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**Author post-print (accepted) deposited by Coventry University's Repository**

**Original citation & hyperlink:**

Hasan, A. O. , Abu-jrai, A. , Turner, D. , Tsolakis, A. , Xu, H. M. , Golunski, S. E. and Herreros, J. M. (2016) Control of harmful hydrocarbon species in the exhaust of modern advanced GDI engines. Atmospheric Environment, volume 129 : 210-217

<http://dx.doi.org/10.1016/j.atmosenv.2016.01.033>

DOI 10.1016/j.atmosenv.2016.01.033

ISSN 1352-2310

Publisher: Elsevier

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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 C<sub>5</sub> - C<sub>11</sub>, 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<sub>x</sub> 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<sub>x</sub> 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 polyaromatic  
50 compounds [6] such as naphthalene are monitored and that their impact (i.e. toxicity and photochemical  
51 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 engines  
55 equipped with a diesel particulate filter, thus there is an increased need to investigate the emission of  
56 PM [7] and PAHs [8] by GDI engines. Due to their low emissions of NO<sub>x</sub> and particulate matter (PM)  
57 as well as their fuel economy benefits, HCCI and lean burn engines have been also seen as enablers for  
58 cleaner vehicles. During lean combustion operation more air than needed for the combustion is induced  
59 to the cylinder in order to favour the complete oxidation, this leads to improvements in fuel economy  
60 and in-cylinder emissions formation. However, the presence of oxygen in the exhaust dramatically  
61 reduces the NO<sub>x</sub> performance of a conventional TWC. On the other hand, in HCCI the target is to  
62 achieve low combustion temperatures and locally lean conditions in order to reduce NO<sub>x</sub> and PM,  
63 although HCCI results in high levels of CO and unburnt total hydrocarbons emissions (THC) due to the  
64 low in-cylinder combustion temperature. Furthermore, lean HCCI leads to high levels of CO and  
65 unburnt HCs as well as the presence of oxygen in the exhaust. Due to this, there has been a growing  
66 interest over the last few years in the study of the carbonyl [9], PAHs [10] and oxygenated emissions,  
67 and their origin [11], in this type of engine running on advanced combustion operation. Most of the  
68 THCs are derived from unburned fuel being released from the crevice volumes during the expansion  
69 stroke, with increasing molecular weight of the fuel increasing the total emissions [12]. The complex  
70 reactions that take place during fuel combustion are not yet fully understood [13], but it is reported that  
71 the air/fuel (A/F) ratio plays a major role in HC emissions formation during combustion [14].  
72 Furthermore, SI (including GDI and HCCI) engines can operate under stoichiometric, lean and rich  
73 conditions, making the function of catalysts in controlling the combustion pollutants challenging,  
74 requiring that catalytic technologies are adapted to take care of pollutants under specific conditions such  
75 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 of  
87 hydrogen are needed, which can be produced on-board the vehicle via catalytic fuel reforming [18][22].

88 In the area of hydrocarbon emissions, speciation studies are required because total elemental  
89 concentration may be uninformative and even misleading. There are no regulations or protocols  
90 established for the sampling and speciation of HC molecules. However, there are methodologies which  
91 have been adopted by international bodies for the measurement of different HC species. The  
92 Environmental Protection Agency (EPA) use the method found in [23] for the measurement of carbonyl  
93 emissions and the standard published in [24] has been used by Karavalakis et al. [25] and Fontaras et  
94 al. [26]. The Auto-Oil Air Quality Improvement Research Program (AQIRP), using capillary GC, [27],  
95 achieved separation of more than 140 compounds in the C<sub>1</sub> - C<sub>12</sub> range. This type of single-column  
96 chromatographic approach has also been used in Europe, where extensive studies have been reported  
97 [12][14]. It is become increasingly clear that speciation of the individual hydrocarbons in gasoline-  
98 engine exhaust can provide valuable information about the fuel combustion process in the engine, the  
99 performance of the emissions control systems [28] and the human and environmental hazards of the  
100 pollutants when they are released to the atmosphere.

101 The overall objectives of this study are to analyse different medium-to-heavy hydrocarbon species  
102 formed under HCCI and SI stoichiometric and lean engine operation, and to understand the influence  
103 of hydrogen addition on a catalyst in reducing these compounds. Hydrocarbon speciation (C<sub>5</sub> to C<sub>11</sub>) of  
104 the exhaust gases from HCCI/SI engine operation before and after the catalyst was therefore carried  
105 out. The parameters studied here are a) engine load effect under HCCI stoichiometric condition, b) air  
106 to fuel ratio (stoichiometric and lean), c) HCCI and SI combustion modes under the same load and d)  
107 hydrogen addition upstream of the catalyst.

## 108 **2. Material and Methods**

109 *Engine* - The experimental engine was a 3L gasoline direct-injection (wall guided) V6 engine; the  
110 specifications are listed in Table 1. The engine was coupled to a Froude EC 38 eddy current  
111 dynamometer. The valve-train was modified to permit operation in HCCI mode by the provision of a

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

124 **Catalyst** - The 3-zone monolith catalyst (supplied by Johnson Matthey as part of the project) was  
125 connected to the actual engine exhaust manifold [31]. The first zone was designed to reduce HC and  
126 NO<sub>x</sub> under lean and stoichiometric engine conditions at high temperatures >400°C, the second zone  
127 was designed to reduce NO<sub>x</sub> by reaction with hydrocarbon under lean engine operation in the  
128 temperature range of 250°C – 400°C. The third catalyst zone was designed to control part of the exhaust  
129 hydrocarbons and CO at temperatures below 300°C.

130 **Gaseous emissions analysis** - A Horiba MEXA 7100 DEGR equipped with a heated line (191°C)  
131 was used to measure total hydrocarbons, carbon monoxide, carbon dioxide, NO<sub>x</sub> and oxygen.

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

134 **Hydrogen addition** - H<sub>2</sub> was added to the engine exhaust upstream of the catalyst and was measured  
135 using a gas chromatograph (Hewlett-Packard Model GC-5890) fitted with a thermal conductivity  
136 detector (GC-TCD).

137 **Hydrocarbon speciation** – There is no standard procedure for measuring specific HC species, as  
138 they are not individually regulated, thus both the sampling and measurement method were optimised  
139 for the experimental conditions and HC species studied. The hydrocarbon speciation of C<sub>5</sub> - C<sub>11</sub> was  
140 carried out using an on-line GC-MS. A Fisons 8000 series GC equipped with direct injector was  
141 connected to a Fisons MD 800 mass spectrometer, used as a detector. The gas samples were introduced  
142 via a heated line into a six-port Valco valve fitted with a 0.1ml sample loop. The gas sampling apparatus  
143 was kept at a constant temperature of 200°C. A 30m long x 0.53mm i.d. DB-1 capillary column with a  
144 3µm film thickness was used for the separation of both the polar and non-polar compounds. The column  
145 head pressure was kept at 10psi. The helium carrier gas flow rate was controlled at a flow rate of  
146 6ml/min. The temperature programme settings (Table 2) were set to flush the heavier hydrocarbons

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

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

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

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

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

178 **Engine operation condition** – Two different engine operating conditions defined by engine speed  
179 and load have been chosen. Those engine conditions selected are representative of a wide range of urban  
180 driving conditions of the vehicle equipped with this engine, where the exhaust conditions (i.e. low  
181 temperature and high HC emissions) are challenging for efficient catalyst operation (Table 5). The  
182 influence of the combustion mode (SI or HCCI), engine load (3bar or 4bar NMEP) and A/F ratio

183 (stoichiometric or lean) in the engine output concentration of NO<sub>x</sub> and the magnitude and speciation  
184 profile of THC emissions has been studied.

### 185 **3. Results and Discussion**

#### 186 *3.1 Engine-out hydrocarbon species emissions*

187 Engine output NO<sub>x</sub> and hydrocarbon speciation comparing HCCI and SI stoichiometric combustion  
188 modes were carried out at 4 bar NMEP engine operation condition. Engine output NO<sub>x</sub> emissions were  
189 reduced around 4x times while the total concentration of C<sub>5</sub>-C<sub>11</sub> hydrocarbon species was approximated  
190 12% higher under HCCI stoichiometric in comparison to stoichiometric SI engine operation (Table 5  
191 and Figure 2). In general terms, the engine output emission concentration for all the studied species  
192 were higher for HCCI combustion with the exception of benzene, ethyl-benzene and iso-octane (Table  
193 6 and Figure 3). The higher unburned hydrocarbon emissions under HCCI combustion are due to the  
194 lower in-cylinder temperature and available energy to drive the complete oxidation reactions of the  
195 hydrocarbons part of the fuel and to also reduce hydrocarbon oxidation post combustion. On the other  
196 hand, the lower concentration of the rest of species under HCCI conditions can be attributed to i) the  
197 conversion of iso-octane to methane [42] (this finding supports the results of a previous study from this  
198 group where high concentration of methane was found under HCCI stoichiometric engine operation  
199 [31]), ii) a higher formation rate of toluene, p-xylene, naphthalene, methyl-naphthalene or any other  
200 compounds derived from benzene due to the higher presence of hydrocarbon to react with, and iii) the  
201 breakdown of the already formed toluene and p-xylene during SI combustion process producing  
202 benzene and ethyl-benzene.

203 The engine operation at lean HCCI combustion enables simultaneous reduction of both NO<sub>x</sub> and the  
204 total hydrocarbon concentration of the species from C<sub>5</sub> to C<sub>11</sub>, compared to HCCI stoichiometric  
205 operation (Figure 2). HCCI lean operation especially reduces very harmful aromatic compounds such  
206 as p-xylene, naphthalene and methyl-naphthalene, while mainly increasing iso-pentane (alkane) and  
207 iso-octane. Total C<sub>5</sub>-C<sub>11</sub> unburned hydrocarbon emissions were reduced when increasing the engine  
208 load under both lean ( $\lambda=1.4$ ) and stoichiometric HCCI operation (Table 5). Under HCCI stoichiometric  
209 operation, increasing the engine load reduces the total hydrocarbon species in the range of C<sub>5</sub> to C<sub>8</sub>,  
210 while increasing the naphthalene and methyl-naphthalene engine output emissions (Table 6). This  
211 phenomenon could be attributed to the higher in-cylinder temperature at high load which could increase  
212 the reaction rate of naphthalene formation through the fusion of two benzene rings. Further reaction  
213 pathways will form methyl-naphthalene, by replacing the hydrogen atoms by methyl groups [41]. A  
214 second mechanism for this could be the cyclisation of long-chain hydrocarbons found in the partial  
215 combustion products. At lean HCCI operation the engine output concentration of all the species are  
216 reduced when engine load is increased (Table 6). It is suggested that the temperature in the post-  
217 combustion phase of the engine cycle, where naphthalene is formed [43], is not high enough to

218 significantly enhance naphthalene formation at any of the studied loads under lean combustion  
219 operation.

### 220 3.2. Catalyst conversion efficiency

221 The NO<sub>x</sub> conversion of the catalyst was significantly decreased under HCCI stoichiometric  
222 operation in comparison to stoichiometric SI (Figure 4). However, the total hydrocarbon conversion  
223 (C<sub>5</sub>-C<sub>11</sub>) at 4bar NMEP for HCCI stoichiometric operation was even higher compared to stoichiometric  
224 SI operation, despite the large reduction in the exhaust gas temperature. Figure 4 also shows that HCCI  
225 lean operation at 4bar NMEP enables an increase in both NO and HC conversion by the catalyst, when  
226 compared to HCCI stoichiometric operation.

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

244 The conversion efficiency for light aromatic HC components, i.e. benzene and toluene was high for  
245 most engine conditions. For the aromatic hydrocarbon p-xylene (a benzene ring with two methyl  
246 substituents), an average of 85% catalyst efficiency was achieved. However, for heavier and more  
247 dangerous aromatic compounds that are known to be difficult to combust catalytically [44], such as  
248 naphthalene and methyl-naphthalene, the catalyst conversion was in the range of 15-80%. The low  
249 conversion could be because the aromatic rings are more susceptible to further dehydrogenation than to  
250 combustion. As a result, the contact time required for catalytic combustion of heavy aromatic species  
251 is longer than that for saturated HCs, which reduces the probability of naphthalene and methyl-  
252 naphthalene decomposition to smaller hydrocarbon species [44][46]. Conversion was improved at  
253 higher temperatures as the kinetic limitations to combustion were overcome [42]. Storage of some of



254 the HC species, including both naphthalene and methyl-naphthalene, is expected to occur in the middle  
255 zone, which contributes to the reduction in the concentration of these species.

### 256 *3.3 Catalyst performance with H<sub>2</sub> addition, HCCI lean operation*

257 The effect of hydrogen has been investigated by injecting approximately 2400 ppm H<sub>2</sub> upstream of  
258 the catalyst, in order to improve the catalyst performance in the reduction of harmful HC species such  
259 as naphthalene (classified as possible carcinogenic by IARC) and methyl-naphthalene.. Comparison is  
260 drawn between the same engine operating condition (lean HCCI combustion at 4bar NMEP) with and  
261 without hydrogen addition, (Figure 6 and 7).

262 From the results it can be observed that hydrogen greatly enhances the catalyst performance by 66%  
263 and 100% respectively (Figure 6) in reducing naphthalene and methyl-naphthalene (Figure 7). There  
264 are several likely causes: (i) Hydrogen oxidation in the first zone increases the catalyst temperature by  
265 5 to 20°C, enhancing the oxidation rate of the aromatic hydrocarbons (ie the exotherm effect of  
266 hydrogen); (ii) We have earlier reported that hydrogen oxidation in for example a Pt/Al<sub>2</sub>O<sub>3</sub> catalysts,  
267 increases the availability of NO<sub>2</sub> that is consequently consumed in the oxidation of the C-containing  
268 species [19]; (iii) Hydrogenation is another possibility, in which H<sub>2</sub> reacts with the aromatic compounds  
269 to form less unsaturated cyclic and aliphatic hydrocarbons that are easier to combust. However,  
270 although the hydrogenation reactions are overall exothermic, there is a high activation barrier to  
271 overcome.

## 272 **4. Conclusions**

273 Engine operation under low temperature combustion and lean engine operation strategies enable the  
274 simultaneous increase in fuel efficiency and a decrease in both NO<sub>x</sub> and particulate matter emissions.  
275 However the CO and unburnt HC emission levels increase, while the low exhaust temperature and  
276 presence of oxygen result in more challenging conditions for conventional aftertreatment devices to  
277 reduce CO and unburnt hydrocarbon emissions.

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

285 The three-zone catalyst reduced most of the hydrocarbon compounds in both (HCCI and SI)  
286 combustion modes, except for methyl-naphthalene and naphthalene, which are known to be hazardous  
287 both to the environment and to human health, and are commonly found in the atmosphere in urban  
288 areas. The catalyst was, therefore, less capable of activating a fused pair of benzene rings than aliphatic

289 or mono-aromatic molecules. However, the addition of hydrogen upstream of the catalyst during HCCI  
290 lean engine operation substantially enhances the conversion of both methyl-naphthalene and  
291 naphthalene species. This is attributed to an increase in the local temperature as a result of hydrogen  
292 oxidation, and due to its reactivity with the aromatic compounds to form molecules that are more readily  
293 oxidised by the catalyst. Therefore, this research work has demonstrated that, through the integration of  
294 advanced combustion technologies with novel aftertreatment systems, it should be possible to achieve  
295 notable benefits in fuel economy and in air quality.

## 296 **Acknowledgements**

297 The DTI (now Innovate UK) and EPSRC (GR/S81964/01) are acknowledged for funding the project  
298 “Controlled Homogeneous Autoignition Supercharged Engine (CHASE), 2004 – 2007”. The School of  
299 Mechanical Engineering at the University of Birmingham (UK) is gratefully acknowledged for the PhD  
300 scholarship to Mr. A.O. Hasan. Johnson Matthey Plc is also thanked for supporting this work and by  
301 supplying the catalysts. Jaguar Land Rover is acknowledged for supporting the work with the research  
302 engine used in this study. Dr. D. Turner thanks Engineering and Physical Science Research Council-  
303 EPSRC project (EP/G038139/1) for supporting the research work.

304

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## Abbreviations

<b>AQIRP</b>	Auto-Oil Air Quality Improvement Research Program
<b>A/F</b>	Air to fuel ratio
<b>Al<sub>2</sub>O<sub>3</sub></b>	Alumina
<b>BOC</b>	British Oxygen Company
<b>CA</b>	Crank Angle
<b>CO</b>	Carbon Monoxide
<b>CPS</b>	Cam profile switching
<b>EGR</b>	Exhaust Gas Recirculation
<b>EPA</b>	Environmental protection agency
<b>GC-MS</b>	Gas chromatography-mass spectrometry
<b>GC-TCD</b>	Gas chromatography-thermal conductivity detector
<b>GDI</b>	Gasoline direct injection
<b>HC</b>	Hydrocarbons
<b>HCCI</b>	Homogeneous charge compression ignition
<b>IARC</b>	International agency for research on cancer
<b>NO<sub>x</sub></b>	Nitrogen oxide
<b>NO</b>	Nitrogen Monoxide
<b>NO<sub>2</sub></b>	Nitrogen dioxide
<b>NMEP</b>	Net Indicated Mean Effective Pressure
<b>OSHA</b>	Occupational Safety and Health Administration
<b>PAH</b>	Polycyclic aromatic hydrocarbon
<b>PM</b>	Particulate Matter
<b>Pt</b>	Platinum
<b>RON</b>	Research Octane Number
<b>SI</b>	Spark Ignition
<b>SV</b>	Space Velocity
<b>THC</b>	Total Hydrocarbon
<b>TWA</b>	Time-weighted average
<b>TWC</b>	Three-way catalytic converter

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**Table 2.** GC operating parameters.

**Table 3.** Retention times of detected compounds.

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**Table 6.** Concentration of hydrocarbon species (C<sub>5</sub> – C<sub>11</sub>) before and after the catalyst for the different engine conditions at 2000rpm engine speed.

**Table 1**

<b>Description</b>	<b>Specification</b>
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**

<b>Instrument Parameters</b>	<b>Description</b>
Column	DB-1; 30m; 0.53mm ID; 3 $\mu$ 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**

<b>Peak NO</b>	<b>Compound</b>	<b>Retention Time (minute)</b>
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**

<b>Chemical Species</b>	<b>Exposure Limits (ppm) TWA</b>
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**

<b>Engine Condition</b>	<b>Mode</b>	<b>HCCI</b>	<b>HCCI</b>	<b>HCCI</b>	<b>HCCI</b>	<b>SI</b>	<b>HCCI+H<sub>2</sub></b>
	$\lambda$	1.0	1.0	1.4	1.4	1.0	1.4
	NMEP (bar)	3.0	4.0	3.0	4.0	4.0	4.0
	O <sub>2</sub> (%)	1.2	1.2	6.29	6.55	1.06	6.55
	CO <sub>2</sub> (%)	12.31	13.92	10.31	10.34	13.81	10.34
	C <sub>5</sub> -C <sub>11</sub> (ppm)	1718	1683	1731	1222	1500	1222
	T <sub>Ex</sub> (°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 <sub>2</sub> $\lambda =1.4,$ $4.0\text{bar}$ (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 <sub>5</sub> -C <sub>11</sub>	1718	508	1683	258	1731	290	1222	159	1500	380	1222	133

B- before catalyst

A- after catalyst

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**Figure 1.** Schematic of experimental setup.

**Figure 2.** Engine output C<sub>5</sub>-C<sub>11</sub> hydrocarbon species and NO<sub>x</sub> at 4bar NMEP and different combustion conditions.

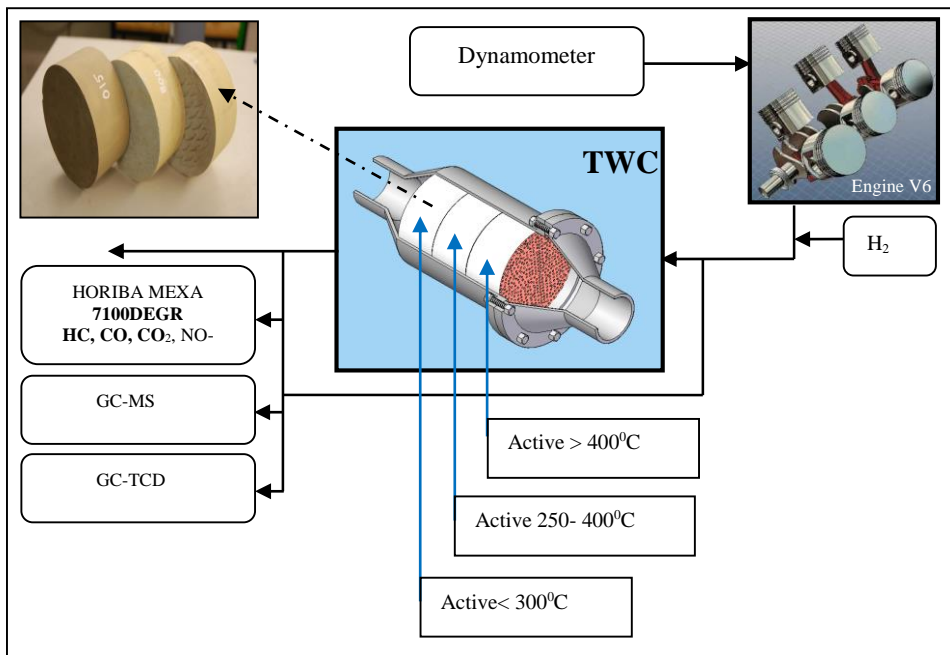
**Figure 3.** Engine output HC species at 4bar NMEP at different combustion conditions.

**Figure 4.** Conversion efficiency of the catalyst at 4bar NMEP and different combustion modes.

**Figure 5.** HC conversion efficiency of the catalyst at different combustion conditions 4bar NMEP (top) and 3bar NMEP (bottom).

**Figure 6.** HC conversion efficiency of the catalyst at 4bar NMEP with and without hydrogen addition.

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



**Figure 1**

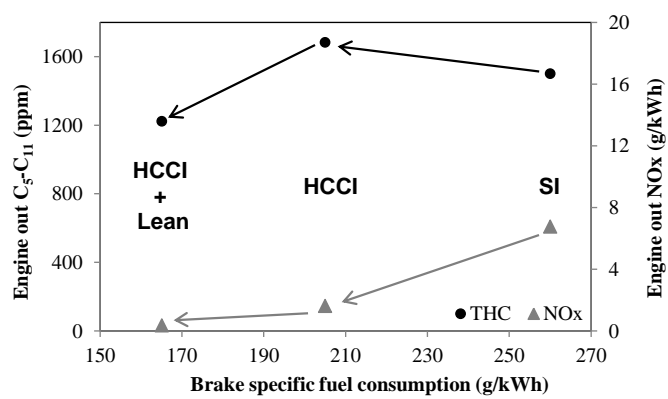
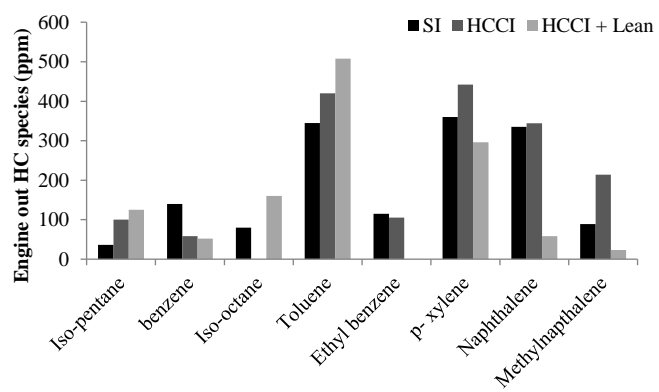
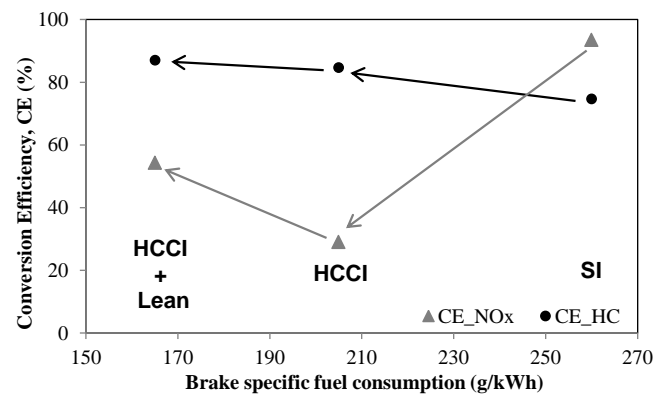


Figure 2

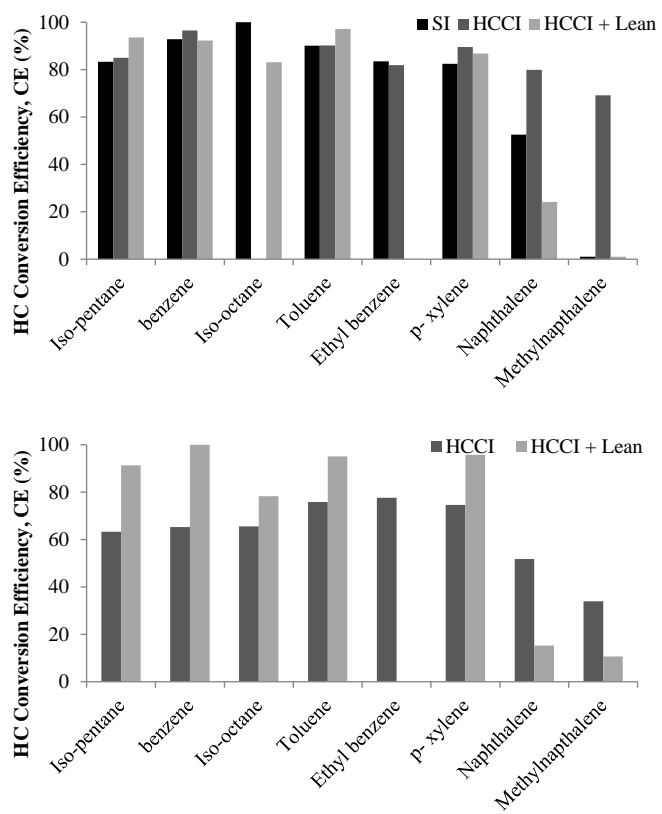




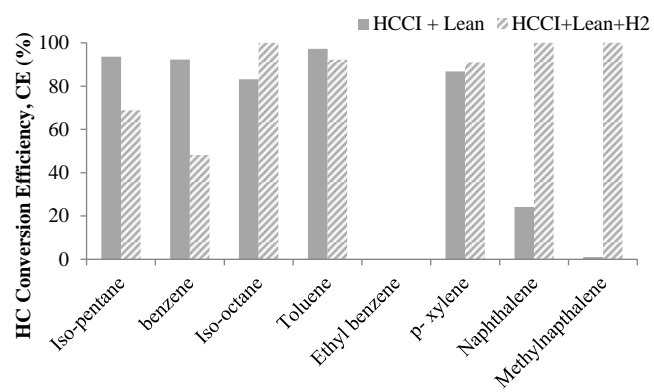
**Figure 3**



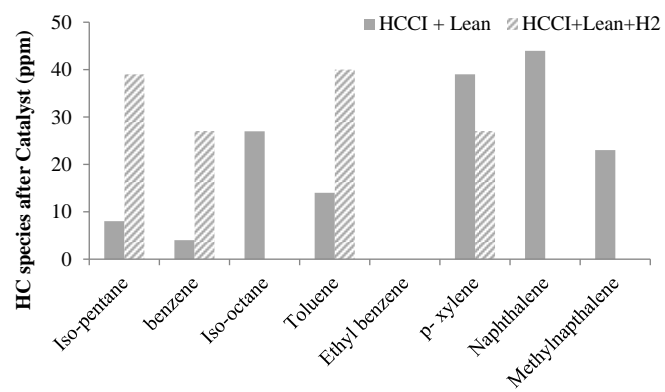
**Figure 4**



**Figure 5**



**Figure 6**



**Figure 7**