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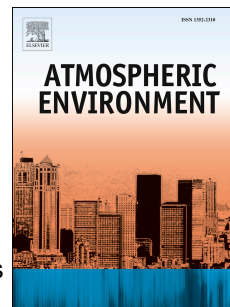
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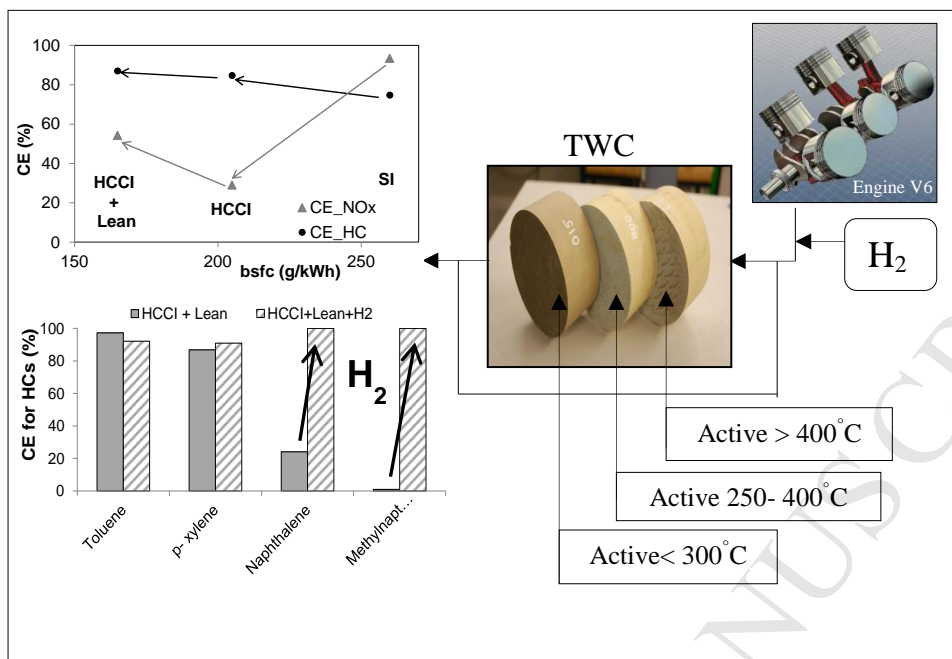
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Control of Harmful Hydrocarbon Species in the Exhaust of Modern Advanced GDI Engines

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Abstract

A qualitative and quantitative analysis of toxic but currently non-regulated hydrocarbon compounds ranging from C₅ - C₁₁, before and after a zoned three-way catalytic converter (TWC) in a modern gasoline direct injection (GDI) engine has been studied using gas chromatography-mass spectrometry (GC-MS). The GDI engine has been operated under conventional and advanced combustion modes, which result in better fuel economy and reduced levels of NO_x with respect to standard SI operation. However, these fuel-efficient conditions are more challenging for the operation of a conventional TWC, and could lead to higher level of emissions released to the environment. Lean combustion leads to the reduction in pumping losses, fuel consumption and in-cylinder emission formation rates. However, lean HCCI will lead to high levels of unburnt HCs while the presence of oxygen will lower the TWC efficiency for NO_x control.

The effect on the catalytic conversion of the hydrocarbon species of the addition of hydrogen upstream the catalyst has been also investigated. The highest hydrocarbon engine-out emissions were produced for HCCI engine operation at low engine load operation. The catalyst was able to remove most of the hydrocarbon species to low levels (below the permissible exposure limits) for standard and most of the advanced combustion modes, except for naphthalene (classified as possibly carcinogenic to humans by the International Agency for Research on Cancer) and methyl-naphthalene (which has the potential to cause lung damage). However, when hydrogen was added upstream of the catalyst, the catalyst conversion efficiency in reducing methyl-naphthalene and naphthalene was increased by approximately 21%. This results in simultaneous fuel economy and environmental benefits from the effective combination of advanced combustion and novel aftertreatment systems.

Keywords: Hydrogen, HCCI, Hydrocarbon Speciation, GDI; Three Way Catalytic Converter

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40 1. Introduction

41 The motor vehicle is a significant cause of air pollution and human health hazards, especially in
42 urban areas. Automotive exhaust emission regulations are, therefore, becoming progressively stricter
43 due to increasing awareness of the hazardous effects of the chemicals released by road traffic. These
44 include environmental issues such as photochemical smog and undesirable health effects, which are
45 caused by hydrocarbon species emitted into the atmosphere. Furthermore, it is well known that skin,
46 lung and bladder cancer is associated with polycyclic aromatic hydrocarbons (PAHs) in the
47 environment [1]. Therefore, in addition to the regulated engine exhaust emissions (i.e. carbon
48 monoxide, hydrocarbons, nitrogen oxides), it is critical that unregulated species such as methane [2],
49 carbonyl compounds [3] including aldehydes [4] and ketones [2], toluene, benzene [5] and
50 polyaromatic compounds [6] such as naphthalene are monitored and that their impact (i.e. toxicity and
51 photochemical reactivity) on the environment is assessed.

52 Gasoline direct injection engines are seen as the future of commercial internal combustion engine
53 powertrains due to their benefits on fuel economy and gaseous emissions. However, it is reported that
54 the levels of PM produced by these engines are higher than port fuel injection engines and diesel
55 engines equipped with a diesel particulate filter, thus there is an increased need to investigate the
56 emission of PM [7] and PAHs [8] by GDI engines. Due to their low emissions of NO_x and particulate
57 matter (PM) as well as their fuel economy benefits, HCCI and lean burn engines have been also seen
58 as enablers for cleaner vehicles. During lean combustion operation more air than needed for the
59 combustion is induced to the cylinder in order to favour the complete oxidation, this leads to
60 improvements in fuel economy and in-cylinder emissions formation. However, the presence of
61 oxygen in the exhaust dramatically reduces the NO_x performance of a conventional TWC. On the
62 other hand, in HCCI the target is to achieve low combustion temperatures and locally lean conditions
63 in order to reduce NO_x and PM, although HCCI results in high levels of CO and unburnt total
64 hydrocarbons emissions (THC) due to the low in-cylinder combustion temperature. Furthermore, lean
65 HCCI leads to high levels of CO and unburnt HCs as well as the presence of oxygen in the exhaust.
66 Due to this, there has been a growing interest over the last few years in the study of the carbonyl [9],
67 PAHs [10] and oxygenated emissions, and their origin [11], in this type of engine running on
68 advanced combustion operation. Most of the THCs are derived from unburned fuel being released
69 from the crevice volumes during the expansion stroke, with increasing molecular weight of the fuel
70 increasing the total emissions [12]. The complex reactions that take place during fuel combustion are
71 not yet fully understood [13], but it is reported that the air/fuel (A/F) ratio plays a major role in HC
72 emissions formation during combustion [14]. Furthermore, SI (including GDI and HCCI) engines can
73 operate under stoichiometric, lean and rich conditions, making the function of catalysts in controlling
74 the combustion pollutants challenging, requiring that catalytic technologies are adapted to take care of
75 pollutants under specific conditions such as cold start and stop-start operation.

76 Catalysts have been used in engine exhaust aftertreatment systems for almost four decades, with
77 continuous research and development leading to some highly effective technologies. However, there
78 remain notable challenges associated with low temperature combustion modes such as low engine-out
79 temperature, high unburned hydrocarbon emissions and the presence of oxygen in the exhaust in
80 conventional TWC [15][16]. Hydrogen has been researched as an additive to improve the combustion
81 process in GDI engines [17] and advanced HCCI combustion operation [18], as well as a low-
82 temperature performance enhancer of different aftertreatment components such as diesel oxidation
83 catalysts [19] and HC-SCR systems [20]. The beneficial effects of hydrogen are attributed to its
84 exothermic oxidation increasing the temperature of the active sites as well as its chemical role as a
85 promoter of catalytic reactions [21]. The main drawback associated with the use of hydrogen on-board
86 a vehicle is its low density. However, it has been previously demonstrated that only small quantities
87 of hydrogen are needed, which can be produced on-board the vehicle via catalytic fuel reforming
88 [18][22].

89 In the area of hydrocarbon emissions, speciation studies are required because total elemental
90 concentration may be uninformative and even misleading. There are no regulations or protocols
91 established for the sampling and speciation of HC molecules. However, there are methodologies
92 which have been adopted by international bodies for the measurement of different HC species. The
93 Environmental Protection Agency (EPA) use the method found in [23] for the measurement of
94 carbonyl emissions and the standard published in [24] has been used by Karavalakis et al. [25] and
95 Fontaras et al. [26]. The Auto-Oil Air Quality Improvement Research Program (AQIRP), using
96 capillary GC, [27], achieved separation of more than 140 compounds in the C₁ - C₁₂ range. This type
97 of single-column chromatographic approach has also been used in Europe, where extensive studies
98 have been reported [12][14]. It is become increasingly clear that speciation of the individual
99 hydrocarbons in gasoline-engine exhaust can provide valuable information about the fuel combustion
100 process in the engine, the performance of the emissions control systems [28] and the human and
101 environmental hazards of the pollutants when they are released to the atmosphere.

102 The overall objectives of this study are to analyse different medium-to-heavy hydrocarbon species
103 formed under HCCI and SI stoichiometric and lean engine operation, and to understand the influence
104 of hydrogen addition on a catalyst in reducing these compounds. Hydrocarbon speciation (C₅ to C₁₁)
105 of the exhaust gases from HCCI/SI engine operation before and after the catalyst was therefore carried
106 out. The parameters studied here are a) engine load effect under HCCI stoichiometric condition, b) air
107 to fuel ratio (stoichiometric and lean), c) HCCI and SI combustion modes under the same load and d)
108 hydrogen addition upstream of the catalyst.

109 2. Material and Methods

110 **Engine** - The experimental engine was a 3L gasoline direct-injection (wall guided) V6 engine; the
111 specifications are listed in Table 1. The engine was coupled to a Froude EC 38 eddy current

112 dynamometer. The valve-train was modified to permit operation in HCCI mode by the provision of a
113 cam profile switching mechanism. This cam profile switching (CPS) system was used to switch
114 between SI and HCCI modes. This system allowed on-line switching of valve lift from 9mm (SI
115 operation) to 3mm (HCCI) operation. The HCCI operation was achieved by internal EGR, using
116 negative valve overlap which trapped exhaust gases in order to retain enough energy for auto-ignition.
117 The variable valve timing system of the engine made it possible to change the valve timing for the
118 inlet and exhaust valves within a 60 crank angle (CA) degree range. More details regarding the engine
119 can be found elsewhere in [29] and [30]. In HCCI mode the engine was operated with a wide open
120 throttle significantly reducing pumping losses. A DSPACE- based system coupled to a computer
121 using MATLAB/SIMULINK software was used to control the engine parameters during operation
122 and data acquisition. The fuel flow rate to the engine was measured with the use of an AVL
123 gravimetric meter. The fuel injection pulse width was adjusted by the engine management system to
124 maintain the required engine operation condition and A/F ratio.

125 **Catalyst** - The 3-zone monolith catalyst (supplied by Johnson Matthey as part of the project) was
126 connected to the actual engine exhaust manifold [31]. The first zone was designed to reduce HC and
127 NO_x under lean and stoichiometric engine conditions at high temperatures >400°C, the second zone
128 was designed to reduce NO_x by reaction with hydrocarbon under lean engine operation in the
129 temperature range of 250°C – 400°C. The third catalyst zone was designed to control part of the
130 exhaust hydrocarbons and CO at temperatures below 300°C.

131 **Gaseous emissions analysis** - A Horiba MEXA 7100 DEGR equipped with a heated line (191°C)
132 was used to measure total hydrocarbons, carbon monoxide, carbon dioxide, NO_x and oxygen.

133 **Fuel** - Unleaded gasoline of 95 RON, composed of 48.3% saturated hydrocarbon, 16.2% olefins,
134 3.7% naphthenes and 30.2% aromatics, was used in this study.

135 **Hydrogen addition** - H₂ was added to the engine exhaust upstream of the catalyst and was
136 measured using a gas chromatograph (Hewlett-Packard Model GC-5890) fitted with a thermal
137 conductivity detector (GC-TCD).

138 **Hydrocarbon speciation** – There is no standard procedure for measuring specific HC species, as
139 they are not individually regulated, thus both the sampling and measurement method were optimised
140 for the experimental conditions and HC species studied. The hydrocarbon speciation of C₅ - C₁₁ was
141 carried out using an on-line GC-MS. A Fisons 8000 series GC equipped with direct injector was
142 connected to a Fisons MD 800 mass spectrometer, used as a detector. The gas samples were
143 introduced via a heated line into a six-port Valco valve fitted with a 0.1ml sample loop. The gas
144 sampling apparatus was kept at a constant temperature of 200°C. A 30m long x 0.53mm i.d. DB-1
145 capillary column with a 3µm film thickness was used for the separation of both the polar and non-
146 polar compounds. The column head pressure was kept at 10psi. The helium carrier gas flow rate was

147 controlled at a flow rate of 6ml/min. The temperature programme settings (Table 2) were set to flush
148 the heavier hydrocarbons from the column. As there is no established reference procedure and in
149 order to ensure the accuracy of the results, standard mixtures of paraffins, olefins and aromatics with
150 known concentrations were used to calibrate the chromatograph. The components of the standards
151 sample were generally stable under the operation conditions used in this analysis. The retention time
152 of each species was calibrated daily before each set of experiments, by the analysis of a 15 component
153 reference gas (sourced from BOC). The total run time was 20 minutes for the retention times of the
154 species given in Table 3. The integrated area of each specific peak in the chromatogram was used to
155 calculate the concentration of the associated component. The VG Mass-Lab software was used to
156 acquire and integrate the basic GC-MS data.

157 **Hydrocarbon species** – The individual compounds that are quantified in this study were chosen
158 because of the impact they have on air quality and ultimately to human health. The Occupational
159 Safety and Health Administration (OSHA) have introduced permissible exposure limits for these
160 species. The limits (are time-weighted average values, calculated for an exposure time of 8 hours. The
161 individual limits are shown in Table 4 [32]. General information regarding the studied species is given
162 below.

163 Iso-octane is studied as it is a major component in gasoline fuels. Iso-pentane is chosen as one of
164 the typical hydrocarbon species derived from iso-octane. Benzene has been chosen as it has been
165 classified as human carcinogen by the Environmental Protection Agency (EPA). Toluene, which is a
166 derivative of benzene, is another major component of gasoline fuels and one of the major volatile
167 compounds in the atmosphere [33]. It has been reported that the higher the content of toluene, iso-
168 octane and aromatic hydrocarbons in the parent fuel the higher the benzene concentration formed
169 during combustion [15][34].

170 Ethyl-benzene has been classified as possible human carcinogenic by the International Agency for
171 Research on Cancer (IARC) [35][36]. It is a major combustion by-product of aromatic species such as
172 xylene isomers during the combustion process [37]. It also participates in the formation of benzene,
173 toluene [38] and PAHs. P-xylene, which is also included in this study, is often formed by the
174 replacement of two hydrogen atoms of benzene by methyl groups, during the combustion process.

175 Naphthalene has been studied as it has been reported to be the most abundant PAHs in polluted urban
176 atmospheres [39]. It has been defined as a hazardous air pollutant by the US environmental protection
177 agency (EPA) [40] and classified as possibly carcinogenic to humans by the international agency for
178 research on cancer (IARC) [35]. Finally, methyl-naphthalene is monitored, which could be formed
179 from two benzene rings joining together while simultaneously a hydrogen from the naphthalene group
180 can be replaced by a methyl group [41].

181 **Engine operation condition** – Two different engine operating conditions defined by engine speed
182 and load have been chosen. Those engine conditions selected are representative of a wide range of

183 urban driving conditions of the vehicle equipped with this engine, where the exhaust conditions (i.e.
184 low temperature and high HC emissions) are challenging for efficient catalyst operation (Table 5).
185 The influence of the combustion mode (SI or HCCI), engine load (3bar or 4bar NMEP) and A/F ratio
186 (stoichiometric or lean) in the engine output concentration of NO_x and the magnitude and speciation
187 profile of THC emissions has been studied.

188 **3. Results and Discussion**

189 *3.1 Engine-out hydrocarbon species emissions*

190 Engine output NO_x and hydrocarbon speciation comparing HCCI and SI stoichiometric
191 combustion modes were carried out at 4 bar NMEP engine operation condition. Engine output NO_x
192 emissions were reduced around 4x times while the total concentration of C₅-C₁₁ hydrocarbon species
193 was approximated 12% higher under HCCI stoichiometric in comparison to stoichiometric SI engine
194 operation (Table 5 and Figure 2). In general terms, the engine output emission concentration for all
195 the studied species were higher for HCCI combustion with the exception of benzene, ethyl-benzene
196 and iso-octane (Table 6 and Figure 3). The higher unburned hydrocarbon emissions under HCCI
197 combustion are due to the lower in-cylinder temperature and available energy to drive the complete
198 oxidation reactions of the hydrocarbons part of the fuel and to also reduce hydrocarbon oxidation post
199 combustion. On the other hand, the lower concentration of the rest of species under HCCI conditions
200 can be attributed to i) the conversion of iso-octane to methane [42] (this finding supports the results of
201 a previous study from this group where high concentration of methane was found under HCCI
202 stoichiometric engine operation [31]), ii) a higher formation rate of toluene, p-xylene, naphthalene,
203 methyl-naphthalene or any other compounds derived from benzene due to the higher presence of
204 hydrocarbon to react with, and iii) the breakdown of the already formed toluene and p-xylene during
205 SI combustion process producing benzene and ethyl-benzene.

206 The engine operation at lean HCCI combustion enables simultaneous reduction of both NO_x and
207 the total hydrocarbon concentration of the species from C₅ to C₁₁, compared to HCCI stoichiometric
208 operation (Figure 2). HCCI lean operation especially reduces very harmful aromatic compounds such
209 as p-xylene, naphthalene and methyl-naphthalene, while mainly increasing iso-pentane (alkane) and
210 iso-octane. Total C₅-C₁₁ unburned hydrocarbon emissions were reduced when increasing the engine
211 load under both lean ($\lambda=1.4$) and stoichiometric HCCI operation (Table 5). Under HCCI
212 stoichiometric operation, increasing the engine load reduces the total hydrocarbon species in the range
213 of C₅ to C₈, while increasing the naphthalene and methyl-naphthalene engine output emissions (Table
214 6). This phenomenon could be attributed to the higher in-cylinder temperature at high load which
215 could increase the reaction rate of naphthalene formation through the fusion of two benzene rings.
216 Further reaction pathways will form methyl-naphthalene, by replacing the hydrogen atoms by methyl
217 groups [41]. A second mechanism for this could be the cyclisation of long-chain hydrocarbons found
218 in the partial combustion products. At lean HCCI operation the engine output concentration of all the

219 species are reduced when engine load is increased (Table 6). It is suggested that the temperature in the
220 post-combustion phase of the engine cycle, where naphthalene is formed [43], is not high enough to
221 significantly enhance naphthalene formation at any of the studied loads under lean combustion
222 operation.

223 3.2. Catalyst conversion efficiency

224 The NO_x conversion of the catalyst was significantly decreased under HCCI stoichiometric
225 operation in comparison to stoichiometric SI (Figure 4). However, the total hydrocarbon conversion
226 (C₅-C₁₁) at 4bar NMEP for HCCI stoichiometric operation was even higher compared to
227 stoichiometric SI operation, despite the large reduction in the exhaust gas temperature. Figure 4 also
228 shows that HCCI lean operation at 4bar NMEP enables an increase in both NO and HC conversion by
229 the catalyst, when compared to HCCI stoichiometric operation.

230 The average conversion of HC species over the catalyst under both SI and HCCI combustion
231 modes was higher than 90% for all engine conditions, except for HCCI stoichiometric operation at
232 3bar NMEP (Figure 5). Figure 5 (bottom) shows that the catalytic conversion was reduced to 60% for
233 most of the hydrocarbon species at HCCI stoichiometric operation. It is as though, at these low
234 exhaust gas temperatures, only the 3rd catalyst is active in oxidation of C-containing species (Table 5,
235 Figure 1), thus under these conditions i) the effective space velocity (SV) is significantly increased as
236 only 1/3 of the catalyst array is active, and the presence of available oxygen is required to catalytically
237 oxidise the HC species in the catalyst active sites. Therefore, the low exhaust temperature and absence
238 of oxygen in stoichiometric HCCI operation at low load resulted in the reduced HC oxidation rates.
239 As expected, hydrocarbon conversion over the catalyst was significantly improved for HCCI lean
240 operation (second zone of the catalyst is also active thanks to the higher oxygen availability) and at
241 high engine load conditions (higher exhaust gas temperatures activating all the three catalyst layers).
242 For instance, the conversion of iso-pentane was approximately 63% during HCCI stoichiometric
243 operation and improved to 93% during HCCI lean operation (Figure 2), this is despite the compound
244 being a saturated alkane (ie with single C-C bonds). Iso-octane conversion was approximately 65%
245 during HCCI stoichiometric operation at low load, and as the temperature was increased (i.e for high
246 load SI mode, Figure 3 condition 5) the net conversion rose to 100%.

247 The conversion efficiency for light aromatic HC components, i.e. benzene and toluene was high
248 for most engine conditions. For the aromatic hydrocarbon p-xylene (a benzene ring with two methyl
249 substituents), an average of 85% catalyst efficiency was achieved. However, for heavier and more
250 dangerous aromatic compounds that are known to be difficult to combust catalytically [44], such as
251 naphthalene and methyl-naphthalene, the catalyst conversion was in the range of 15-80%. The low
252 conversion could be because the aromatic rings are more susceptible to further dehydrogenation than
253 to combustion. As a result, the contact time required for catalytic combustion of heavy aromatic
254 species is longer than that for saturated HCs, which reduces the probability of naphthalene and

255 methyl-naphthalene decomposition to smaller hydrocarbon species [44][46]. Conversion was
256 improved at higher temperatures as the kinetic limitations to combustion were overcome [42]. Storage
257 of some of the HC species, including both naphthalene and methyl-naphthalene, is expected to occur
258 in the middle zone, which contributes to the reduction in the concentration of these species.

259 *3.3 Catalyst performance with H₂ addition, HCCI lean operation*

260 The effect of hydrogen has been investigated by injecting approximately 2400 ppm H₂ upstream of
261 the catalyst, in order to improve the catalyst performance in the reduction of harmful HC species such
262 as naphthalene (classified as possible carcinogenic by IARC) and methyl-naphthalene,. Comparison
263 is drawn between the same engine operating condition (lean HCCI combustion at 4bar NMEP) with
264 and without hydrogen addition, (Figure 6 and 7).

265 From the results it can be observed that hydrogen greatly enhances the catalyst performance by
266 66% and 100% respectively (Figure 6) in reducing naphthalene and methyl-naphthalene (Figure 7).
267 There are several likely causes: (i) Hydrogen oxidation in the first zone increases the catalyst
268 temperature by 5 to 20°C, enhancing the oxidation rate of the aromatic hydrocarbons (ie the exotherm
269 effect of hydrogen); (ii) We have earlier reported that hydrogen oxidation in for example a Pt/Al₂O₃
270 catalysts, increases the availability of NO₂ that is consequently consumed in the oxidation of the C-
271 containing species [19]; (iii) Hydrogenation is another possibility, in which H₂ reacts with the
272 aromatic compounds to form less unsaturated cyclic and aliphatic hydrocarbons that are easier to
273 combust. However, although the hydrogenation reactions are overall exothermic, there is a high
274 activation barrier to overcome.

275 **4. Conclusions**

276 Engine operation under low temperature combustion and lean engine operation strategies enable
277 the simultaneous increase in fuel efficiency and a decrease in both NO_x and particulate matter
278 emissions. However the CO and unburnt HC emission levels increase, while the low exhaust
279 temperature and presence of oxygen result in more challenging conditions for conventional
280 aftertreatment devices to reduce CO and unburnt hydrocarbon emissions.

281 In this research a catalytic system was evaluated with the aim of oxidising the HC species
282 produced under those fuel-efficient, but challenging exhaust conditions. Exhaust hydrocarbons have
283 been speciated, and the efficiency with which they are oxidised by the catalyst has been assessed
284 under different engine operation conditions. Species such as iso-octane, benzene, and ethyl-benzene
285 are mainly found in the engine exhaust during SI engine operation, while heavier species such as
286 naphthalene and methyl-naphthalene are present in higher concentrations under stoichiometric HCCI
287 engine operation.

288 The three-zone catalyst reduced most of the hydrocarbon compounds in both (HCCI and SI)
289 combustion modes, except for methyl-naphthalene and naphthalene, which are known to be hazardous

290 both to the environment and to human health, and are commonly found in the atmosphere in urban
291 areas. The catalyst was, therefore, less capable of activating a fused pair of benzene rings than
292 aliphatic or mono-aromatic molecules. However, the addition of hydrogen upstream of the catalyst
293 during HCCI lean engine operation substantially enhances the conversion of both methyl-naphthalene
294 and naphthalene species. This is attributed to an increase in the local temperature as a result of
295 hydrogen oxidation, and due to its reactivity with the aromatic compounds to form molecules that are
296 more readily oxidised by the catalyst. Therefore, this research work has demonstrated that, through
297 the integration of advanced combustion technologies with novel aftertreatment systems, it should be
298 possible to achieve notable benefits in fuel economy and in air quality.

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307

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430

Abbreviations

AQIRP	Auto-Oil Air Quality Improvement Research Program
A/F	Air to fuel ratio
Al₂O₃	Alumina
BOC	British Oxygen Company
CA	Crank Angle
CO	Carbon Monoxide
CPS	Cam profile switching
EGR	Exhaust Gas Recirculation
EPA	Environmental protection agency
GC-MS	Gas chromatography-mass spectrometry
GC-TCD	Gas chromatography-thermal conductivity detector
GDI	Gasoline direct injection
HC	Hydrocarbons
HCCI	Homogeneous charge compression ignition
IARC	International agency for research on cancer
NO_x	Nitrogen oxide
NO	Nitrogen Monoxide
NO₂	Nitrogen dioxide
NMEP	Net Indicated Mean Effective Pressure
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic aromatic hydrocarbon
PM	Particulate Matter
Pt	Platinum
RON	Research Octane Number
SI	Spark Ignition
SV	Space Velocity
THC	Total Hydrocarbon
TWA	Time-weighted average
TWC	Three-way catalytic converter

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Table 1

Description	Specification
Engine type	V6, 24-V, GDI
Bore	89mm
Stroke	79.5mm
Fuel	Gasoline, RON 95
Compression ratio	11.3
Intake valve timing	Variable
Exhaust valve timing	Variable
Intake temperature	Variable

Table 2

Instrument Parameters	Description
Column	DB-1; 30m; 0.53mm ID; 3 μ m film
Detector	MS; Source 200°C
Oven Temperature	40°C initial; 5 min hold, 10°C/min to 240°C; 5 min hold,
Flow Rate	6ml/minute; He

Table 3

Peak NO	Compound	Retention Time (minute)
1	iso-pentane	3.77
2	benzene	7.04
3	iso-octane	7.85
4	toluene	9.42
5	ethyl-benzene	11.54
6	p-xylene	11.72
7	naphthalene	18.19
8	methyl-naphthalene	20.66

Table 4

Chemical Species	Exposure Limits (ppm) TWA
iso-pentane	1000
Benzene	1
iso-octane	300
Toluene	200
ethyl-benzene	100
p-xylene	150
Naphthalene	10
methyl-naphthalene	N.A

TWA- time weighted average

Table 5

Engine Condition	Mode	HCCI	HCCI	HCCI	HCCI	SI	HCCI+H₂
	λ		1.0	1.0	1.4	1.4	1.0
NMEP (bar)		3.0	4.0	3.0	4.0	4.0	4.0
O ₂ (%)		1.2	1.2	6.29	6.55	1.06	6.55
CO ₂ (%)		12.31	13.92	10.31	10.34	13.81	10.34
C ₅ -C ₁₁ (ppm)		1718	1683	1731	1222	1500	1222
T _{Ex} (°C)		385	413	349	386	661	406

Table 6

Compound	HCCI $\lambda=1, 3.0\text{bar}$ (ppm)		HCCI $\lambda=1, 4.0\text{bar}$ (ppm)		HCCI $\lambda=1.4, 3.0\text{bar}$ (ppm)		HCCI $\lambda=1.4, 4.0\text{bar}$ (ppm)		SI $\lambda=1, 4.0\text{bar}$ (ppm)		HCCI+H ₂ $\lambda=1.4, 4.0\text{bar}$ (ppm)	
	B	A	B	A	B	A	B	A	B	A	B	A
iso-pentane	150	55	100	15	174	15	125	8	36	6	125	39
benzene	72	25	58	2	68	0	52	4	140	10	52	27
iso-octane	151	52	N.A	N.A	180	39	160	27	80	0	160	N.A
toluene	597	144	420	41	616	30	508	14	345	34	508	40
ethyl-benzene	130	29	105	19	N.A	N.A	N.A	N.A	115	19	N.A	N.A
p-xylene	454	115	442	46	476	20	296	39	360	63	296	27
naphthalene	114	55	344	69	170	144	58	44	335	159	58	0
methyl-naphthalene	50	33	214	66	47	42	23	23	89	89	23	0
Total C ₅ -C ₁₁	1718	508	1683	258	1731	290	1222	159	1500	380	1222	133

B- before catalyst

A- after catalyst

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Figure 7. Hydrocarbon concentration downstream of the catalyst with and without hydrogen addition.

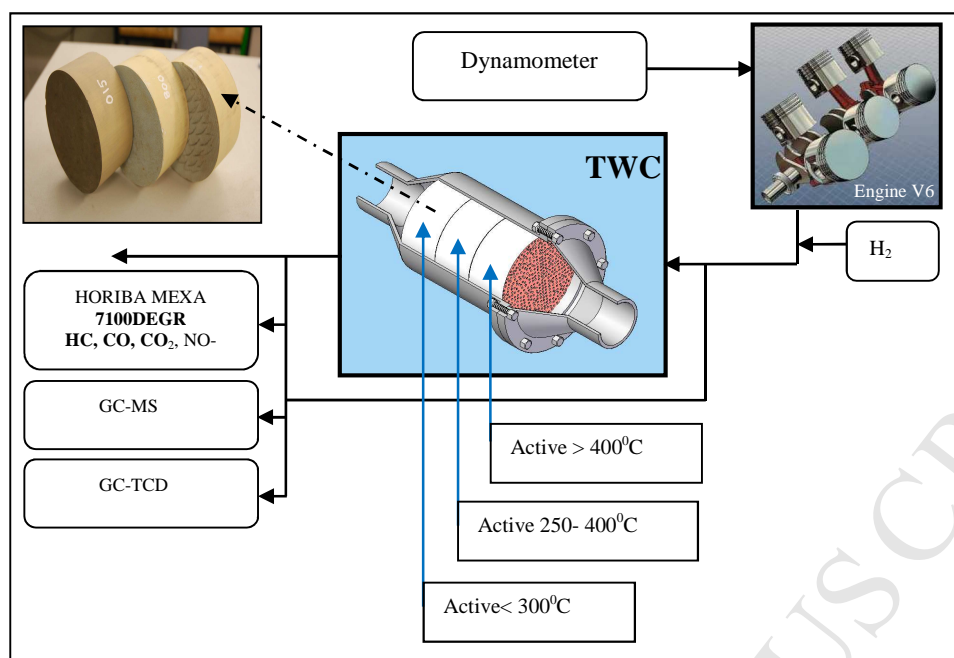


Figure 1

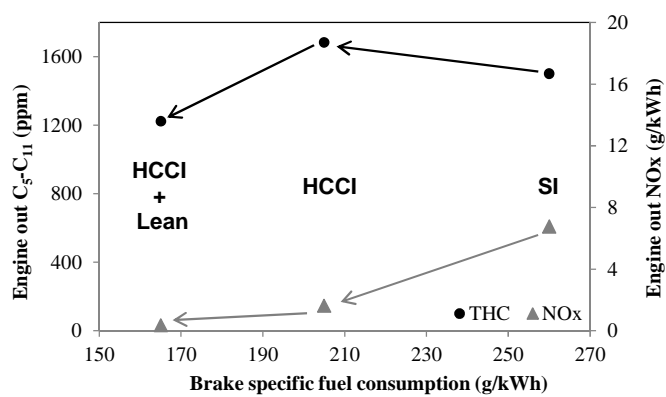


Figure 2

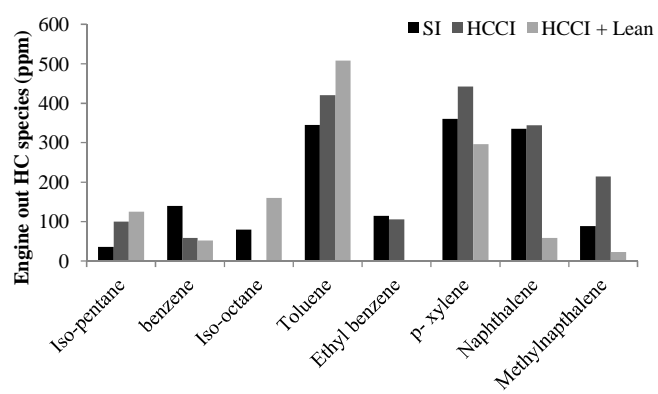


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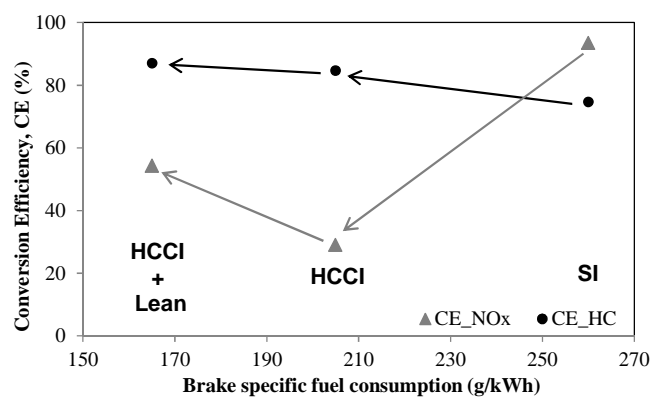


Figure 4

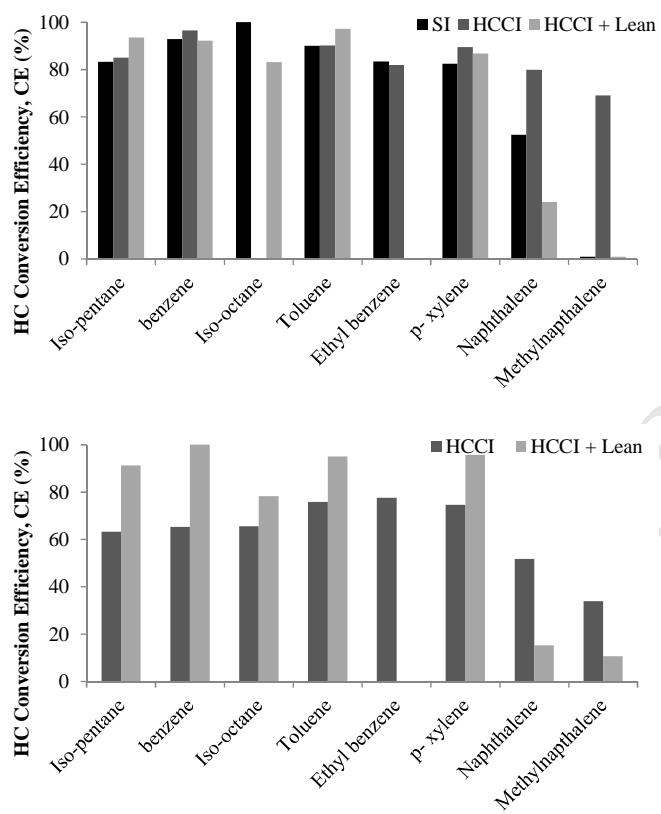
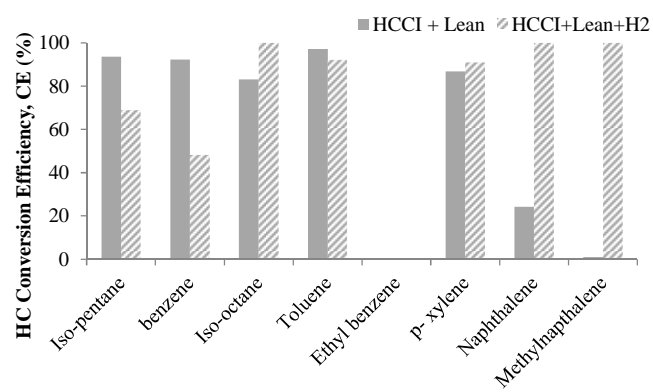


Figure 5

**Figure 6**

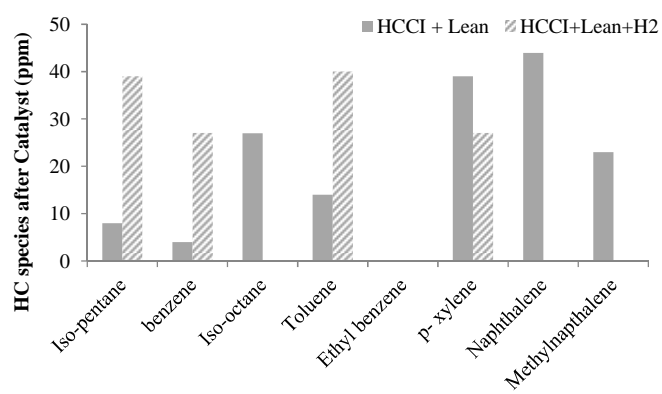


Figure 7

Toxic non-regulated hydrocarbon compounds C₅ - C₁₁ from modern GDI engine were analysed

The analysis was carried out for stoichiometric and lean combustion engines.

The catalyst ability to control heavy HC (C₅ – C₁₁) was also studied

Naphthalene and methylnaphthalene were the most resistant compounds

Hydrogen addition in the catalyst improved methylnaphthalene and naphthalene reduction