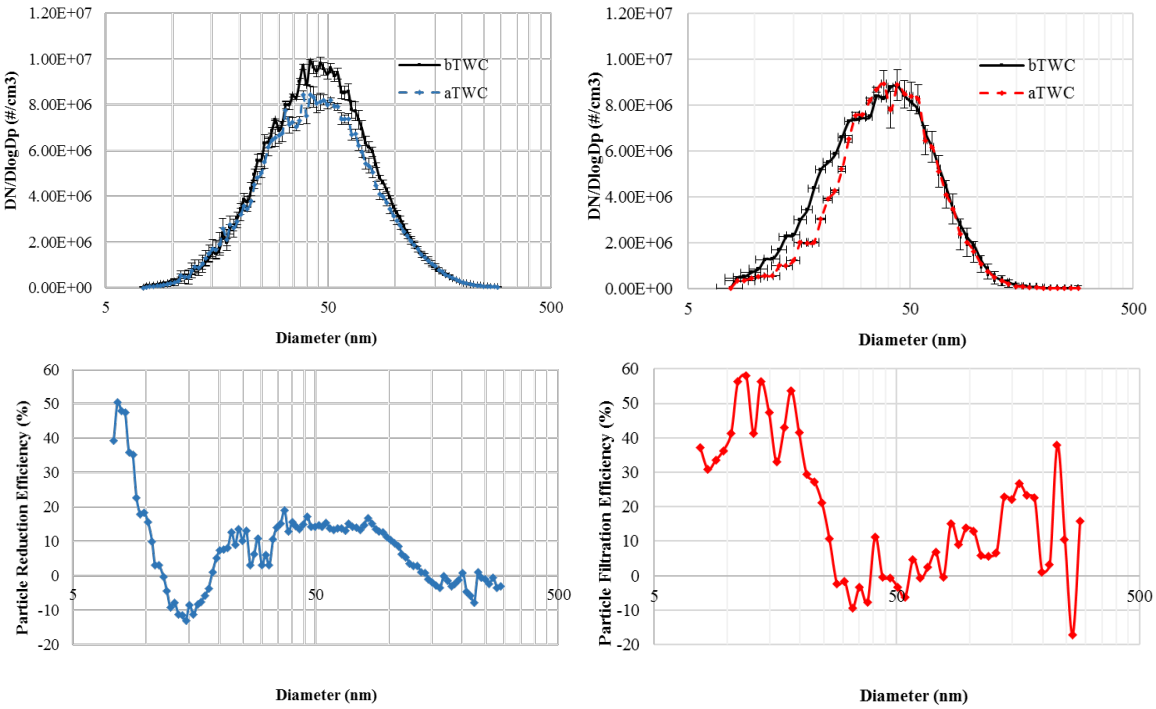
530 **Figure 6**



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533 **Figure 7**

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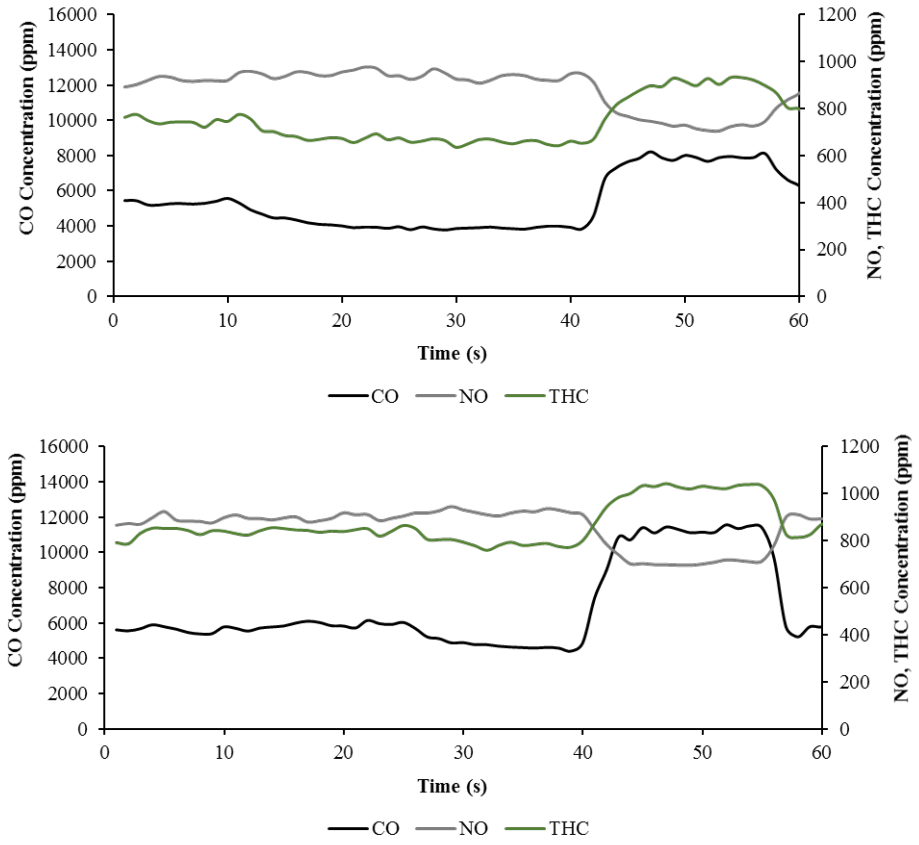

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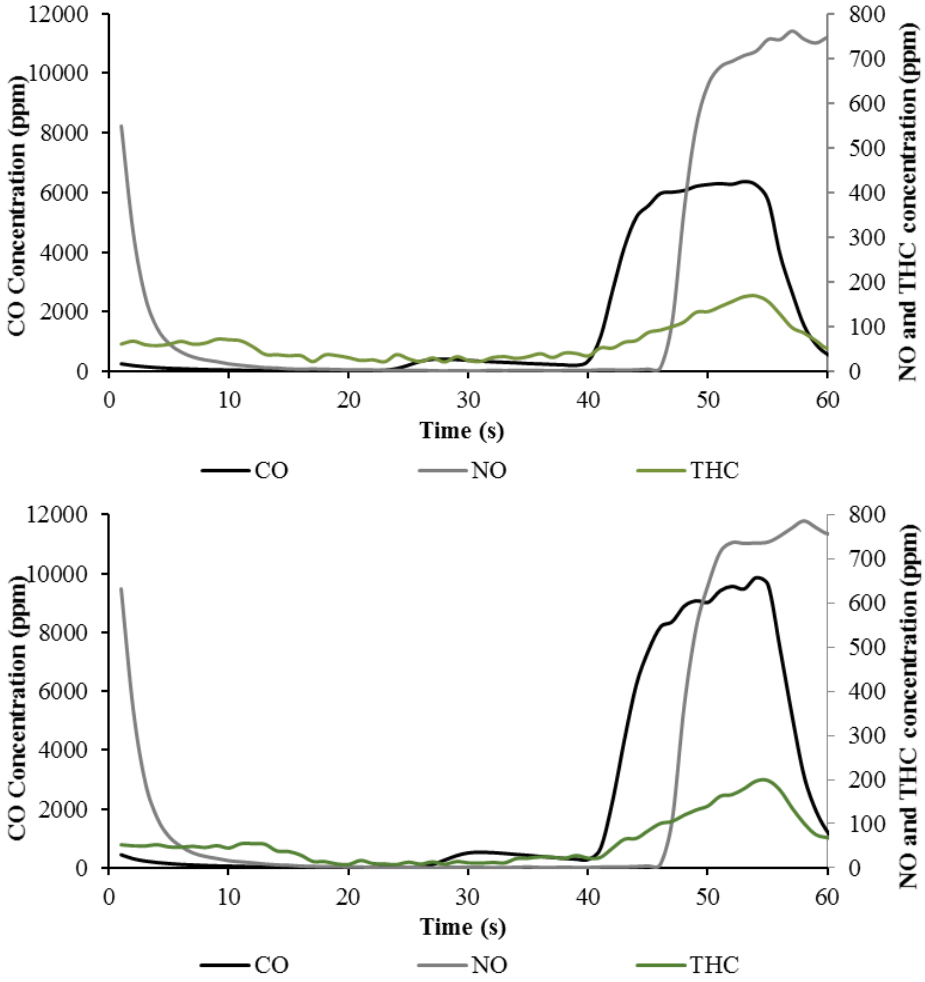

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Figure 9

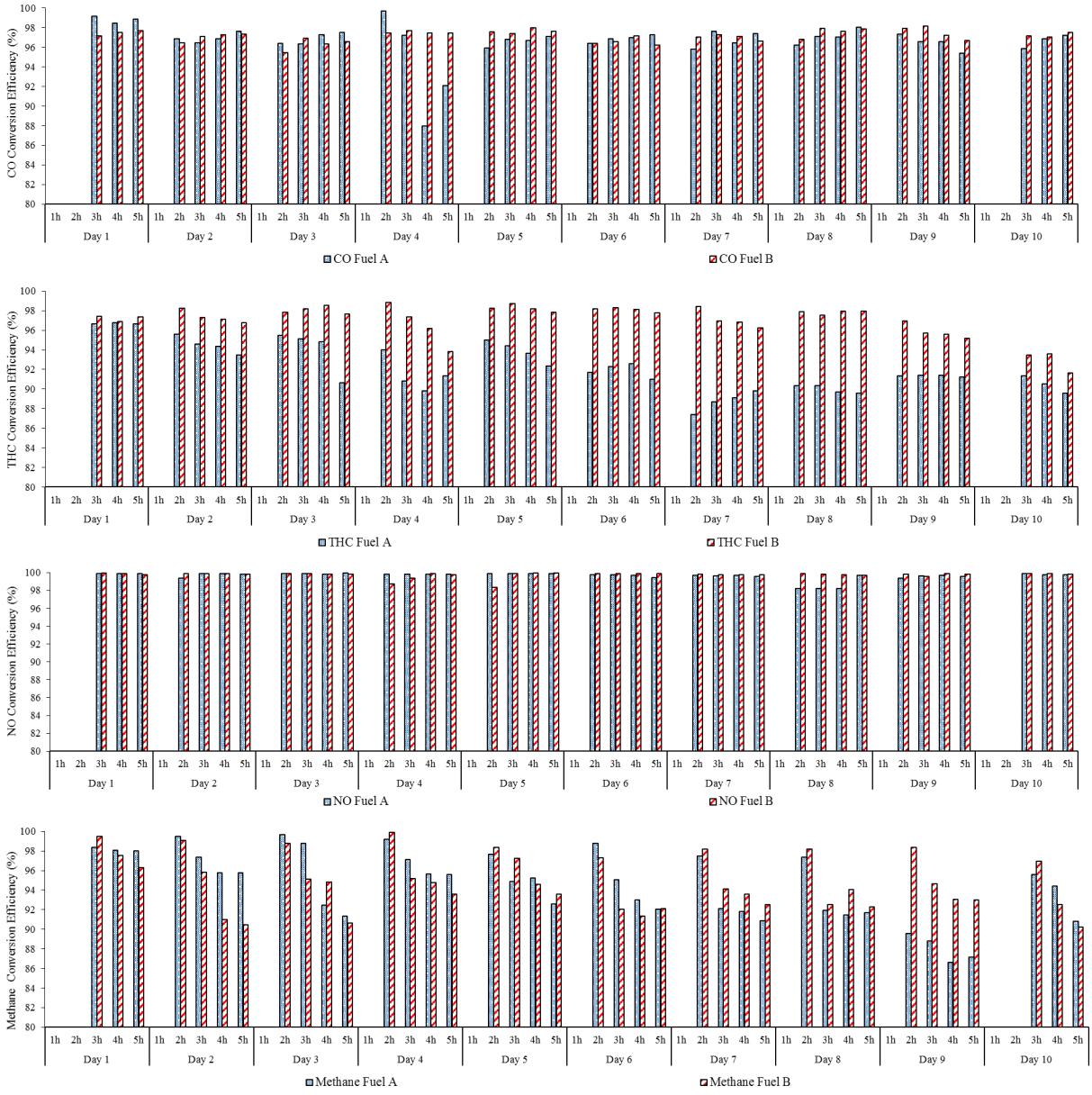
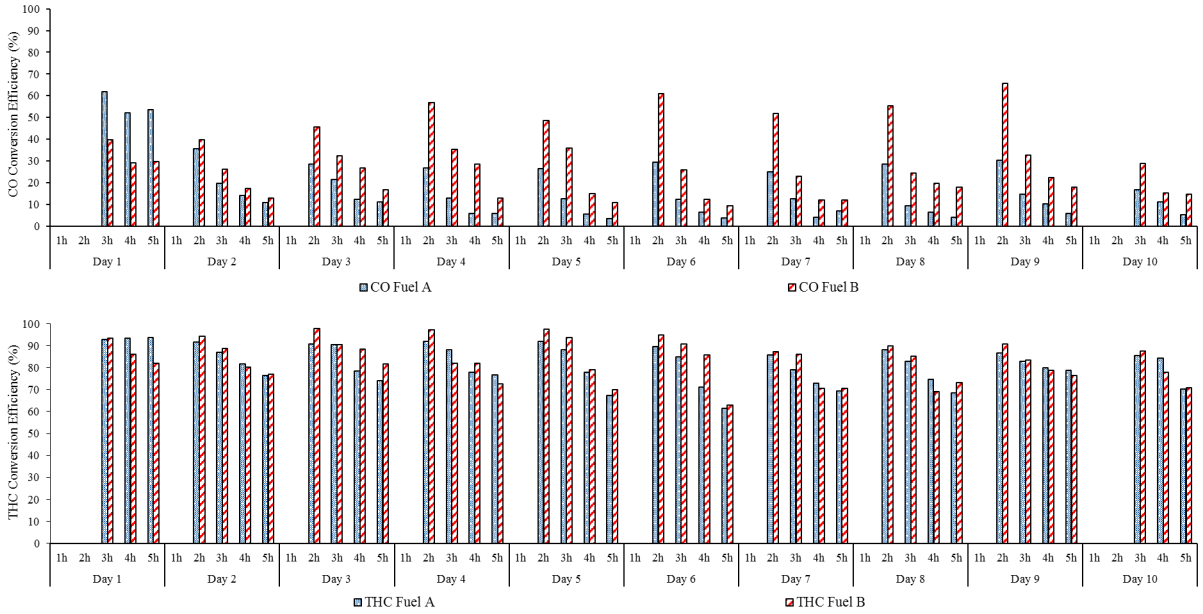

CO Conversion Efficiency (%)
THC Conversion Efficiency (%)
NO Conversion Efficiency (%)
Methane Conversion Efficiency (%)
1h 2h 3h 4h 5h
Day 1
Day 2
Day 3
Day 4
Day 5
Day 6
Day 7
Day 8
Day 9
Day 10
CO Fuel A
CO Fuel B
THC Fuel A
THC Fuel B
NO Fuel A
NO Fuel B
Methane Fuel A
Methane Fuel B

Figure 10



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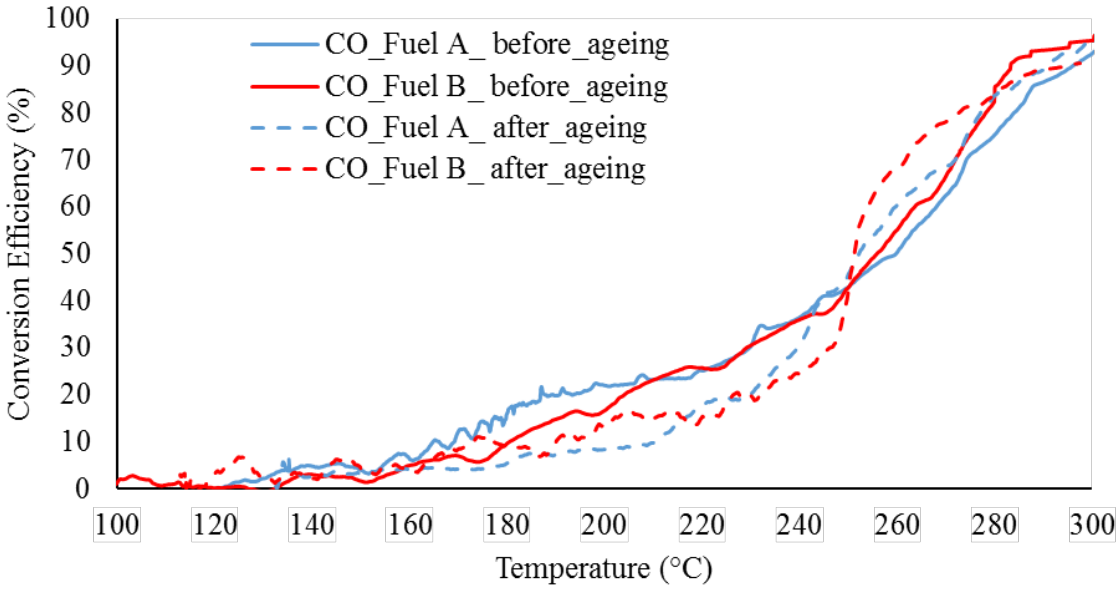
547 **Figure 11**



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549 **Figure 12**

List of Tables

556 **Table 1**

Specification	Value
Compression Ratio	10:1
Bore × Stroke	87.5 × 83.1 mm
Turbocharger	Borg Warner K03
Rated Power	149 kW at 6000 rpm
Rated Torque	300 Nm At 1750-4500 rpm
Engine Management	Bosch Me17

561 **Table 2**

Property	Standard	Units	Min	Max	Fuel B Base	Fuel A Additivated
Research Octane Number (RON)	ASTM D 2699-18a	-	98.0	-	98.1	99.5
Motor Octane Number (MON)	ASTM D 2700-18a	-	85.0	-	87.8	87.8
Density @ 15 °C	ASTM D 4052-18	kg/m^3	720	775	734.9	736.8
Vapour pressure (DVPE)	ASTM D 5191-15	kPa	50	80	71.9	71.9
Distillation curve	ASTM D 86-17					
Evaporated @ 70 °C (E70)		% v/v	22	56	32.0	33.2
Evaporated @ 100 °C (E100)		% v/v	46	74	55.9	57.2
Evaporated @ 150 °C (E150)		% v/v	75	-	82.6	83.8
Final Boiling Point		ºC	-	210	191	198
Residuals		% v/v	-	2	1.1	1.0
Sulphur	ASTM D 4294-16e1	mg/kg	-	10	< 10	< 10
Lead	UNE EN 237:2005	mg/l	-	5.0	< 0.003	< 0.003
HC composition	UNE EN ISO 22854:2016					
Olefins		% v/v	-	18.0	11.4	11.5
Aromatics		% v/v	-	35.0	24.5	24.7
Benzene		% v/v	-	1.0	0.68	0.69
Oxygen		% m/m	-	2.7	2.32	2.38
Methanol		% v/v	-	3	< 0.01	< 0.01
Ethanol		% v/v	-	5	0.65	0.66
Isopropyl alcohol		% v/v	Limited by maximum oxygen content		0.13	0.17
Tert-butyl alcohol		% v/v	-		< 0.01	< 0.01
Iso-butyl alcohol		% v/v	-		< 0.01	< 0.01
MTBE		% v/v	-		< 0.1	< 0.1
ETBE		% v/v	-		13.2	13.5
Ether compounds longer than C5					14.2	14.5
Other oxygenated compounds		% v/v	-		< 0.1	< 0.1

562 **Table 3**

TWC Characteristics		
Monolith	**Substrate (cpsi/mil)**	**Dimensions (inch)**
Full scale TWC	400/4.3	ϕ4.66×4.5
Scaled-down TWC	400/4.3	ϕ1×4.5

563 **Table 5**

Time (seconds)	Engine Air/Fuel Ratio	Secondary oxygen (air) injection
1-40	Stoichiometric	None
41-45	Rich with lambda = 0.94	None
46-55	Rich with lambda = 0.94	3% (± 1%)
56-60	Stoichiometric	3% (± 1%)

564