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1 **Influence of composite after-treatment catalyst on particle-bound polycyclic aromatic**
2 **hydrocarbons–vapor-phase emitted from modern advanced GDI engines**

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41 **Abstract**

42 With mutagenic and carcinogenic potential polycyclic aromatic hydrocarbons (PAHs) generated
43 from engine source which have contributed to a substantial share of air toxic, so in order to
44 characterize and eliminate the PAHs emissions of commercial engine fuelled, an experimental
45 study has been carried out on a V6 gasoline engine working in spark-ignition (SI) and
46 homogeneous charge compression ignition (HCCI) equipped with smart three-way catalyst
47 converter (TWC). The particle phase and gas phase of PAHs in engine exhaust, downstream
48 and upstream the catalyst were collected by stainless-steel cartridges containing XAD-2 resin
49 to capture PAHs species. The vapour phase and particulate bound PAHs compounds observed
50 with two and three rings to exist almost entirely in the gas phase, on the other hands, five or
51 more fused rings are predominantly adsorbed on soot particles, the intermediate – 4 ring
52 PAHs exist in the two PAHs phases, naphthalene is the most abundant polycyclic aromatic
53 hydrocarbon that was detected in the exhaust vapour- phase on both engine modes. The
54 prototype catalytic converter eliminates most of the polycyclic aromatic hydrocarbons species
55 in both PAHs phases, particle phase and gas phase, except for NAP species. A prototype
56 catalyst showed higher efficient conversion on PAHs particulate-bound phase than vapor
57 phase for both engine modes. However, when hydrogen was added upstream of the catalyst,
58 the catalyst conversion efficiency in reducing naphthalene was increased by approximately
59 20%.

60

61 **Keywords:** Polycyclic aromatic hydrocarbons; Emissions control systems; HCCI/SI engine;
62 Three-way catalytic converter.

63

64 **1. Introduction**

65

66 Multi-ring organic species are called “Polycyclic Aromatic Compounds” (PAC). Within this
67 wide range, there are species containing heteroatoms (S, N, and O) as well as those containing
68 only carbon and hydrogen which is identified mainly in automotive emissions and automotive
69 fuels. Polycyclic aromatic hydrocarbons (PAHs) are comprised of carbon and hydrogen atoms
70 in two or more aromatic rings [1]. They are a group of ubiquitous persistent organic pollutants
71 possessing carcinogenic, mutagenic, and immune-toxic properties [2]. PAHs are currently
72 unregulated pollutants in automotive exhaust emissions, they are emitted to the atmosphere
73 either in the vapor phase or associated with fine particles They occur in the atmosphere due to
74 emissions from gasoline and diesel-powered vehicles and other sources such as coal, biomass,
75 gas, and oil combustion [3–5]. PAHs thermally very stable and therefore PAH is abundant
76 molecules in the combustion zone. Therefore, they are always formed in combustion
77 processes and are attributed to unburned, paralyzed, or partially oxidized fuel and lubricant oil
78 that are transferred from the gas phase to the particulate phase by adsorption and condensation
79 on to the existing particles or by nucleation of new particles when the exhaust cools [2].
80 Despite the extensive work and literature relating to the area of automotive PAHs emissions,
81 there has been a surprising lack of definitive investigations into the link between fuels PAHs
82 content and measured PAHs emissions. There has also been a limited amount of work
83 investigating total PAHs emissions, i.e. particulate bound plus vapor phase emissions. Most
84 research has, instead, concentrated on particulate bound PAHs. The nature of gasoline
85 emissions, i.e. predominantly vapor, and the collection systems used, means that results given
86 are closer to “totals”, or “total targeted PM and vapor phase” PAHs. However, in a real
87 engine, there is always some level of in homogeneity which leads to some level of PM
88 emissions. That PM emissions from a DI HCCI engine lie between emissions from diesel and
89 SI engines and therefore, may not be negligible. The influence of air/fuel ratio (λ) on engine

90 lean operation and on the emission of specific pollutants is not very well established. PM
91 emissions are related to air-to-fuel ratio. When the air-to-fuel ratio is increased, PM diameter
92 shifted towards smaller diameters [6]. Certain individual polycyclic aromatic hydrocarbons
93 (PAHs) have been classified by the International Agency for Research on Cancer as
94 carcinogenic to animals and probably carcinogenic to humans. Evidence for the
95 carcinogenicity of some other PAHs is equivocal; for others, there is no evidence of
96 carcinogenic potential, whilst many others have not so far been tested. PAHs have attracted
97 much attention in the studies on air pollution recently because some of them are highly
98 carcinogenic or mutagenic. In particular, benzo (a) pyrene has been identified as a highly
99 carcinogenic. The occurrence of PAHs in the urban air has caused particular concern because
100 of the continuous nature of the exposure and the size of the population at risk [7-9].
101 Homogeneous Charge Compression Ignition (HCCI) engines are being investigated widely
102 because they can provide both high diesel-like efficiencies and ultra-low NO_x and particulate
103 emissions. A specific case of HCCI is gasoline-fuelled HCCI. It is attractive due to the
104 simplicity of implementing such a technology into existing SI engines as well as the existing
105 fueling infrastructure. However, gasoline is a complicated mixture of many different
106 hydrocarbons which results in rather poor auto-ignition properties, there are several technical
107 challenges that must be overcome before this promising technology is commercially viable.
108 One significant challenge is that HCCI engines produce emissions of unburned hydrocarbon
109 (HC), oxygenated hydrocarbons (OHC), and carbon monoxide (CO) and polycyclic aromatic
110 hydrocarbon PAH_s. Aldehydes are mainly produced by industrial processes and combustion
111 sources including automobile engines, the direct release of aldehydes come from internal
112 combustion engines. Incomplete combustion of fuels and atmospheric oxidation of organic
113 compounds are the major sources of carbonyl compounds, these pollutants have multiple
114 sources, but motor exhaust gas is considered as one of the most important [10-12]. The gas

115 contains specific pollutants such as alcohols and carbonyl compounds in gasoline emissions
116 especially in HCCI engines have not been thoroughly investigated. The influence of air/fuel
117 ratio (λ) on engine lean operation and on the emission of specific pollutants is not very well
118 established [13-15]. The scope of such pyro synthesis reactions are very familiar - engines
119 running on both gasoline (molecules typically in the C5 – C10 range) and diesel fuel
120 (molecules typically in the C12 – C24 range) produce emissions ranging from methane (C1)
121 to soot (upwards of a million C atoms per particle). Such reactions easily have the potential
122 to create sufficient PAHs to account for those found in exhaust emissions [16-17]. Thus it is
123 possible that new regulatory requirements might be considered for selected compounds
124 including polycyclic and aldehydes, they continue to receive scientific and regulatory
125 attention as toxic air contaminants, and carcinogens, the international agency for research on
126 cancer (IARC) has classified formaldehyde as known carcinogen to humans [18]. However,
127 regardless of the ability to minimize engine-out HC and CO emissions by altering engine
128 operations or changing engine design. HCCI engines will likely require advanced exhaust
129 emission control device, thus, engine exhaust after-treatment systems are widely considered.
130 Catalyst technology for HC and CO removal is well understood and used in gasoline-fueled
131 automobiles for twenty-five years. Although some oxidation catalysts were introduced much
132 earlier, it was not until the 1980s that the Three-Way-Catalyst (TWC) was developed by
133 which NO_x, CO and HC can be converted simultaneously [19]. Catalytic converters are being
134 widely used in automobile and considered to be the most effective technique in reducing
135 harmful emissions from internal combustion engines. It is evidenced that future emission
136 regulations (i.e. CO₂ limits) will see encourage HCCI and lean (i.e. O₂ presence) engine
137 operation in addition to stoichiometric SI. A suitable exhaust after-treatment system would be
138 required in order to reduce HC, CO, NO_x and possibly PM emissions within allowable limits
139 of the SI/HCCI dual mode engine. The current exhaust gas 3-way catalytic converters are

140 ineffective in reducing NO_x (and maybe certain hydrocarbons) under lean or HCCI engine
141 operation conditions where the exhaust temperature is lower [20-23].
142 This paper describes the concentration of 16 individual PAHs in semi-volatile gas phase and
143 in PM generated by a V6 SI/HCCI engine, PAH concentrations will be identified and
144 quantified downstream and upstream the smart treatment catalyst. The commercial gasoline
145 fuel was used in this investigation, in order to understand the emissions gases emitted from
146 the HCCI engine and compare it to SI engines. It has also been an important aim of this study
147 to see whether a prototype catalyst has the potential to reduce specifically naphthalene,
148 acenaphthylene, acenaphthene, and fluorene emissions together with the other polycyclic
149 aromatic hydrocarbons compounds. Analysis for both HCCI/SI engine modes, under lean and
150 stoichiometric engine operation has been carried out. Emission measurements and PAHs
151 analysis of the exhaust gases in the vapor phase and particulate-bound from HCCI/SI engine
152 operation have been carried out at five engine conditions. The variables studied were engine
153 load effect under HCCI stoichiometric operation, air to fuel ratio, HCCI and SI combustion
154 modes under the same load, and hydrogen addition upstream of the catalyst.

155

156 **2. Experimental**

157 **2.1 Engine**

158 The multi-cylinder engine used for this research is the Jaguar AJV6 direct injection research
159 engine having swept volume of 3 L with the specification given in Table (1). The engine
160 Figure (1) used in this work has been described in a previous publication [24-27]. A positive
161 displacement supercharger is connected to the engine to be used when needed, but throughout
162 this research natural aspiration was implemented. The engine is equipped with cam profile
163 switching mechanism to switch between profiles required for SI and HCCI. The variable cam
164 timing systems give the possibility of changing the cam timing of the intake and exhaust cams

165 within a range of 60 crank angle degrees. Negative valve overlap was used to increase the
166 amount of exhaust gas retained in the cylinder to achieve HCCI combustion. The engine is
167 connected to an EC38 eddy current dynamometer. A DSPACE-based system coupled to a
168 computer using MATLAB/SIMULINK software is used to control the engine parameters
169 during operation and to record engine data.

170 The HCCI mode starting procedure involves a warming-up period when the engine was
171 operated in SI mode first until the crankcase lubricant and coolant temperatures reached 90°C.
172 In HCCI mode the engine was operated with the throttle wide open. The temperature of the
173 intake air was controlled by a thermal management system. Fuel flow was measured by an
174 AVL controls gravimetric meter, and fuel direct injection pulse width is adjusted by the
175 engine management system to maintain the required value of air/ fuel ratio (Table 2).

176 **2.2 Catalyst**

177 The prototype 3-zone monolith catalyst (supplied by Johnson Matthey) (Figure 1) was
178 connected to the actual engine exhaust manifold [27]. The first zone was designed to reduce
179 HC and NO_x under lean and stoichiometric engine conditions at high temperatures >400°C,
180 the second zone was designed to reduce NO_x by reaction with hydrocarbon under lean engine
181 operation in the temperature range of 250°C – 400°C. Both zones contain non-precious metal
182 catalyst supported on alumina or zeolite. The third catalyst zone (Pt-based) was designed to
183 control part of the exhaust hydrocarbons and CO at temperatures below 300°C. Diluter tunnel
184 was used to trap the PAHs bounded to PM and a stainless steel cartridge was used to trap the
185 vapor-phase PAHs.

186

187

188

189 2.3 Fuel

190 Standard unleaded gasoline of RON 95 was used in this study which composed of H/C =
191 1.86; composition (saturated = 48.26%, olefins = 16.2%, naphthenes = 3.66%, aromatic =
192 30.2%). Clarifying the hydrocarbon components in conventional gasoline fuel is considered to
193 be the key step in speciating of HCs in the engine exhaust. By using the retention times of
194 some known compounds chromatograms and the NIST library together, the peaks in gasoline
195 chromatograms could be identified. The hydrocarbons in gasoline consist primarily of light
196 aliphatic hydrocarbons (butane, pentane, methyl-pentane, hexane, methyl-hexane, heptane and
197 octane) and aromatic compounds (toluene, xylenes, and trimethyl-benzenes), with smaller
198 amounts of olefinic hydrocarbons (pentenes, hexenes, heptenes, octenes and nonenes). The
199 GC-MS characterization of the main components in the used gasoline fuel is shown in Figure
200 (2).

201 2.4 Emissions analysis

202 Horiba MEXA 7100 DEGR (THC, CO, NO_x, CO₂, and O₂) analyzer equipped with the heated
203 line was used to measure total hydrocarbons, carbon monoxide, carbon dioxide NO_x and
204 oxygen.

205 **PAH compounds:** There is no standard procedure for measuring specific PAHs compounds
206 species as they are not individually regulated, so both the sampling and measurements method
207 were optimised for the experimental conditions and PAHs study. The PAHs was performed
208 using GC-MS. The retention time for each species was calibrated daily before each set of an
209 experiment by the analysis of 16 PAHs compounds in acetonitrile solvent (PAHs Mixture;
210 Supelco, Bellefonte, PA, USA). The total run time was 50 min for a retention time of the
211 species given in (Table 3), the integrated area of each specific peak in the chronogram was
212 used to calculate the concentration of the associated component. The VG mass-lab software

213 was used acquire and integrate the basic GC-MS data. PAH Standards and measured samples
214 were injected into a J & W DB-5 column. The oven temperature was increased from 60°C and
215 fixed for 2 min, and then increased to 300°C at a rate of 10°C/min, held at 300°C for 20 min
216 with a total runtime of about 50 min. The components of the standards sample solution were
217 generally stable under the operation conditions of GC used in these analyses. Complete
218 separations of the standard sample species were obtained. The well-known sampling method
219 used to identify semi-volatile organic species is the trapping of these species on a solid
220 sorbent; different sorbents could be used for this analysis, according to previous study XAD-2
221 (Supelco) is an excellent trapping media for PAHS, for many applications, though it was
222 selected for trapping and collecting PAHs from engine exhaust emission. The XAD-2 resin
223 was loaded in stainless-steel cartridge to retain the PAHs on the vapor phase; the cartridge is
224 split into three zones, 10 g of XAD-2 resin (50 mm) was inserted between 25 mm and 10 mm
225 quartz wool plugs. Quartz wool is used at the inlet of the cartridge to filter particulate matter
226 that could contaminate the resin, and at the outlet of the cartridge to fix the resin and to
227 prevent escaping the resin to the flow meter [28]. The flow rate of sampling was 1.0 l/min for
228 30 min and immediately after collecting the sample; the cartridges were soaked in
229 dichloromethane sonic bath to extract the trapped species (3550B methodology of Misonix
230 [29,30]). Ultrasonic Processor-XL was carried out at 20 Hz for 30 min immersed in an ice
231 bath, and then concentrated by rotary evaporation at 20°C, then after extraction samples were
232 purified.; using NH₂-C18 column [15]. Acetonitrile was used to elute the PAHs from the
233 clean-up column. The recovery efficiencies for PAH were tested through same experimental
234 procedure applied to the samples. The recovery-efficiency of PAHs varied between 74% and
235 119%.

236

237

238 **2.5 Sampling**

239 The sampled PAHs underwent a classical Soxhlet extraction, and then the extract
240 concentration was performed using a rotary evaporator and micro-concentration under gentle
241 nitrogen stream before the GC–MS analysis. (PAH Mixture; Supelco, Bellefonte, PA, USA)
242 A standard solution containing 16 EPAPAH compounds in acetonitrile solvent was used to
243 calibrate the GC–MS. Table (2) shows the characteristic parameters and the retention time for
244 the standard 16 PAH compounds. The particulate matter is consisting of soluble and insoluble
245 components; the Soluble Organic Fraction (SOF) presents the proportion of particles that are
246 soluble in commonly used solvents such as dichloromethane. The insoluble part can be
247 evaluated by comparison the weight of the filter before and after the extraction. The sampling
248 rate of the diluted exhaust was 100 l/min and the collection time was 30 and 90 min for SI and
249 HCCI modes respectively. The sampled PAHs underwent a classical Soxhlet extraction,
250 PAHs in filter samples were extracted in dichloromethane and quantified by GC–MS. Filter
251 disks were ultrasonicated in high-grade dichloromethane. The identification and quantification
252 of PAHs were carried out using the same temperature program as in the previously mentioned
253 case of PAH₅ analysis with GC–MS method.

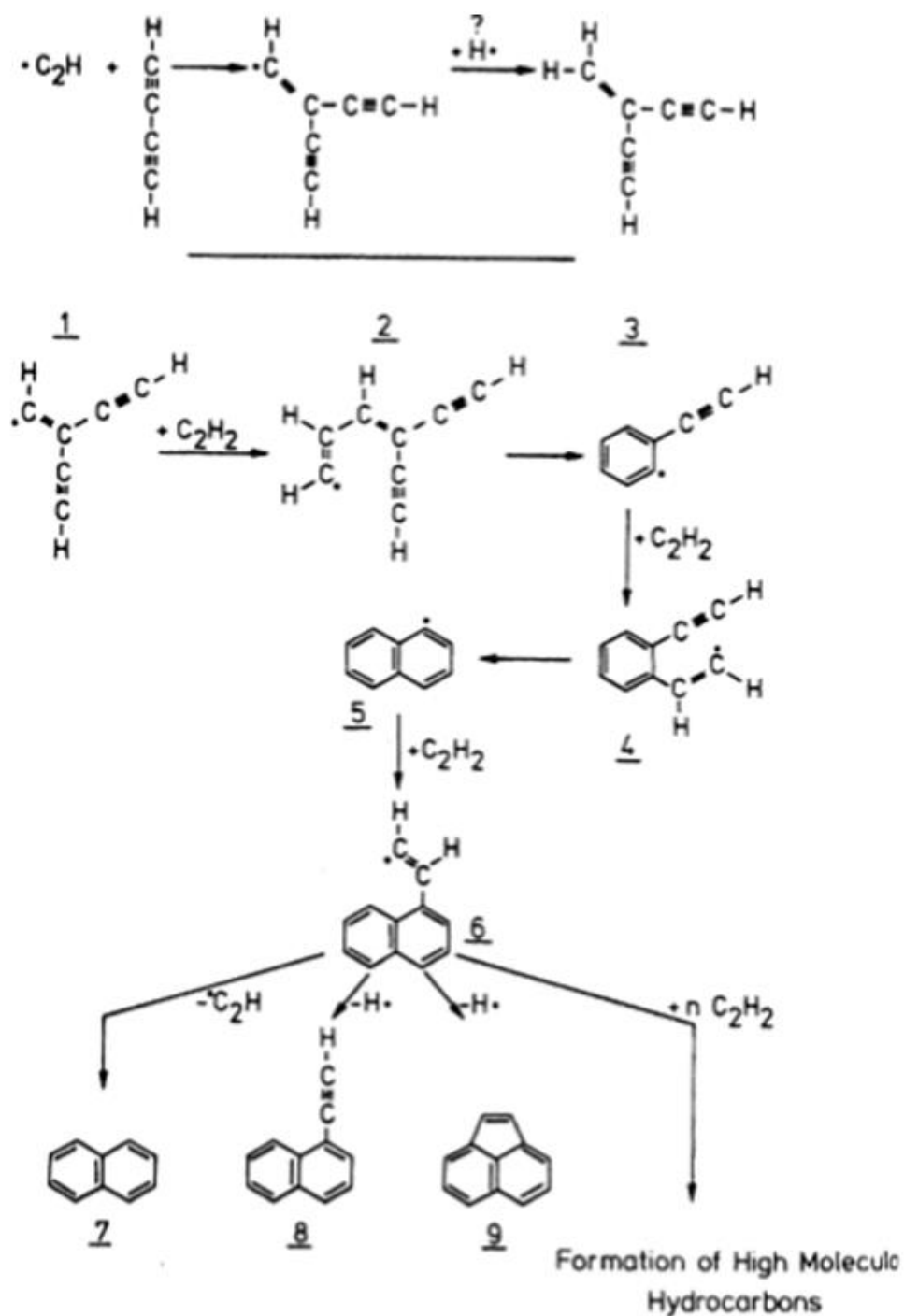
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255 **3- Results and Discussion**

256 3-1 Engine out PAH species emissions

257 Experimental work indicates that favorable kinetics and thermodynamics lead to PAHs
258 formation from non-PAH₅; including non-aromatic, fuel components, and a substantial
259 fraction of the exhaust PAH₅ could be formed by pyro synthesis. PAH₅ are readily created
260 during the partial combustion of non-PAH₅ and even non-aromatic hydrocarbons. This can
261 be attributed both to favorable combustion kinetics and to the thermodynamic stability of
262 PAH. Few authors have attempted to correlate fuel composition/PAH levels with those

263 measured in the exhaust or have included any measurement of PAHs in the test fuels used
264 [31, 32]. The thermodynamic stability of PAHs (especially pre-condensed ones) makes them
265 likely products of incomplete combustion (also known as pyrolysis); irrespective of the
266 molecular structure of the fuel (i.e. the fuel need not contain PAHs for there to be PAHs in the
267 flame). This is particularly true under fuel rich conditions such as those found close to the
268 surface of an evaporating fuel droplet in a hot environment. It is also generally believed that
269 PAHs are important intermediates on the route to soot formation [33,34]. A scheme of the
270 chemical pathways suggested a reaction sequence beginning with diacetylene and C_2H
271 forming a branched hydrocarbon radical followed by acetylene attack and ring closure leading
272 to a phenylacetylene radical including the formation of larger polycyclic aromatics [28] as
273 shown by the following mechanism:



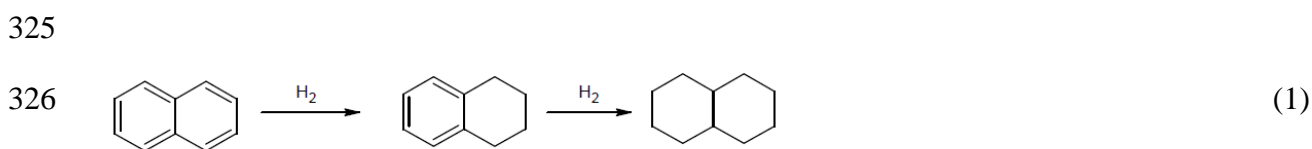
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275 Naphthalene has been studied as it has been reported to be the most abundant PAHs in
 276 polluted urban atmospheres [35]. It has been defined as a hazardous air pollutant by the US
 277 environmental protection agency (EPA) (USEPA (USE environmental Protection Agency),
 278 2000) and classified as possibly carcinogenic to humans by the international agency for
 279 research on cancer (IARC) [36]. In our study in both engine modes HCCI/SI PAHs are
 280 distributed between vapor and particulate phases. Most of the low molecule mass and high

281 vapor pressure (2,3 rings) PAHs are presented in the vapor phase, On the contrary, 4-ring
282 PAHs having a low vapor pressure were present in the particulate phase (Tables 4 & 5). In SI
283 mode, under the same engine conditions ($\lambda=1$, load, 4bar), see Figures (3 & 4) vapor phases,
284 compounds species with 2-3 cyclic rings (NAP, ACY) presented with high concentration
285 comparing to HCCI mode, naphthalene engine output emissions increased (Table 4). This
286 phenomenon could be attributed to the higher in-cylinder temperature at high load, changing
287 to higher load in HCCI stoichiometric (Table 5) did not have a big impact on 4,5 cyclic rings
288 concentration (e.g. PYR, BAA, BAP and BKF), on the other hand changing to HCCI lean
289 mode Figure (5) increased the species concentrations three times the stoichiometric in some
290 species, this is due to (i) the fact that, the in-cylinder temperature HCCI lean is lower than the
291 stoichiometric mode (ii) the residual gases left in the cylinder from the previous end stroke.
292 During combustion, gas particles, including those of fuel vapor, are absorbed by the deposits
293 on the walls of the combustion chamber. The amount of absorption is a function of gas
294 pressure, so the maximum occurs during compression and combustion. Later in the cycle,
295 when the exhaust valve opens and cylinder pressure is reduced, the absorption capacity of the
296 deposited material is lowered and gas particles are desorbed back into the cylinder. These
297 particles, including some HC, are then expelled from the cylinder during the exhaust stroke.
298 The total PAHs emissions from SI was about 900 ppm, the corresponding value from HCCI
299 was 820 ppm C1 equivalent (Table 4). The SI mode generated more PAHs species in the
300 vapor phase, as well as the total amounts of PAHs, are higher compared to that produced from
301 HCCI operation mode. NAP is the most abundant polycyclic-aromatic hydrocarbon presented
302 in large quantity in the exhaust vapor phase, the definition of “PAH” is rather loose and what
303 to some may seem like the “creation” of a PAH may, to others, seem more akin to “survival”.
304 For example, either case could be made for fuel naphthalene molecules which undergo pyro
305 synthetic reactions resulting in the formation of phenanthrene, which may then pass to the

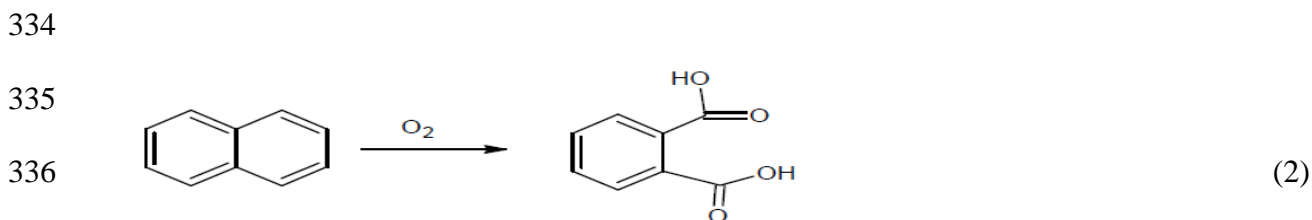
306 exhaust. ACY (Table 4) was the second abundant compound in the vapor phase in both
307 modes. There are some compounds which are not part of the used fuel have been detected in
308 the vapor-phase, these species could be formed as a result of the reaction of the active species
309 that produced from thermal cracking of fuel through Pyro synthetic pathway.
310 Species with four cyclic rings (FLT) (Table 4) was detected from HCCI lean and SI
311 stoichiometric. PYR is observed mainly in HCCI lean mode and SI engine operation mode.
312 These two compounds believed to be formed through the pyro synthetic pathway and were
313 presented with very low concentration when the engine was operating on HCCI low load.
314 PAHs bounded to particulate phase concentrations compound species with 4 and 5 cyclic ring
315 were detected (e.g. PYR, BAA, CRY, BBF, and BAP) in both modes SI and HCCI (Table 5,
316 Figures 3 & 4). Since these polycyclic-aromatic compounds are not part of the fuel, then they
317 should be formed in the combustion process of the fuel in the combustion chamber. In
318 general emissions of PAH found to be more surviving in vapor phase than bound to
319 particulate phase. Several proposals were made regarding the nature of the formation of
320 PAHs; one of these proposals is the formation of the first aromatic ring under pyrolysis
321 conditions from the reactive olefins and has been studied by various groups [37-39].

322 The wide majority of the NAP recovered in fuel combustion under certain conditions is formed
323 from other sources than the original NAP found in the fuel (40). The same conclusion is presented
324 about the formation of other aromatic hydrocarbons that were part of the fuel.

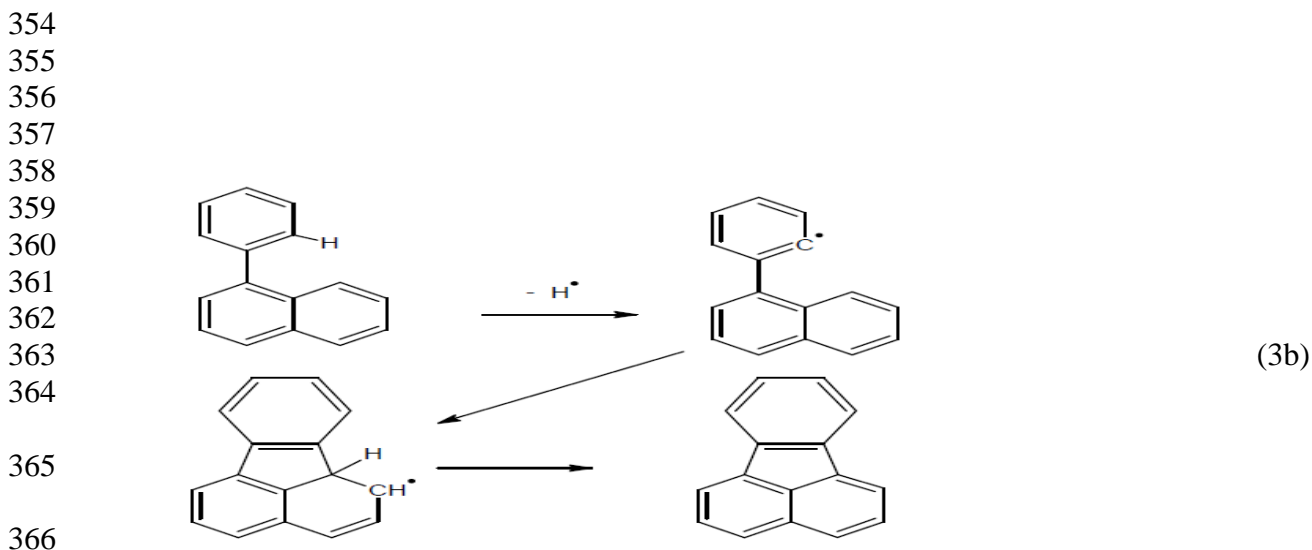
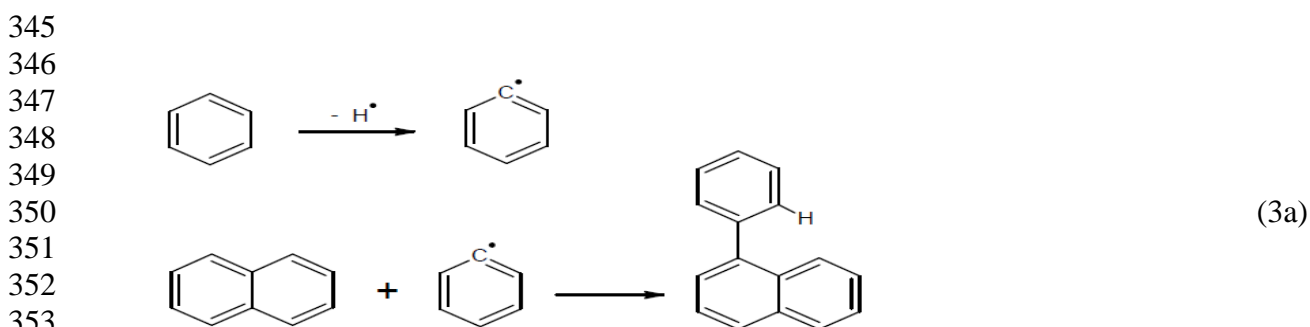


328 Parallel to aromatics growth is aromatic oxidation, an example is the hydrogenation of NAP.
329 Hydrogen can be formed through many different routes in fuel combustion process, and hence can
330 be involved in the dehydrogenation of aromatics. Eq. (1) is represent the partial (formation of
331 Tetrahydronaphthalene) and complete hydrogenation of NAP (formation of

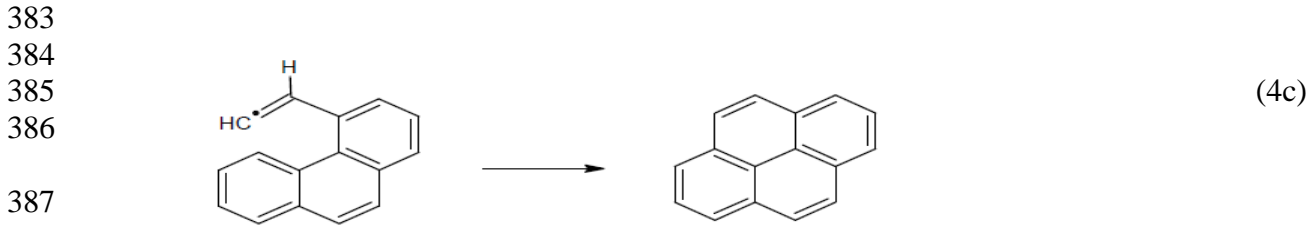
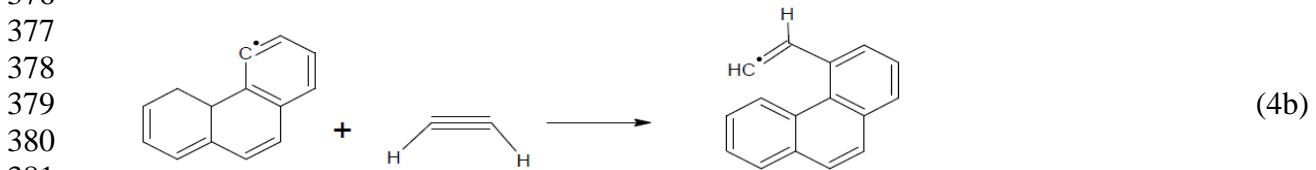
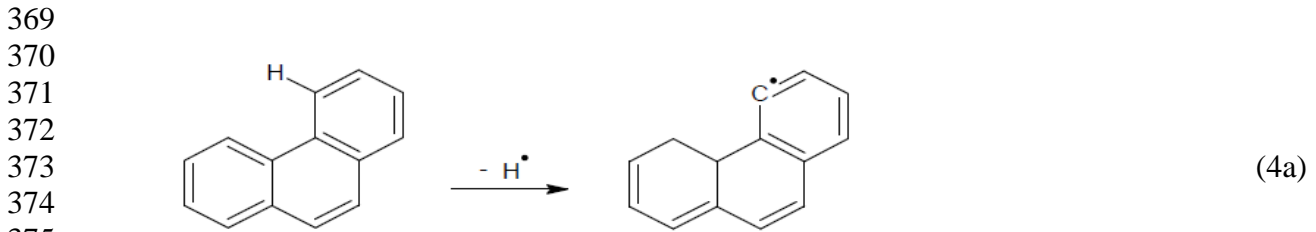
332 Decahydronaphthalene). Aromatics also can go through oxidation process to form mono- and
333 dicarboxylic acids (reaction 2).



338 Not many researchers have investigated the formation of these species, but the oxidation and
339 reduction of aromatics are unavoidable in the combustion process. FLT and PYR were not part of
340 the fuel used, but they were traced in the emission of different loads in both engine modes
341 HCCI/SI. The concentrations of these two compounds, as well as the concentration of other
342 aromatics, were higher from SI relative to their emissions from HCCI. FLT formation
343 mechanisms involve the reaction of NAP with a phenyl radical (reaction 3a) followed by
344 cyclization (3b).



367 Formation of PYR involves hydrogen abstraction from PHE (4a), followed by acetylene
368 addition (4b) and then cyclization (4c).



388

389 Since PM nucleation mechanisms depend strongly on the gas and liquid phase fuel
390 concentrations as well as temperature (41-44) so that decreased concentration of both fuel
391 phases combined with decreased in-cylinder temperature results in a sharp decrease in the
392 amount of PM nucleated as the load in HCCI decreased.

393 As more hot exhaust gas remains in the cylinder, the intake temperature rises and the results
394 in more rapid evaporation of liquid fuel, in contrast with the low consumption of the fuel at
395 low loads in HCCI mode, then less PM.

396 It has been reported that nano-particles form in three stages during combustion (45). The first
397 stage involves PAH formation and growth that showed and explained above. The second
398 stage is the nucleation of PAHs to form nuclei. The last stage involves the collision of nuclei
399 to form particles.

400 In this process, Inlet valve timing has been kept constant at IVO = 65°a TDC. During
401 presented tests, the in-cylinder TR content has been firstly increased by advancing the exhaust
402 valve (EVC has been shifted from 86°b TDC to 91°b TDC) and secondly reduced by
403 retarding the exhaust valve (EVC has been shifted from 86°b TDC to 76°b TDC). When the
404 amount of TR has increased, the load and NO_x emissions have reduced. UHC emissions have
405 been almost the same. A reverse trend has been observed when TR content has been reduced;
406 load and NO_x emissions have risen, and UHC emissions have fallen.

407

408 **3.2. Catalyst conversion efficiency**

409

410 The identified PAH_s compounds in both phases and their concentrations in the engine – out
411 and tailpipe exhaust at different load levels were shown in Tables (4 & 5) respectively. Three
412 and four cyclic rings were detected in the vapor phase at the meantime five and six cyclic
413 rings were found in the bound to particulate phase. Main compounds species were identified
414 in engine-out emission at low engine load of 3 bar in vapor phase such as NAP, ACY and
415 ACE, while a higher concentration of the same compound species was presented in a higher
416 load of HCCI stoichiometric operation. The catalyst conversion efficiency in SI mode Figure
417 (6) vapor phase reached over 90% efficiency of compounds with three and five cyclic rings
418 (e.g. ACY, ACE, and ANT), and reduced around 80% when five and six cyclic rings
419 compound were involved in the conversions operation. The most abundant compound among
420 the species was NAP which resists the catalyst conversion up to 60%. When switching engine
421 mode to HCCI, under the same engine conditions, catalyst efficiency improved sharply up to
422 92% for most of the compound species Figure (6), this could be attributed to the three zones
423 of the smart catalyst which covered three ranges of temperature (low, medium, and high
424 temperature). Similar conversion efficiency existed in HCCI lean Figure (6) except for NAP
425 conversion which did not reach 30%, in SI mode stoichiometric most of the species with four

426 and five cyclic rings were found in high concentration Figure (6). In the bound to particulate
427 phase, the catalyst showed more conversion capability Figure (7), up to 100% efficiency for
428 some compound species such as BAA, BKF, and BAP was found.

429

430 **3.3 Catalyst performance with H₂ addition, HCCI lean engine operation**

431

432 The effect of hydrogen has been investigated by injecting approximately 2000 ppm H₂
433 upstream of the catalyst, in order to improve the catalyst performance in the reduction of
434 harmful HC species such as naphthalene (classified as possibly carcinogenic by IARC) [18].
435 The comparison is drawn between the same engine operating condition (lean HCCI
436 combustion at 4 bar NMEP) with and without hydrogen addition (Table 4 & 5). From the
437 results it can be observed that hydrogen greatly enhances the catalyst performance 20% more
438 Figure (8 & 9) in reducing naphthalene There are several likely causes: (i) hydrogen oxidation
439 in the first zone increases the catalyst temperature by (5-20 °C), enhancing the oxidation rate
440 of the aromatic hydrocarbons (i.e. the exothermal effect of hydrogen); (ii) it has been reported
441 earlier that hydrogen oxidation in for example a Pt/Al₂O₃ catalysts, increases the availability
442 of NO₂ that is consequently consumed in the oxidation of the C-containing species [46]; (iii)
443 hydrogenation is another possibility, in which H₂ reacts with the aromatic compounds to form
444 less unsaturated cyclic and aliphatic hydrocarbons that are easier to combust. However,
445 although the hydrogenation reactions are overall exothermic, there is a high activation barrier
446 to overcome.

447 **Conclusions:**

448 (i) Engine-out emissions: air/ fuel ratio (λ) in the vapour phase has a higher impact on species
449 with two and three cyclic rings (e.g. NAP, ACY , and ACE) condensable emissions presented
450 in HCCI lean operation while (λ) has less effect on species with four and five cyclic rings
451 (e.g. PYR, BBF , and BKF). PAH_s species are heavily dependent on engine operation and

452 combustion mode (i.e. HCCI or SI). PAHS species (e.g. FLU, ACY) concentrations were
453 found to be higher in the SI mode, while PAH_S species such as PYR was mainly found in the
454 exhaust of both engine modes. Analysis showed that the PAH_S species concentration of HCCI
455 lean exhaust contained more of the two cyclic rings species than during HCCI stoichiometric
456 operation (e.g. NAP).

457 (ii) Post-catalyst emissions: A prototype catalyst showed more efficient conversion on PAHS
458 species with three and four cyclic rings in the exhaust vapor phase and five and six cyclic
459 rings in the bound particulate for both engine modes. During lean operation, regardless of the
460 low exhaust temperature, most of the PAH_S species emissions in the tailpipe exhaust were
461 eliminated except for the Naphthalene, the catalyst conversion was reduced. The catalyst was,
462 therefore, less capable of activating a fused pair of benzene rings than aliphatic or mono-
463 aromatic molecules

464 (iii) The addition of hydrogen upstream of the catalyst during HCCI lean engine operation
465 substantially enhances the conversion of naphthalene species. This is attributed to an increase
466 in the local temperature as a result of hydrogen oxidation, and due to its reactivity with the
467 aromatic compounds to form molecules that are more readily oxidized by the catalyst.

468 Therefore, this research work has demonstrated that, through the integration of advanced
469 combustion technologies with novel after treatment systems, it should be possible to achieve
470 notable benefits in fuel economy and in air quality.

471

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479

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