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1 **Understanding the Impact of Cavitation on Hydrocarbons in the** 2 **Middle Distillate Range**

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8 9 **Abstract**

10 Hydrocarbons in the middle distillate range (C₈–C₂₆) have been treated with ultrasound at 20
11 kHz – a frequency sufficient to drive acoustic cavitation. The high temperatures experienced
12 as a result of the implosion of fuel vapour bubbles are sufficient to produce pyrolytic
13 degradation and dehydrogenation, as well as a growth mechanism that results in the
14 formation of small particles that have similarities with the primary soot particles produced
15 during diesel combustion. These nanosized particles agglomerate as a result of kinetically
16 driven collisions during cavitation to form a dispersion of micron sized particles in the treated
17 hydrocarbon. The particles are carbonaceous in character, being a mixture of amorphous and
18 graphitic-like carbon. The mass of material produced increases with the C/H atomic ratio of
19 the hydrocarbon undergoing cavitation and is decreased through the addition (1–3 %v/v) of
20 low boiling paraffinic hydrocarbons, possibly as a result of lowering the temperature
21 developed inside imploding cavities. Dispersions of microparticles contain equilibrated
22 levels of nanoparticles. If sufficiently high numbers of these smaller primary particles are
23 present they agglomerate due to thermally driven collisions during post-cavitation storage.
24 When this happened a sharp rise in the number of 1–2 μm particles was seen after only a few

25 days. Some evidence is presented for the behaviour of ultrasonically treated hydrocarbons
26 being related to the degradation of diesel fuel exposed to hydrodynamic cavitation in the fuel
27 systems of modern common rail direct injection diesel engines.

28

29 **Keywords:** Cavitation, microparticles, middle distillate hydrocarbons, nanoparticles,
30 pyrolytic degradation, ultrasound.

31

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34

1. Introduction

35
36 Ultrasound has become a common laboratory tool used to generate acoustically driven
37 cavitation and chemical reactions in liquids (sonochemistry) [1,2]. The compression and
38 rarefaction of the sound waves when passed through a liquid produces bubbles; the
39 formation, growth and collapse of which is known as cavitation. These bubbles, which are
40 comprised of vapour and dissolved gases, shrink and expand under the influence of the
41 acoustic field. Individual bubbles experience interference from their surroundings and
42 consequently expansion to an unstable size can result, followed by an implosive collapse.
43 This produces localised hot spots (~5,000 K) which are characterised by very rapid heating
44 and cooling rates ($>10^9$ K s⁻¹) [3–7].

45 The acoustic sonication of a range of hydrocarbons that fall within the middle distillate
46 range (C₈–C₂₆) has now been studied as a means of simulating some of the chemistry that
47 may occur in diesel fuel whilst in the high pressure fuel systems of modern common rail
48 direct injection compression ignition engines. The cavitation of fuel in these systems is
49 hydrodynamic in origin, as opposed to acoustic, and can result from the pressure drop across
50 an orifice or when fast moving flows turn sharp corners. Some of the first reports of non-
51 aqueous sonochemistry were published over fifty years ago and suggest that the sonication of
52 aromatic and heterocyclic compounds produces ring cleavage and acetylene production
53 [8–10]. Subsequently Suslick and co-workers found that alkanes undergo sonochemical
54 reactions which are similar to high temperature ($>1,200$ °C) pyrolysis [11]. For example, the
55 products of *n*-decane sonolysis are hydrogen, methane, acetylene and a series of alkenes
56 including ethylene, propylene, butene, pentene, etc. This is consistent with the operation of a
57 radical chain Rice mechanism [12]. Riesz and Misik in related work trapped and identified
58 the radicals produced during the sonolysis of a number of different organic liquids, including
59 *n*-alkanes. Their results were also consistent with a pyrolysis mechanism [13,14].

60 Cataldo found that the prolonged sonication of benzene, toluene, styrene and tetralin
61 produced insoluble dark matter [15]. Infrared spectroscopy of the material from benzene
62 sonolysis suggested that the product contained a cross-linked structure similar to radiation-
63 damaged polystyrene. Decalin and tetralin sonication caused aromatization reactions,
64 although decalin was also cracked to *o*-xylene and ethylene. Somewhat similar findings have
65 also been reported by Katoh and co-workers, who produced C₆₀ fullerene from benzene
66 sonolysis [16]. In subsequent work, the same group produced carbon nanotubes by applying
67 ultrasound to liquid chlorobenzene containing suspended ZnCl₂ particles [17]. A large
68 number of sono-polymerisation reactions have also been reported [18–22].

69 Four different types of reaction have therefore been observed in the ultrasonic
70 destruction of non-aqueous liquids: Radical pyrolysis, thermal cracking, radical
71 polymerisation and dehydrogenation. This results in the possibility of both larger and smaller
72 molecules being formed in hydrocarbons that have undergone cavitation.

73 In 1995 Price and co-workers explored the possibility of using ultrasound for accelerated
74 aging of diesel fuels in an attempt to predict long-term storage stability [23,24]. Common
75 rail high pressure diesel injection systems were not widely available in the market at this
76 time. Experiments with dodecane showed evidence for thermal cracking after 20 hours of
77 sonication, with detection of C₇–C₁₀ species by gas chromatography mass spectrometry.
78 After automotive grade diesel was sonicated for >6 hours, sediment was produced with an
79 average molecular weight of 40,000 amu. The material was deep brown in colour, almost
80 completely soluble in tetrahydrofuran (THF) and had a UV-Vis absorption spectrum
81 characteristic of aromatic species. Infrared analysis suggested the presence of ester carbonyl
82 groups, unsaturated hydrocarbons and possibly indole-like groups.

83 More recently an experimental investigation into the impact of hydrodynamic cavitation
84 on diesel has been reported by Lockett and Jeshani [25]. Samples of commercial diesel were

85 subjected to 40 hours of cavitation across an injector at a pressure of 550 bar. The fuel was
86 cooled to 70 °C after cavitation before being re-cycled through the injector. The optical
87 absorptivity of each diesel at 405 nm was observed to increase as a result of chemistry
88 undergone by aromatic hydrocarbons present in the fuels. The increase in absorptivity was
89 found to be greater for fuel exposed to both cavitation and temperature than for fuel
90 maintained at 70 °C for 40 hours in a water bath. Additionally it was found that a greater
91 increase in absorptivity during cavitation was observed for fuel that had been stored for a
92 year before testing.

93 This paper reports the results of ultrasound experiments on a number of pure
94 hydrocarbons (1-methylnaphthalene, decalin, tetralin, hexadecane) and hydrocarbon mixtures
95 (diesel and 1-methylnaphthalene combined with a range of different aromatic, naphthenic and
96 paraffinic hydrocarbons to make two component mixtures). The formation of insoluble
97 products generated by cavitation has been studied along with the critical physical and
98 compositional properties of the liquids that control the chemistry taking place. This is related
99 to the behaviour of diesel fuel in the high pressure fuel systems of common rail direct
100 injection compression ignition engines.

101

102 **2. Experimental**

103 **2.1 Ultrasound treatment of hydrocarbons**

104 Sonication experiments were carried out with a VCX 500 ultrasonic processor (ex.
105 Sonics Materials Inc.) and a 13 mm extender horn which delivers ultrasound to a 50 mL
106 sample of hydrocarbon contained within a jacketed glass beaker. Cold water (5 °C) was
107 passed through the jacket to keep the liquid hydrocarbon below its flash point – for safety
108 reasons a cut-off temperature was set at 55 °C. A PTFE lid was used to prevent splashing
109 whilst dry air was blown over the surface of the fuel to ensure that there was no condensation

110 inside the reaction vessel (Fig. 1). The whole apparatus was housed inside a box fitted with a
111 safety cut-out mechanism and insulated to reduce acoustic noise.

112 {Fig.1 here}

113 Ultrasound is produced at a frequency of 20 kHz and when the amplitude of the
114 processor is set to 65% the transfer of energy to the hydrocarbon occurs at $6 \text{ kJ mL}^{-1} \text{ h}^{-1}$. The
115 probe is made of titanium alloy (Ti 6Al-4V) and consists of 90% titanium, 6% aluminium and
116 4% vanadium. This material is susceptible to cavitation erosion and becomes tarnished
117 during use. The probe was polished on silicon carbide paper between each experiment to
118 maintain a smooth and shiny tip surface.

119 In a typical experiment 50 mL of hydrocarbon was sonicated for a set period of time,
120 during which a darkening occurred due to the build-up of a dispersion of carbonaceous
121 particles. Gravimetric analysis of these particles was carried out by adding 50 mL of *n*-
122 heptane to the sonicated hydrocarbon and shaking. The sample was then split between two
123 centrifuge tubes and spun at $4,000 \text{ r min}^{-1}$ for 20 minutes. The deposit sediment was
124 collected, dried and weighed on a $0.7 \text{ }\mu\text{m}$ Whatman glass microfiber filter (Grade GF/F).

125

126 **2.2 Hydrocarbon materials**

127 Hydrocarbons were sourced from the Sigma-Aldrich Corporation in their highest
128 available purity. The diesel fuel used was an EN590 'zero' sulphur diesel (sulphur $<10 \text{ ppm}$,
129 density 0.844 g cm^{-3} , viscosity $2.8 \text{ mm}^2 \text{ s}^{-1}$ at $40 \text{ }^\circ\text{C}$, water content 45 mg/kg , mono-
130 aromatics 27.1 \%m/m , di-aromatics 3.5 \%m/m , tri-aromatics 0.4 \%m/m , carbon 86.4 \%m/m ,
131 hydrogen 13.1 \%m/m , oxygen $<0.04 \text{ \%m/m}$) which contained no performance additives or
132 fatty acid methyl ester (FAME). Before treatment with ultrasound all samples were filtered
133 through a $0.7 \text{ }\mu\text{m}$ Whatman glass microfiber filter (Grade GF/F).

134

135 **2.3 Laser particle counting**

136 Particle analysis was carried out using a Spectrex LPC-2200 laser particle counter
137 (Spectrex Corporation, Redwood City, CA.) which makes measurements based on the
138 principle of near-angle light scattering. A revolving laser beam is passed through the walls of
139 a glass container; any particles present in the fuel sample cause the beam to scatter. The
140 extent of scattering is proportional to the number and size of the particles, which are reliably
141 counted in the 1 to 100 μm size range. Samples were agitated on a mechanical shaker (300 r
142 min^{-1} , 1 minute) before standing to allow any air bubbles to settle. Particle counts were then
143 based on the average of three consecutive measurements.

144 When the number concentration is higher than $1,000 \text{ cm}^{-3}$ there is a risk of overlap
145 between particles in the third dimension (i.e. closer to or further from the detector) which
146 may lead to two or more small particles being counted as a single large particle. Sample
147 dilution with chromatography grade *n*-heptane, which has a very low background particle
148 count ($< 20 \text{ cm}^{-3}$), prevents this artefact from occurring.

149

150 **2.4 Transmission Electron Microscopy (TEM)**

151 Samples were prepared for TEM analysis by mechanically agitating the sonicated liquids
152 for 1 hour before taking a 3 mL aliquot and diluting with 15 mL of *n*-heptane. The resulting
153 suspension was then filtered onto a holey carbon film 300 mesh copper TEM grid and de-
154 oiled using a capillary heptane wash. Imaging was carried out in transmission mode using a
155 JEOL 2100 TEM (JEOL Ltd, Tokyo) at 200 kV beam voltage. TEM-EDX analyses were
156 made using an Oxford Instruments INCA system with an X-max-80 silicon drift detector
157 (Oxford Instruments Ltd, Oxford, UK).

158

159 **2.5 X-ray Diffraction (XRD) and SEM-EDX**

160 Samples were prepared for XRD by filtration from the sonicated liquids onto 0.4 μm
161 track-etched membrane filters (Whatman Nuclepore-type) from which the solids were
162 transferred onto low-diffraction silicon substrates. XRD measurements were made using Ni-
163 filtered Cu K α radiation in a PANalytical X'pert Pro diffractometer (PANalytical B.V.,
164 Almelo, The Netherlands). In some cases, SEM-EDX measurements were made of the
165 approximate composition of the samples prepared for XRD, while still in place on the XRD
166 substrate, using a Zeiss EVO60-XVP SEM (Carl Zeiss Ltd, Cambridge, UK) equipped with
167 an Oxford Instruments INCA system with an X-max-80 silicon drift detector (Oxford
168 Instruments Ltd, Oxford, UK).

169

170 **2.6 X-ray Photoelectron Spectroscopy**

171 XPS was carried out using a purpose-built ultra-high vacuum system equipped with a
172 Specs PHOIBOS 150 electron energy analyser and Specs FOCUS 500 monochromated Al
173 K α X-ray source (Specs GmbH, Berlin, Germany). As for XRD, samples were prepared for
174 analysis by filtration and subsequent drying from heptane slurry onto clean gold foil
175 substrates.

176

177 **3. Results**

178 Ultrasound treatment (1 h) of liquid hydrocarbons in the middle distillate boiling range
179 produced a variety of visual changes. Hexadecane (b.p. 287 °C) and decalin (b.p. 189°C)
180 changed from colourless to pale yellow. The yellow diesel fuel (b.p. 162–362 °C) darkened
181 in colour, whereas the pale yellow 1-methylnaphthalene (b.p. 240 °C) turned black as a result
182 of the formation of a suspension of fine particles (Fig. 2). The particulate matter dispersed in
183 the 1-methylnaphthalene was removed by centrifuge and filtration, allowing the mass of
184 material to be determined.

185 {Fig. 2 here}

186 The morphology of the particles formed by ultrasound cavitation is presented in the three
187 TEM images in Fig. 3. The lowest magnification (Fig. 3a) shows that the sample consists of
188 irregular shaped material of varying contrast ranging from 500 nm to 5 μm in size. Images at
189 higher magnification reveal the presence of smaller primary nanoparticles (Fig. 3b). There is
190 also evidence that these primary particles can overlap and agglomerate, and that they have an
191 internal morphology (Fig. 3c). This is reminiscent of the graphitic planes that are observed in
192 diesel combustion soot or carbon black. TEM-EDX was used to determine the elemental
193 composition of the material. Copper, present in the support grid and sample holder was
194 ignored to give the elemental composition of the material shown in Fig. 3a as carbon 96.4,
195 oxygen 3.5 and sulphur 0.1 atomic %. Significant proportions of the carbon detected will
196 have arisen from the carbon grid upon which the particles were captured. Hydrogen is not
197 detected by this technique and is therefore excluded from the atomic % values given here and
198 subsequently in this work.

199 XRD was carried out on a larger sample prepared by sonicating 1-methylnaphthalene for
200 2 hours followed by centrifuge and filtration onto a track-etched membrane filter. The
201 diffraction pattern shows a broad background feature between 10° and 30° with a peak at
202 approximately 23° – this is positioned at a lower angle (larger interplanar spacing) than
203 expected for pure graphite (26.4°) and is indicative of disordered graphitic-like carbon (Fig.
204 3d). From the other peaks in the spectrum it is possible to make an unambiguous
205 identification of titanium crystals, which are present as a consequence of cavity induced
206 erosion of the ultrasound probe tip. Analysis by SEM-EDX after accounting for the
207 substrate, confirmed the carbonaceous character of the material with an elemental
208 composition of carbon 88.0, oxygen 9.9, titanium 1.1, fluorine 0.3, sulphur 0.3 and nickel 0.2
209 atomic %, with traces of copper, vanadium, calcium and iron.

210

{Fig. 3 here}

211 XPS analysis of further samples prepared in the same way gave elemental composition
212 consistent with the SEM-EDX analysis and also showed a low level of nitrogen (carbon 88.0,
213 oxygen 11.0 nitrogen 0.6 and sulphur 0.4 atomic %). In a similar fashion to TEM-EDX and
214 SEM-EDX, hydrogen is not detected by this technique and the results are therefore given
215 excluding this element. The carbon 1s photoelectron spectrum comprised of a main peak
216 (285.0 eV) with slight asymmetry on the high binding energy side (Fig. 4a). An X-ray
217 excited carbon KVV Auger spectrum was also collected and the shape and kinetic energy of
218 the high energy onset were consistent with a proportion of graphitic-like material being
219 present (Fig. 4b) [26]. Highly ordered graphite would be expected to show a prominent $\pi-\pi^*$
220 shake-up feature at 291.7 eV in the XPS – this was not present suggesting that the graphite-
221 like material in the sample may only have short-range order. Curve-fitting on the high energy
222 side of the main carbon 1s peak is consistent with carbon-oxygen bonding and in samples
223 generated from diesel fuel was attributed more specifically to C–O (286.5 eV), C=O (287.8
224 eV) and C(O)O (289.3 eV) ester or acid groups. Likewise the oxygen 1s photoelectron peak
225 was fitted with two components representing single and double bonds to carbon.

226

{Fig. 4 here}

227 Ultrasound experiments in which the probe was not placed directly into the hydrocarbon
228 being treated were also conducted in order to avoid titanium contamination of the samples
229 and to make sure that the production of particles was not due to the metal acting as a
230 dehydrogenation catalyst. A cup-horn was used to transfer ultrasound through the walls of a
231 small conical flask filled with 25 mL of hydrocarbon – an arrangement somewhat akin to that
232 of a high intensity ultrasonic bath. The efficiency with which energy was transferred was
233 approximately a factor of ten lower than when placing a sonication probe directly into the
234 hydrocarbon. 1-Methylnaphthalene was treated by this method for 5 hours, over which time

235 a black suspension of particles was formed. TEM imaging (Fig. 5) showed the morphology
236 of the material to be similar to that generated in earlier experiments. The elemental
237 composition determined by TEM-EDX was also the same, although in this instance no
238 titanium was present. A further sample was produced in which the treatment of 1-
239 methylnaphthalene with ultrasound was carried out under a nitrogen atmosphere. The
240 hydrocarbon was not fully degassed and therefore still contained small levels of dissolved air.
241 The formation of black particles again took place.

242 {Fig. 5 here}

243 The relationship between deposit mass and length of sonication time was found to be
244 linear for 1-methylnaphthalene (Fig. 6). However, the varying degree of colour change
245 observed between different fuels suggests that the deposit-forming tendency is also
246 dependent on the degree of unsaturation in the molecular structure of the hydrocarbon being
247 treated. Fig. 7 presents the gravimetric analysis after 1 hour ultrasound treatments of four
248 different fuels: 1-methylnaphthalene and mixtures of 80% v/v 1-methylnaphthalene with 20%
249 v/v of tetralin, decalin and hexadecane. Deposit formation appears to be linearly dependent
250 on C/H atomic ratio. EN590 market diesel typically has a C/H of 0.50–0.55 but is comprised
251 of different generic classes of hydrocarbons, the atomic ratios of which are presented as
252 horizontal grey bars marked below the x-axis in Fig. 7.

253 {Fig. 6 and 7}

254 Samples of 1-methylnaphthalene were prepared with 1, 2 and 3% v/v of *n*-octane, *n*-
255 decane, dodecane, tetradecane, hexadecane, ethylbenzene, *n*-propylbenzene, indan and
256 indene. The fuels were treated with ultrasound for 1 hour in a randomised order which
257 included ten repeat tests on 1-methylnaphthalene to establish a baseline level of deposit
258 formation and an indication of the repeatability of the test method. The relative standard
259 deviation of the deposit mass from 1-methylnaphthalene was 2.8% (n=10).

260 The change in deposit mass resulting from the incorporation of different hydrocarbons
261 was found to be minimal for the aromatic hydrocarbons (indan, indene, *n*-propylbenzene and
262 ethylbenzene) (Fig. 8). In contrast the presence of paraffinic hydrocarbons reduced the
263 amount of deposit, with this trend becoming more pronounced as the alkane chain length
264 became shorter. Generally, but not always, the suppression of deposit formation increased
265 with the blend ratio of the alkane.

266 {Fig. 8 here}

267 A 'zero' sulphur diesel fuel which contained no performance additives or FAME was
268 treated with ultrasound for different periods of time, up to 80 minutes. This was followed by
269 a determination of the 1–100 μm particle count in each sample. 1-Methylnaphthalene was
270 sonicated for 5 minutes before carrying out a similar analysis. Fig. 9 shows a monotonically
271 increasing particle count in the diesel fuel as the exposure to ultrasound was increased. The
272 particle count in the 1-methylnaphthalene sample treated for 5 minutes was 30% higher than
273 the equivalent diesel sample; however the variation of number concentration with particle
274 size for these two samples was quite different (Fig. 10). The majority of the particles (>98%)
275 were <16 μm in size but the mean particle diameter ($d_{1,0}$) in diesel fuel was smaller (2.1–2.7
276 μm) than in 1-methylnaphthalene (6.6 μm). This indicates a higher particle mass
277 concentration for 1-methylnaphthalene, consistent with the previously established high
278 deposit-forming tendency of the di-aromatic when exposed to cavitation.

279 {Fig. 9 and 10}

280 All the samples were allowed to stand under ambient conditions in the laboratory and
281 periodically the particle count measurements were repeated over 33 days. Diesel fuel that has
282 not undergone cavitation has a low particle count of <1,000 cm^{-3} which does not significantly
283 change with storage time (Fig. 11 and Table 1). The initial particle count for the 5 minute
284 sample was higher (7,000 cm^{-3}) but again did not change. The diesel sample treated for 20

285 minutes underwent a small increase in particle count after 1 day, the count then became
286 stable. This initial increase in particle count for the diesel sample exposed to ultrasound for
287 80 minutes was more pronounced, but again stabilised after 1 day. The sonicated 1-
288 methylnaphthalene sample showed distinctive behaviour in that the particle count increased
289 fourfold after 1 day. This rapid increase continued and after 7 days storage the particle count
290 had increased by a factor of 14; beyond this storage time the rate of increases slowed and the
291 count eventually stabilised. This increase in number concentration was combined with a drop
292 in the mean diameter of the particles present from 7 μm to 2 μm .

{Fig. 11 and Table 1 here}

295 **4. Discussion**

296 **4.1 The impact of hydrocarbon composition and physical properties on deposit** 297 **formation**

298 Two key parameters associated with fluid cavitation are the number of bubbles generated
299 and the intensity of the bubble collapse (which is related to the speed of collapse and the
300 magnitude of the temperature and pressure generated). The critical parameters that have a
301 controlling influence are:

302 *Ambient pressure:* Increasing the external pressure raises the threshold of cavitation as larger
303 negative pressures are required to separate molecules to form a bubble.

304 *Fuel vapour pressure:* When bubbles form they contain fuel vapour and any dissolved gases
305 that are present. High vapour pressures actually soften the collapse of bubbles and reduce the
306 harshness of the conditions that develop, i.e. lower peak temperature and pressure.

307 *Viscosity:* Liquids with higher viscosity have stronger cohesive forces and are consequently
308 harder mediums in which to induce cavitation.

309 *Surface tension:* Decreasing surface tension makes the formation of cavities more likely to
310 occur, however the relationship is complex and not well understood.

311 *Temperature:* Increasing temperature decreases surface tension and viscosity and increases
312 vapour pressure. All three changes make cavitation more likely.

313 *Dissolved gasses and suspended particles:* These can act as nuclei for bubble formation.

314 The maximum pressure and temperature that occur inside a collapsing bubble have been
315 defined by assuming adiabatic conditions [27,28]:

$$p_{max} = p (p_c (\gamma - 1)/p)^{\gamma/(\gamma-1)} \quad (1)$$

$$T_{max} = T_0 (p_c (\gamma - 1)/p) \quad (2)$$

316 where T_0 is the ambient temperature (K) of the liquid, γ is the ratio of heat capacity of the
317 bubble gas at constant pressure (C_p) and volume (C_v), p is the pressure (N m^{-2}) in the bubble
318 at its maximum size (assumed to be the vapour pressure of the liquid) and p_c is the pressure
319 (N m^{-2}) in the liquid at the moment of collapse (which is the sum of the ambient liquid
320 pressure and the ultrasound amplitude during sonication).

321 The conditions generated during collapse are extreme, however an important observation
322 from sonochemistry studies is that as the temperature of the fluid being cavitated is raised the
323 vapour pressure (p) inside the bubble increases and consequently T_{max} decreases (equation 2).
324 Therefore, the reaction rates of the chemistry taking place within a collapsing bubble are
325 counter intuitively slowed by raising the temperature (T_0) and increasing the vapour pressure
326 (p) of the liquid. This has been clearly demonstrated by Suslick and co-workers who
327 measured depletion of 2,2-diphenyl-1-picrylhydrazyl (DPPH) used to trap the radicals
328 formed by cavitation collapse in a number of organic liquids exposed to ultrasound [29]. The
329 rate of depletion of DPPH is proportional to the rate of radical production by cavitation and
330 was found to be inversely related to the vapour pressure of hydrocarbon being treated.

331 From the data present in Fig. 7 and 8 it is apparent that the rate of cavity induced deposit
332 formation is related to both the degree of unsaturation (C/H ratio) and the vapour pressure of
333 the hydrocarbon undergoing sonication. The fuels from Fig. 8 all underwent standard
334 analysis to define three properties: flash point (related to the vapour pressure of the fuel),
335 kinematic viscosity at 40 °C and C/H atomic ratio. In an empirical treatment of the data,
336 deposit mass determined by gravimetric analysis was correlated against fuel compositions
337 and properties. Carbon-to-hydrogen atomic ratio is the single most influential fuel property
338 with respect to deposit formation, followed by flash point and lastly viscosity. However, the
339 best regression of the data ($R^2 = 0.73$) is achieved when using all three properties (Fig. 12)

$$\text{Deposit mass} = (28.05 * C/H) + (0.02 * f_p) - (2.77 * V_k) - 22.15 \quad (3)$$

340 where f_p is flash point (°C), V_k is the kinematic viscosity (mm^2s^{-1}) at 40 °C and C/H is the
341 atomic carbon-to-hydrogen ratio.

342 {Fig. 12 here}

343 The coefficients in equation 3 are consistent with a physical understanding of cavitation
344 in that:

- 345 1. As C/H ratio increases the fuel becomes more aromatic in nature and is more likely to
346 react during bubble collapse to form carbon particles (c.f. the impact of aromatic content
347 in diesel soot formation).
- 348 2. A flash point increase (and therefore vapour pressure decrease) results in more severe
349 cavity collapse (higher T_{max}) producing higher levels of pyrolytic degradation and deposit
350 formation.
- 351 3. As viscosity increases so does the cohesive forces between molecules, making it harder to
352 form cavities. The reduction in the number of bubbles should result in less deposit
353 formation.

354

355 4.2 Mechanisms of particle growth

356 The violent collapse of bubbles generates shear forces at the tip of the acoustic probe and
357 therefore promotes kinetically driven particle-particle collisions of the primary nanoparticles
358 that are formed during cavitation. This leads to aggregation and the formation of larger
359 particles with diameters in the micron range. Kinetically driven agglomeration rates are
360 defined by

$$J_{ok} = dN/dt = -2\alpha\gamma_s d^3 N^2/3 \quad (4)$$

361 where J_{ok} is the orthokinetic rate ($\text{m}^{-3} \text{s}^{-1}$) of change in primary particle number, N is the
362 primary particle number concentration (m^{-3}), γ_s is rate of shear (s^{-1}), d is the primary particle
363 diameter (m) and α is the collision efficiency (between 0 and 1).

364 If a constant rate of nanoparticle production from cavitation is assumed, it follows that

$$dN/dt = R_p - 2\alpha\gamma_s d^3 N^2/3 \quad (5)$$

365 where R_p is the rate of primary particle formation ($\text{m}^{-3} \text{s}^{-1}$) during sonication.

366 Equation 5 allows the primary particle number concentration to be defined as a function
367 of sonication time. A value for the rate of particle formation (R_p) (assuming $\gamma_s = 1,000 \text{ s}^{-1}$, d
368 = 20 nm, $\rho = 2,000 \text{ kg/m}^3$ and $\alpha = 1$) can be set such that the predicted deposit mass (of
369 micron sized agglomerated material) matches that observed experimentally in the data from
370 Fig. 6. The results of this exercise are shown in Fig. 13 and reveals a good match between
371 measured and predicted deposit mass out to 120 minutes of sonication. An equilibrium
372 concentration of primary particles is established when

$$R_p = 2\alpha\gamma_s d^3 N_{eq}^2/3 \quad (6)$$

373 where N_{eq} is the equilibrated number concentration of primary particles (m^{-3}).

374 If the time required for this equilibrium (t_{eq}) to be established is short (~ 5 minutes) then
375 the mass of deposit essentially becomes proportional to the length of the ultrasound

376 treatment, as indeed is observed experimentally. The time required for the concentration of
 377 primary particles to reach equilibrium (t_{eq}) is shortened if the size of the particles (d),
 378 formation rate (R_p) or shear rate (γ_s) is increased. N_{eq} decreases if particle size (d) or shear
 379 rate (γ_s) is reduced but increases with higher rates of formation (R_p). A reduction in collision
 380 efficiency (α) will increase both t_{eq} and N_{eq} . From this exercise the primary particle number
 381 concentration for sonicated 1-methylnaphthalene can be estimated to be in the region of 10^{12}
 382 cm^{-3} .

383 {Fig. 13 here}

384 Once sonication is complete particle-particle collisions only occur as a consequence of
 385 thermally induced motion. The Brownian movement of particles that gives rise to particle
 386 agglomeration is described by

$$J_{pk} = dN/dt = -4\alpha kTN^2/3\eta \quad (7)$$

387 where J_{pk} is the perikinetic rate ($\text{m}^{-3}\text{s}^{-1}$) of change in primary particle number, N is the particle
 388 number concentration (m^{-3}), k is Boltzmann's constant (J K^{-1}), T is temperature (K), α is the
 389 collision efficiency (between 0 and 1) and η is the dynamic viscosity (Nsm^{-2}) of the liquid.

390 Integration of equation 7 gives

$$N = N_0 / (1 + 4\alpha kTN_0t/3\eta) \quad (8)$$

391 From which the half-life of the primary particles can be determined

$$t_{1/2} = 3\eta/4\alpha kTN_0 \quad (9)$$

392 Particle half-life is plotted as a function of particle number concentration in Fig. 14 based
 393 upon a temperature of 300 K and a dynamic viscosity of $2 \times 10^{-3} \text{ Nsm}^{-2}$. A high concentration
 394 of primary particles (10^{12} cm^{-3}) will therefore undergo an initial rapid agglomeration to form
 395 larger particles. However, further agglomeration of these larger particles will be slowed by
 396 the drop in particle number and eventually the dispersion will become stable. It would
 397 therefore appear that samples of diesel fuel sonicated for relatively short periods of time do

398 not contain sufficiently high numbers of primary particles for growth of secondary particles
399 in the micron size range. However the contrasting behaviour of the sonicated 1-
400 methylnaphthalene is consistent with a very high primary particle number concentration that
401 is initially not detectable with the laser particle counter. During storage these nanoparticles
402 grow into larger microparticles that fall within the detection limit of the technique and give
403 rise to the sharp increase in the count of 1–2 μm particles.

404 {Fig. 14 here}

405

406 **4.3 Implication for diesel fuel in modern common rail direct injection diesel engines**

407 Fuel is known to undergo cavitation in injector nozzles, resulting in the formation of
408 bubbles in regions where the liquid pressure falls below the fuel's vapour pressure [30-32].
409 This can occur at a pressure drop across an orifice or when fast moving flows turn sharp
410 corners. If these bubbles return to high ambient pressure they collapse and produce areas of
411 extreme temperature and pressure as a result of the adiabatic compression of the fuel vapour,
412 in a manner analogous to that observed during acoustic cavitation.

413 Over the last six years there has been a growing awareness of field issues involving
414 injector sticking in modern common rail compression ignition engines [33–36]. This is
415 caused by the formation of internal diesel injector deposits (IDID), the occurrence of which
416 has increased as fuel rail pressures ($>2,000$ bar) and injector nozzle temperatures ($>200^\circ\text{C}$)
417 have become higher [36,37]. These conditions result in stressed fuel, some of which is
418 recycled back into the fuel tank rather than being burned.

419 Three main types of deposits have been identified, all of which are distinct from the
420 coke-like material that forms in nozzle holes and which has historically been controlled
421 through the use of detergent additives:

- 422 1. Soap deposits: Soft opaque material that is typically water soluble and comprised of metal
423 (sodium, sometimes calcium) carboxylates or sodium chloride [35,38].
- 424 2. Lacquer deposits: Hard brown material that is insoluble in most solvents. Fourier
425 transform infrared spectroscopy (FTIR) has identified the presence of amides ($-C(O)NH-$
426) leading to the origins of these deposits being linked to detergent molecules (in particular
427 low molecule weight polyisobutylene succinimides, PIBSI) [33,35,39].
- 428 3. Carbonaceous deposits: Black material that has been observed on fuel filters and nozzle
429 springs [40] as well as being linked to the reported phenomenon of black diesel fuel [41].
430 The origins of this material have proved to be somewhat difficult to identify, although
431 there are reports of the material resembling combustion soot and being comprised of
432 graphitic carbon [42–44].

433

434 A diesel vehicle (2008 registration plate) known to have an intermittent fault in which
435 engine stalls occurred when it slowed to a standstill at junctions was sourced. The vehicle
436 had been driven just over 100,000 miles on 191 tanks fills in a time period of three years.
437 Examination of the vehicle revealed a fuel filter coated in black deposits and a visible
438 suspension of fine material in samples of fuel taken from the tank – some of this material
439 formed sediment when left to stand. TEM images show material that is similar to that
440 generated by the ultrasound treatment of hydrocarbons, being comprised of small primary
441 particles linked together into larger structures (Fig. 15). High magnification reveals the
442 internal structure of these particles, within which can be seen layers of graphitic-like carbon
443 (Fig 15b). The XRD spectrum of these deposits has a strong graphite peak at $\sim 26.5^\circ$ (Fig.
444 15c). The iron oxide-hydroxide ($FeO(OH)$), lepidocrocite was also found and is indicative of
445 the presence of rust. Peaks consistent with calcium carbonate were cross matched with a
446 small number of lozenge shaped particles seen in some of the TEM images. There are two

447 other peaks present which give a good fit to solid linear waxy saturated hydrocarbons (i.e.
448 $-(CH_2)_n-$).

449 {Fig. 15 here}

450 The phenomenon of cavitation in the high pressure fuel systems of modern common rail
451 diesel vehicles is therefore proposed as an explanation for the formation of deposits
452 comprising of fine particles. This material is observed to build up in the fuel over extended
453 periods of use. If large enough ($>4 \mu m$) it will be captured by the filter typically positioned
454 between the tank and the pump that delivers fuel into the high pressure rail that feeds each of
455 the injectors. Smaller sized material will however pass through this filter and be carried into
456 the injectors. If it migrates into regions within the injectors where there are low clearances
457 between moving surfaces ($\sim 1 \mu m$) an impact upon injector response and function is possible.

458

459 **5. Conclusions**

460 Acoustically driven cavitation has been used to study the degradation chemistry that takes
461 place in hydrocarbons that fall within the middle distillate (C_8-C_{26}) range. The following
462 conclusions can be drawn from these experiments:

- 463 1. The high temperature produced by the implosion of bubbles that contain hydrocarbon
464 vapour and dissolved gases produces carbonaceous material (typical carbon levels of ca.
465 90 atomic % excluding H). These deposits form as dispersed micron sized particles that
466 are themselves comprised of agglomerated nanoparticles which have similarities to the
467 primary soot particles that are produced during the diffusion flame combustion of diesel
468 fuel. The carbon is a mixture of amorphous and graphitic material which also contains
469 significant quantities of oxygen (ca. 10 atomic % excluding H) in the form of hydroxyl,
470 carbonyl and ester or acid groups present on the particle surfaces.

- 471 2. The deposit-forming tendency of a hydrocarbon is strongly coupled to the number of
472 unsaturated carbon-carbon bonds that are present or its C/H atomic ratio. The di-aromatic
473 1-methylnaphthalene produces high levels of deposit during cavitation, whereas the paraffin
474 hexadecane produces very few deposits.
- 475 3. The formation of the deposits can be reduced by increasing the flash point of the
476 hydrocarbon. This increases the vapour pressure inside the bubbles and reduces the
477 temperature (and pressure) that results from their implosion, slowing the reaction rates of
478 the chemistry leading to particle formation. This reduction in deposit formation is most
479 significant when the lower boiling hydrocarbon is paraffinic, as opposed to aromatic, in
480 character.
- 481 4. During cavitation a mixture of primary nanoparticles and larger micron sized particles is
482 produced. The dispersion of this material is stable if the particle number concentration of
483 the primary particles is below a threshold value. However if high numbers of
484 nanoparticles are present they can start to agglomerate to form additional numbers of
485 micron sized particles during the storage of the sonicated liquid.
- 486 5. The chemistry and formation of deposits observed during the acoustic treatment of middle
487 distillate hydrocarbons has been found to be similar to that seen during the hydrodynamic
488 cavitation of fuel in modern common rail direct injection compression ignition engines.
489 The material formed in these sonication experiments is compositionally similar to a
490 suspension of particles sampled from fuel in the tank of a common rail diesel vehicle. The
491 material is also consistent with the black deposits that are generally reported to build up on
492 fuel filters and around the nozzle springs of injectors. Such material can affect the passage
493 of fuel through the filter and possibly the correct function of the injectors.

494

495 **Acknowledgements**

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497 acoustic cavitation to study the degradation of middle distillate hydrocarbons and the
498 contribution of Grant Middleton in the running of ultrasound experiments and the preparation
499 of samples for analysis. The work has been financed by Shell Global Solutions.

500

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601

602 **Figure Captions**

603 Colour figures in electronic versions only.

604

605 **Fig. 1.** Schematic of the experimental apparatus used for the sonication of hydrocarbon
606 liquids.

607 **Fig. 2.** 1-Methylnaphthalene (50 mL) before (a) and after (b) 20 kHz ultrasound treatment (6
608 kJ mL⁻¹) for 1 h. An addition of 50 mL of *n*-heptane was made before centrifuging the
609 suspension (4,000 r min⁻¹ for 20 minutes) and filtration through a 0.7 μm microfiber paper
610 (c).

611 **Fig. 3.** TEM images (a, b and c) and XRD pattern (d) of particles formed in sonicated 1-
612 methylnaphthalene.

613 **Fig. 4.** Carbon 1s XPS (a) and the X-ray excited carbon KVV Auger spectra (b) of four
614 samples (S1-4) of particles all produced by the sonication of 1-methylnaphthalene.

615 **Fig. 5.** TEM images of particles formed in 1-methylnaphthalene when ultrasound is
616 delivered indirectly using a cup-horn. The low (a) and high (b) magnification images show
617 similar features to those presented in Fig. 3.

618 **Fig. 6.** Relationship between deposit mass and the sonication time (6 kJ mL⁻¹ h⁻¹) of 50 mL
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620 **Fig. 7.** Deposit mass produced by the 1 h sonication (6 kJ mL⁻¹) of 50 mL volumes of 1-
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622 decalin or tetralin as a function of C/H atomic ratio. The bars show the typical C/H range for
623 the different generic classes of hydrocarbons present in diesel fuel. (TriAr – tri-aromatics,
624 NdiAR – naphthenic-di-aromatics, DiAr – di-aromatics, NmoAr – naphthenic mono-
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626 **Fig. 8.** The change in deposit mass produced by blending 1-3% (v/v) of a second
627 hydrocarbon into 1-methylnaphthalene and treating with ultrasound ($6 \text{ kJ mL}^{-1} \text{ h}^{-1}$). Repeat
628 measurements of the deposit mass produced from just 1-methylnaphthalene had a relative
629 standard deviation of 2.8% (n=10).

630 **Fig. 9.** Total particle number concentration in diesel fuel and 1-methylnaphthalene (50 mL)
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632 **Fig. 10.** Particle number concentration as a function of particle diameter in diesel fuel and 1-
633 methylnaphthalene (50 mL) after 0–80 minutes sonication ($6 \text{ kJ mL}^{-1} \text{ h}^{-1}$).

634 **Fig. 11.** Change in particle number concentration with storage time for diesel fuel and 1-
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636 **Fig. 12.** The correlation between measured and empirically predicted deposit mass.

637 **Fig. 13.** Deposit formation in 1-methylnaphthalene and the predicted equilibrated
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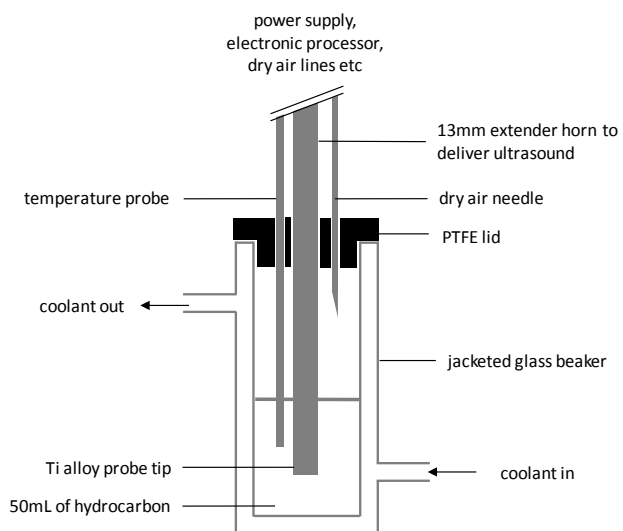
641 **Fig. 15.** TEM images (a and b) and XRD pattern (c) of particles taken from the fuel tank of a
642 diesel vehicle.

643

644 **Table titles**

645 **Table 1.** Number concentration (cm^{-3}) and mean diameter (μm) (in italics) of particles
646 produced by the cavitation ($6 \text{ kJ mL}^{-1} \text{ h}^{-1}$) of diesel fuel and 1-methylnaphthalene (1-MN)
647 followed by storage.

648

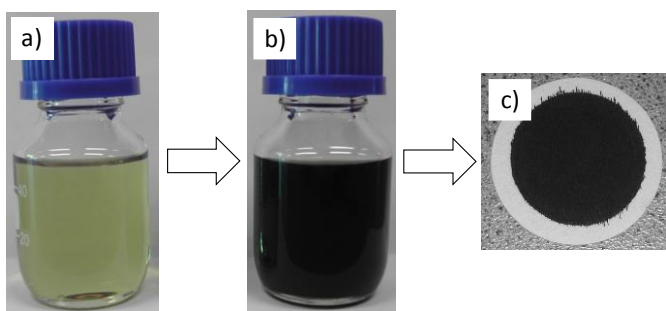


649

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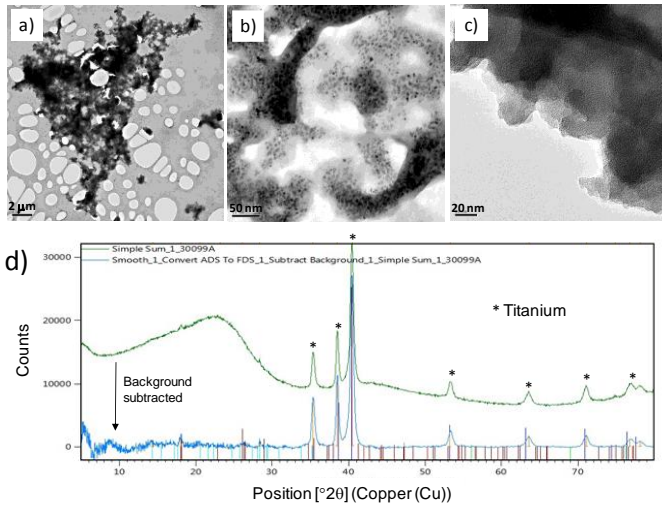
651 liquids.

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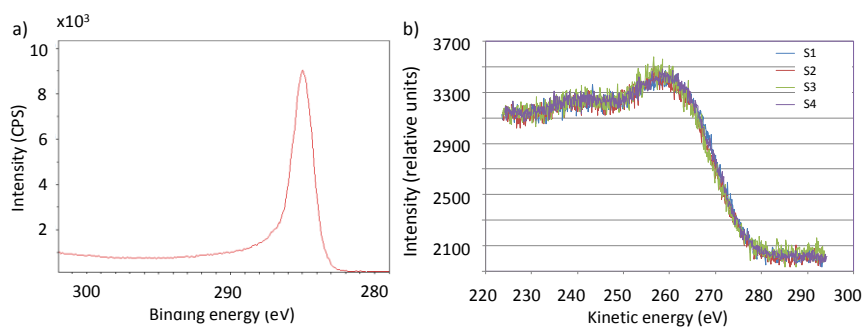
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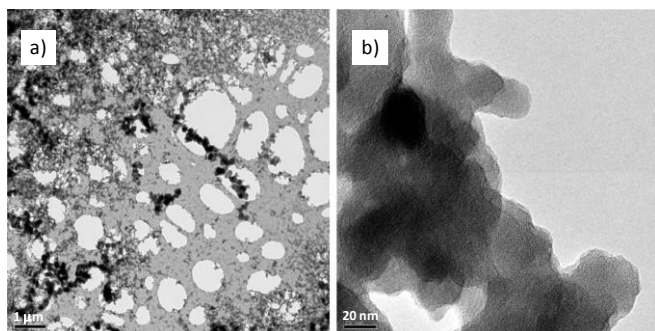


662

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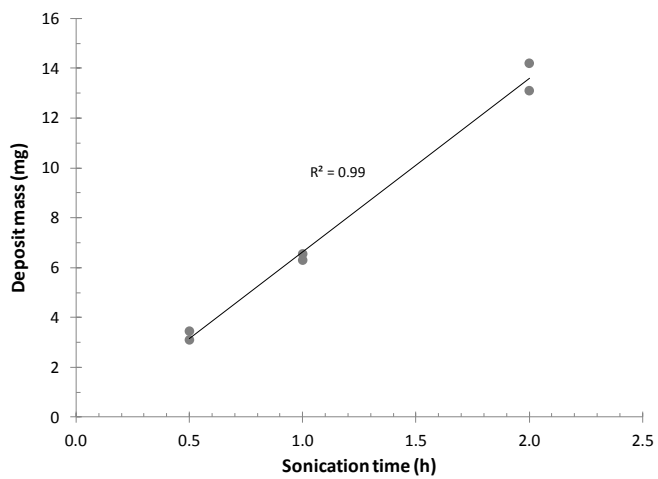
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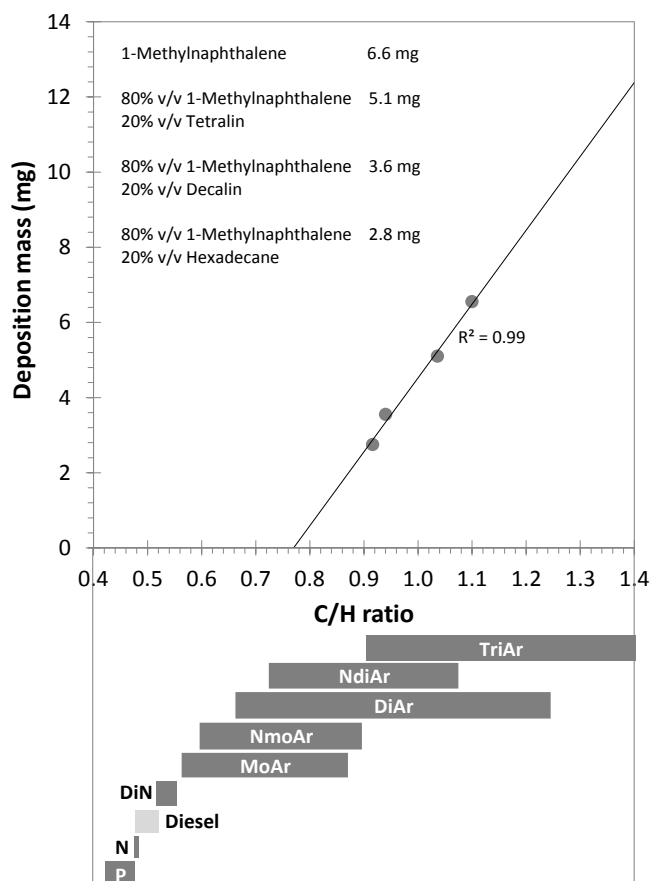


671

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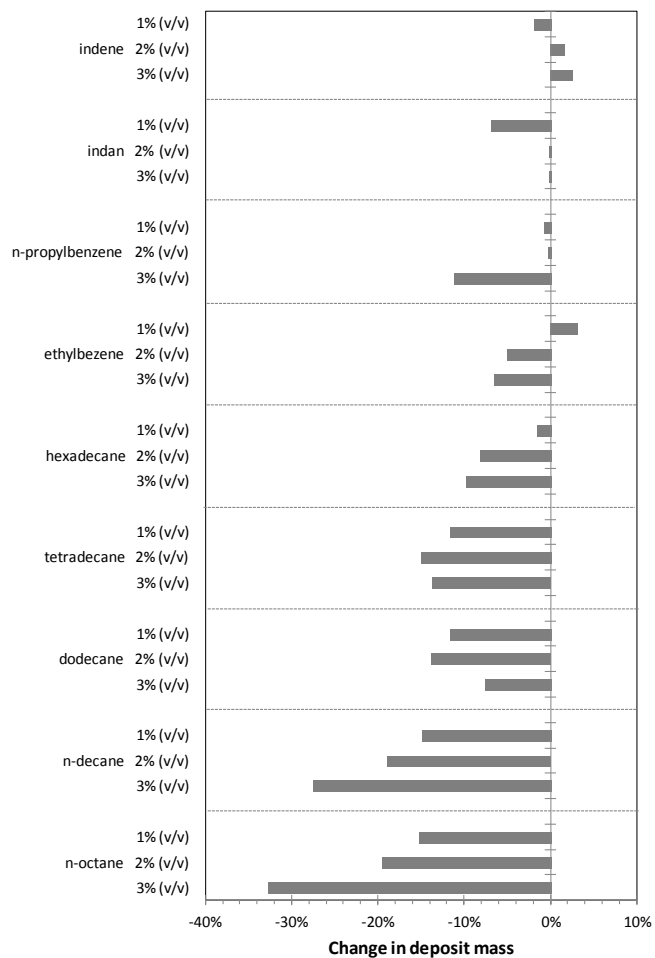
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675

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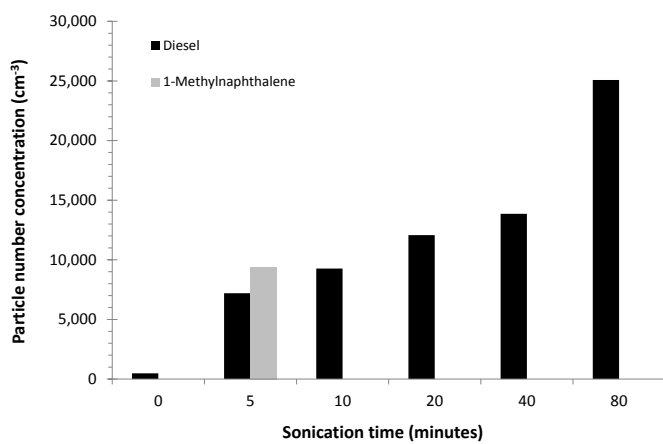
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683

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 685 hydrocarbon into 1-methylnaphthalene and treating with ultrasound ($6 \text{ kJ mL}^{-1} \text{ h}^{-1}$). Repeat
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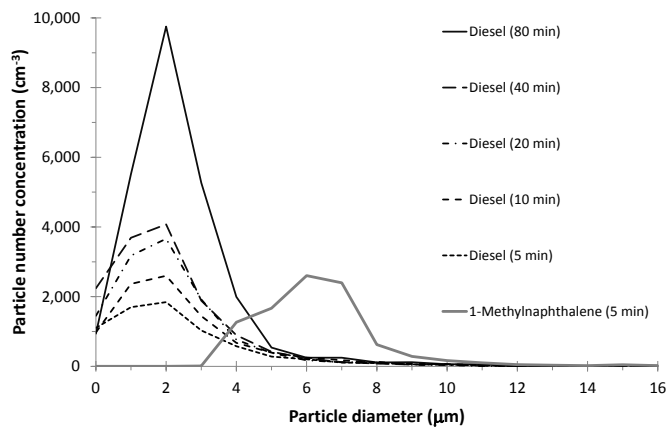


689

690 **Fig. 9.** Total particle number concentration in diesel fuel and 1-methylnaphthalene (50 mL)

691 after 0–80 minutes sonication ($6 \text{ kJ mL}^{-1} \text{ h}^{-1}$).

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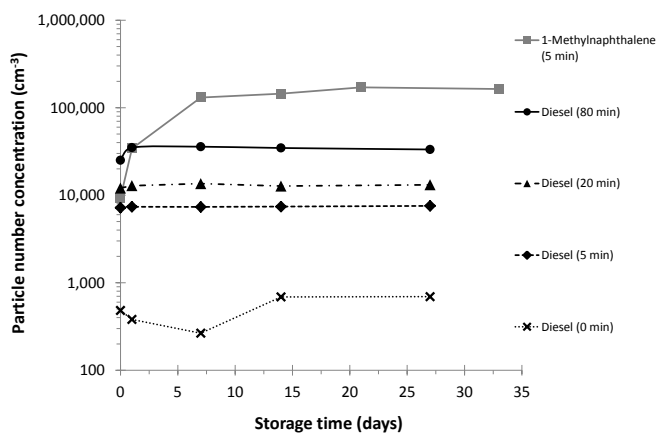


693

694 **Fig. 10.** Particle number concentration as a function of particle diameter in diesel fuel and 1-

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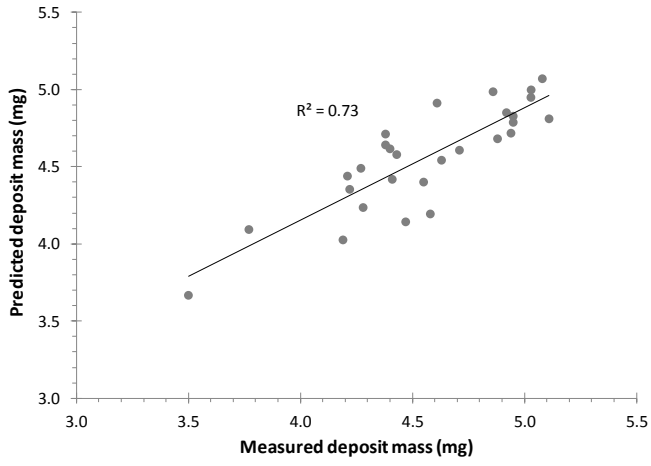
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697

698 **Fig. 11.** Change in particle number concentration with storage time for diesel fuel and 1-
 699 methylnaphthalene after sonication ($6 \text{ kJ mL}^{-1} \text{ h}^{-1}$).

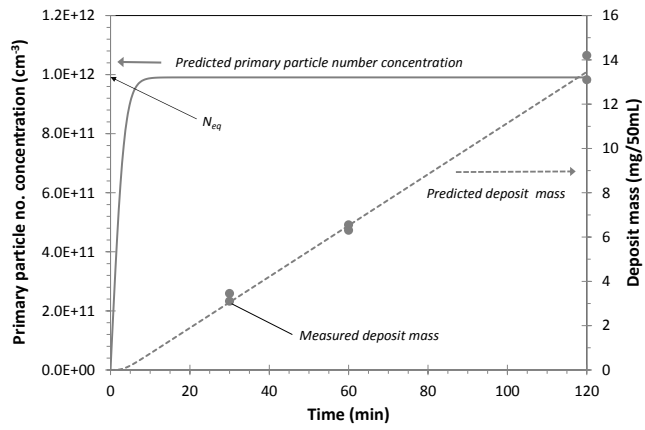
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702 **Fig. 12.** The correlation between measured and empirically predicted deposit mass.

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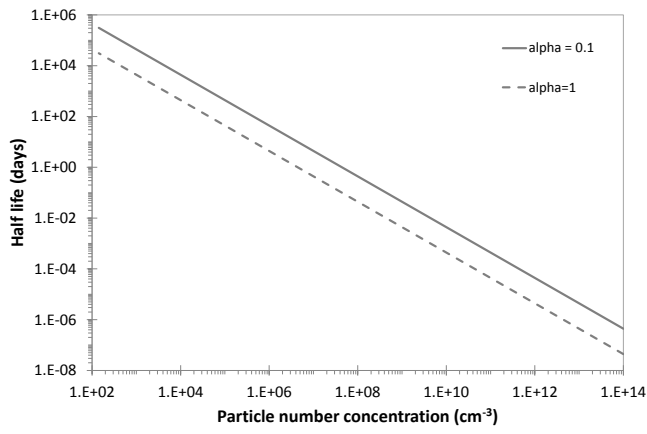
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Fig. 13. Deposit formation in 1-methylnaphthalene and the predicted equilibrated

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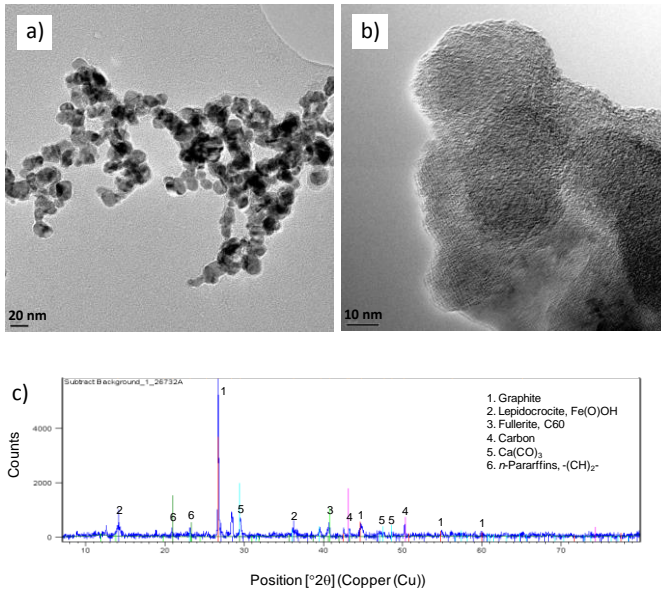


708

709 **Fig. 14.** Relationship between half-life and primary particle number concentration ($T = 300$

710 K and $\eta = 2 \times 10^{-3} \text{ N s m}^{-2}$).

711



712

713 **Fig. 15.** TEM images (a and b) and XRD pattern (c) of particles taken from the fuel tank of a

714 diesel vehicle.

715

716 **Table 1.** Number concentration (cm^{-3}) and mean diameter (μm) (in italics) of particles
 717 produced by the cavitation ($6 \text{ kJ mL}^{-1} \text{ h}^{-1}$) of diesel fuel and 1-methylnaphthalene (1-MN)
 718 followed by storage.

Storage time (days)	Diesel cavitation time (min)						1-MN cavitation time (min)
	0	5	10	20	40	80	5
0	482 <i>2.3</i>	7,196 <i>2.7</i>	9,271 <i>2.7</i>	12,070 <i>2.5</i>	13,856 <i>2.1</i>	25,086 <i>2.6</i>	9,397 <i>6.6</i>
1	381 <i>1.6</i>	7,388 <i>2.7</i>	11,030 <i>3.6</i>	12,848 <i>2.1</i>	15,909 <i>2.7</i>	35,021 <i>3.0</i>	34,160 <i>5.0</i>
7	265 <i>4.2</i>	7,354 <i>2.6</i>	10,799 <i>2.7</i>	13,576 <i>2.5</i>	16,378 <i>2.2</i>	35,868 <i>3.6</i>	134,745 <i>1.8</i>
14	689 <i>4.1</i>	7,413 <i>3.0</i>	10,711 <i>3.0</i>	12,733 <i>2.3</i>	15,267 <i>2.0</i>	34,671 <i>3.6</i>	144,878 <i>2.3</i>
21	– –	– –	– –	– –	– –	– –	170,955 <i>1.6</i>
27	694 <i>3.8</i>	7,556 <i>2.6</i>	11,477 <i>2.8</i>	13,158 <i>2.3</i>	16,225 <i>2.4</i>	33,341 <i>2.9</i>	– –
33	– –	– –	– –	– –	– –	– –	163,468 <i>1.9</i>

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