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1

2 **EXPLORING HOMOLYTIC AROMATIC SUBSTITUTION AS A**

3 **DRIVER FOR FUEL DEPOSITION WITH QUANTUM CHEMISTRY**

4 **AND EXPERIMENTS**

5

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12

13 Abstract

14 Liquid phase insoluble formation in fuels can cause performance and safety issues. To

15 understand the formation of insolubles in fuels from first principles, a series of density

16 functional theory (DFT) calculations were run to calculate the energetic barriers of the

17 autoxidation and coupling reactions for several common fuel aromatics/heteroatoms.

18 The six compounds chosen were phenol, toluene, naphthalene, pyrrole, quinoline, and

19 indole. Using a combination of DFT calculations and gravimetric and petroxy experimental

20 work, a novel homolytic aromatic substitution (HAS) coupling pathway was identified for

21 each compound. While previous studies have treated deposition steps implicitly, our detailed

22 calculations of HAS reactions and bulk fuel (RH) oxidation reaction barriers afforded the

23 development of bespoke pseudo-detailed mechanisms for each aromatic compound with
24 explicit reaction steps. These mechanisms were then used to predict trends in deposition
25 behavior of the compounds tested in a simple *n*-dodecane surrogate. The novel HAS
26 mechanism suggested for fuels was proposed to start with the reaction of an aromatic radical
27 ($\text{Ar}\cdot$) to an aromatic (ArH), which then formed a radical ($\text{ArHAr}\cdot$) σ -intermediate. It
28 was then found that hydroperoxides (ROOH) could re-aromatize the radical intermediate
29 ($\text{ArHA}\cdot$), forming a deposit dimer (ArAr). Although our sensitivity analysis revealed that
30 alkyl fuel radical and fuel alkoxy radical abstraction steps influenced the final mass of the
31 deposit, the $\text{Ar}\cdot + \text{ArH}$ HAS coupling step was found to have the largest influence. Finally,
32 an aromatic/heteroatom model containing phenol and toluene was built, which showed that
33 phenol suppressed deposition from toluene, and peaked in deposit mass at a phenol:toluene
34 ratio of 25:75. Although our study was limited to Ar self-reactions, we hypothesize that bulk
35 fuel – aromatic coupling could also be governed by HAS reactions, allowing researchers to
36 move towards a more first-principles based deposition model..

37 Keywords: Density Functional Theory, Homolytic Aromatic Substitution, Thermal Stability,
38 Jet Fuel, Pseudo-detailed Mechanism

39

40

41 1. Introduction

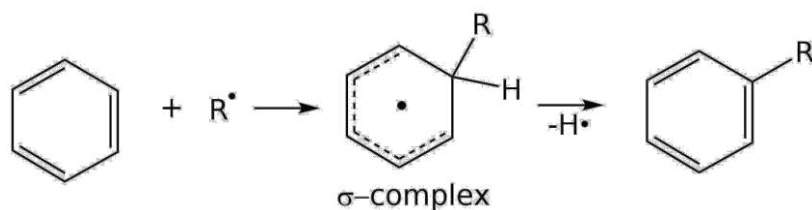
42 The formation of insolubles in the liquid-phase of jet fuels is mainly driven by the formation
43 of oligomers from fuel components.[1, 2] Oligomers successively grow starting from dimers,
44 trimers, tetramers and so on. Each oligomer growth step is predominantly characterized by
45 the formation of C–C and C–O bonds. Previous research has emphasized the termination of
46 antioxidant and/or fuel aromatic components ($\text{Ar}\cdot + \text{Ar}\cdot \rightarrow \text{Ar}_2$) as a key source of fuel

47 insolubles, and by that extension C–C/C–O bond formation.[3, 4, 5] This has led Heneghan
48 and Zabarnick to highlight an inverse correlation between the ease of oxidation and the
49 formation of deposits. In other words, a fuel with a lower oxidation rate arises from the
50 higher concentration of chain-breaking Ar· radicals, and therefore have a higher
51 concentration of Ar· to undergo termination steps producing deposit.[3] However, in some
52 instances, this relation does not always hold. Notably, some nitrogen compounds like
53 pyrroles and indoles tend to show low/no effects on autoxidation rates yet are severe deposit
54 promoters.[6, 7, 8] To explain these exceptions, Heneghan and Zabarnick propose that some
55 fuels produce termination Ar–Ar products with a higher solubility.[3] Nevertheless, there
56 may be other chemical factors that need to be explored.

57 The formation of Ar–Ar via the termination of two free-radicals Ar· in solution is part of an
58 oxidative coupling process. However, it is possible to form Ar–Ar without a termination step
59 under oxidative conditions. Focusing on transition metal free processes, homolytic aromatic
60 substitution (HAS) has received considerable attention as a method for cross-coupling
61 aromatic compounds under free-radical conditions.[9, 10, 11, 12] Additionally, HAS
62 mechanisms have been used as a way to understand the rate of radical reactions.[13, 14] The
63 general mechanism of HAS is shown in Figure 1.1. First, an attack of an aryl radical to an
64 arene compound generates a σ -intermediate. The σ -intermediate is then re-aromatized via
65 elimination of a leaving group forming a dimer. In this sense, HAS reactions are analogous
66 to electrophilic aromatic substitution (EAS) reactions, except that the σ -intermediate is not
67 charged. EAS reactions have been proposed as a mechanism in the formation of jet fuel
68 deposits.[15] However, in aprotic non-polar jet fuel, the stabilization of charged EAS σ -
69 intermediates is precluded.[16] By contrast, HAS reactions have been shown to readily occur
70 in non-polar aprotic solvents between arenes under molecular oxygen.[17] In general HAS
71 reactions have presented a challenge to organic chemists due to poor selectivity, leading to

72 intractable mixtures.[11] Nevertheless, in the context of jet fuel fouling, fuel deposits and
73 gums are characterized by highly disordered coupled products composed of mainly aromatic
74 groups.[18, 19] Overall, the HAS reactions between aromatic fuel species should be
75 investigated as possible route to deposits. Particularly as HAS offers a route to form C–C
76 bonds without terminating the free-radical chain mechanism, and can instead be considered
77 a propagation step.

78



79

80 Figure 1.1: Generalized HAS mechanism, where an Ar^\bullet radical attacks a generic aromatic
81 species. This attack subsequently forms a sigma-complex, which is in a doublet state. The
82 sigma complex is re-aromatized by the loss of a hydrogen *via* an unspecified mechanism.

83

84 Several reactions for the formation of insolubles/deposits are represented in pseudo-detailed
85 mechanisms in the public literature.[5, 20] However, at present, they are implicit. As a result,
86 they do not represent specific chemical transformations, but are composed of 'pseudo'
87 species with parameters fitted to experiments. In the future, a wider range of fuel chemistries
88 and blends will require predictive mechanisms with greater sensitivity to the starting
89 components, without relying too heavily on fitting parameters. However, due to complexity
90 and range of insoluble structures, a compromise needs to be met between the range of
91 reactions and products represented.

92 In recent years, density functional theory (DFT) has become a popular tool to build pseudo-
93 detailed mechanisms jet fuel deposition from 'first-principles'. [21, 22] DFT allows direct
94 calculations of thermochemical and kinetic data, and evaluation of competing chemical
95 reaction pathways. By contrast, previous pseudo-detailed mechanisms have been produced
96 by producing activation energies from fitted experimental data. [5, 20] However, this leads
97 to mechanisms which are only suitable for specific types of fuel.

98 It is the aim of this paper to: 1) explore the possibility of HAS as a route to insolubles
99 formation and 2) attempt to predict insoluble formation tendencies using DFT methods. First,
100 several two-component fuels containing bulk and heteroatoms will be stressed to produce an
101 insoluble mass. Then, the energetic pathways from fuel heteroatoms and bulk species to
102 dimers are calculated and compared to insolubles generated by the surrogate fuels. As a
103 means of understanding the deposition process further, the solubility of oligomers will be
104 considered too.

105 2 Methods and Materials

106 2.1 Surrogate Fuels for this Study

107 Six surrogate fuels were built with a range of compounds designed to represent the different
108 heteroatom and aromatic compounds found in fuels. Out of the nitrogen class of compounds
109 pyrrole (Sigma Aldrich, >98% purity), quinoline (Oakwood chemicals, >98% purity), and
110 indole (Sigma Aldrich, >99% purity) were selected.

111 Pyrrole and indole are two 5-membered nitrogen heteroatom compounds known to promote
112 insoluble formation, with pyrrole being a particularly problematic insoluble promoter. [8, 23]
113 Quinoline has been shown to also promote insolubles, but to a lesser degree than pyrrole and

114 indole.[8, 7] Next, phenol (ACROS Organics, >99%) was chosen to represent the phenolic
115 class of compounds, again shown to promote insolubles in a variety of real and surrogate
116 fuels.[8, 24, 25, 26] Finally, two aromatic components, naphthalene (Fluorochem, >99%)
117 and toluene (SLS, 99.5%) were chosen for their presence in the mono-aromatic and di-
118 aromatic class in fuels.[27] Each of the above six components were added as 0.1 mol l⁻¹ to
119 *n*-dodecane (ACROS Organics, >99%).

120 The authors acknowledge that the chosen concentration of 0.1 mol l⁻¹, equivalent to
121 approximately 20,000 ppm of aromatics, is significantly higher than the heteroatom levels
122 typically found in real fuels, which generally range from 100 to 1000 ppm.[51] However,
123 even at this high concentration, the amount of deposit generated from 5 ml of surrogate fuel
124 was relatively low. Therefore, the fuel needed to be spiked with this level of deposit for the
125 study given the sensitivity of the gravimetric deposit measurement equipment. Furthermore,
126 the primary focus of this study was to investigate the coupling between aromatics in the
127 presence of hydrogen abstraction and addition reactions, hence the requirement for a high
128 concentration of aromatic species to ensure dominant Ar-Ar reactions. Nevertheless, in a
129 real fuel scenario, fuel-aromatic reactions would likely be more prevalent. While homolytic
130 aromatic substitutions would still be relevant (including for fuel-Ar reactions), their impact
131 on the coupling reactions between different species would be more challenging to validate
132 due to the increased complexity of coupling pathways.[14]

133 Another aspect of the design of the surrogate fuels in this study which differ from real fuels
134 was the selection of unsubstituted aromatics. Real fuel aromatics have multiple alkyl-
135 substitutions round the ring aromatic ring. We chose to investigate unsubstituted compounds
136 as a 'base-case' for the coupling reactions here. This base-case was chosen here so that gross
137 differences in aromatic classes could be explored. Future studies adding substituted groups

138 would add another dimension to the work, where the effect of substitutions *within and*
139 *between* each compound class could be explored. Moving beyond the base-case towards a
140 more realistic fuel molecule, additional alkyl- substitutions would likely have two effects
141 based on EAS and HAS theory: 1) block reactive sites where alkyl- substitutions are present
142 and 2) act as weak directing groups.[11] There is also the possibility that alkyl-substitutions
143 would affect the solubility, which can be explored in future work via the methods detailed
144 in section 2.2.

145 2.2 Method of Thermal Stressing and Deposit Measurement

146 To produce the insoluble masses, 5 ml of fuel was added to a 50 ml borosilicate round bottom
147 pressurized flask. The flask was heated to 140°C for 24 h under 1 bar constant oxygen supply.
148 The flask was sealed to all gases aside from the supplied oxygen. After heating, the flask
149 was allowed to cool and insolubles were then filtered through a 0.1 µm glass fibre filter to
150 give the total weight of insolubles in the bulk. The flask was then washed with trisolvant and
151 then washed into a flask. The flask was then dried in a vacuum oven to remove any liquid
152 residue, weighed, and then compared with the weight of the clean flask- giving the total
153 weight of adherent insolubles left in the flask.[28] The sum of the insolubles weights on the
154 filter and in the flask gave a mass total insolubles per surrogate. The deposit experiments
155 were repeated at least 3 times for each surrogate to improve the accuracy of the total
156 insolubles measurement.

157 A petroOxy device was used to produce oxygen depletion curves for each surrogate fuel.
158 The petroOxy device is a sealed gold-lined chamber in which 5 ml of fuel is thermally

159 stressed at 140°C. The headspace above the heated fuel is depleted as the fuel is stressed,
160 giving a measure of the rate of oxygen consumption in the bulk fuel.

161 2.3 Hansen Solubility Parameters and Computational Details

162 All calculations were performed in Gaussian09 (E.01) using the B3LYP
163 functional.[29][30] Grimme's DFT-D3(BJ) dispersion correction was applied to all the
164 calculations to account for long-range effects.[31] A PCM solvation model, with n-
165 dodecane as the chosen solvent, was selected to replicate the hydrocarbon bulk.[32] The
166 basis set chosen was cc-pVTZ on an ultrafine grid. This basis set adds polarization
167 functions, allowing orbital hybridization to be taken into account.[33] Transition states
168 were optimized using the QST1/3 method depending on the reaction studied. All transitions
169 states were verified by the presence of one imaginary frequency corresponding to the
170 saddle point. Additionally, intrinsic reaction coordinate (IRC) calculations were performed
171 to verify the transition state corresponded to the expected reactants and products.
172 Unrestricted (broken symmetry) calculations were performed on open-shell systems, where
173 the HOMO and LUMO were mixed (guess=mix option). Entropy values were corrected
174 using the GoodVibes script, which employs a quasi-harmonic correction corrected at
175 298K.[34, 35, 36]

176 In Hansen solubility theory, three Hansen solubility parameters (HSPs) are assigned to
177 each molecule: D for dispersion, P for polarity, and H for hydrogen bonding. As a
178 consequence, each solvent exists in a 3-dimensional space of HSPs. The HSP distance
179 between two molecules in the 3d HSP space is given by:

180
$$Ra^2 = 4(D_1 - D_2)^2 + (P_1 - P_2)^2 + (H_1 - H_2)^2 \quad (1.1)$$

181 Where R_a is the Hansen distance.

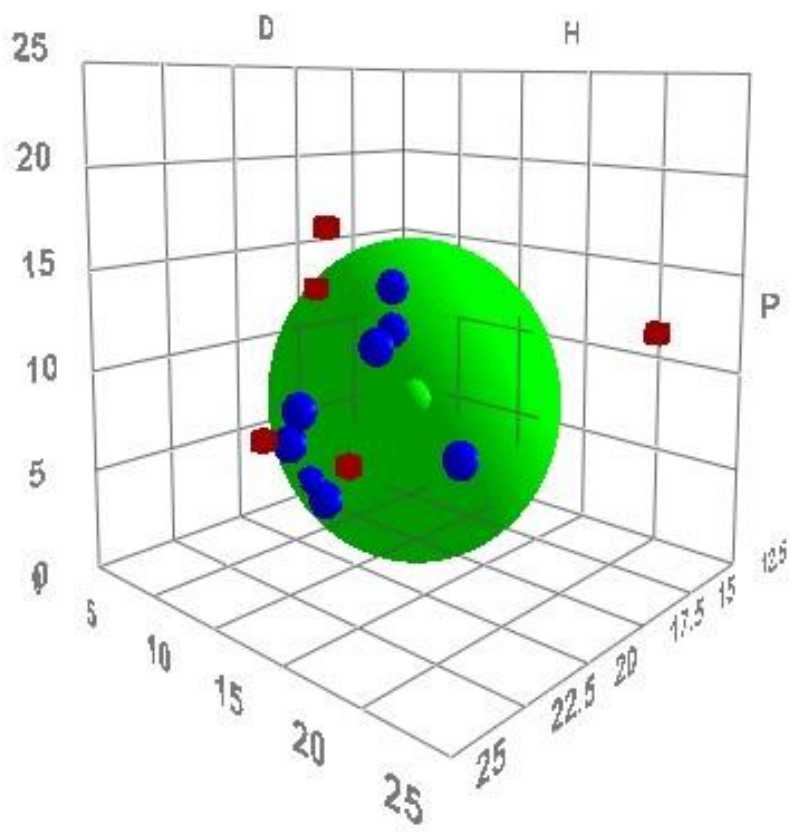
182 The HSP parameters for the test solvents were either obtained from the HSPIP dataset or
183 calculated using the software. The HSPIP software requires a series of test solvents/solutes,
184 tested for their solubility in the *n*-dodecane. A score 0 is assigned to insoluble solvents and
185 a score of 1 is assigned to soluble solvents.

186

187 In each case, 0.1 mol l⁻¹ of each test compound was added to 5ml of *n*-dodecane. Resulting
188 from the series of tests is a 'sphere' in 3d HSP space, whose dimensions are determined by
189 the solubility of the sphere (Figures 2.1 and 2.2). The radius of sphere R_0 is then used to
190 assess the solubility of a proposed solvent, where R_a of the test molecule is used in the
191 following equation:

192
$$RED = R_a/R_0. \quad (10.2)$$

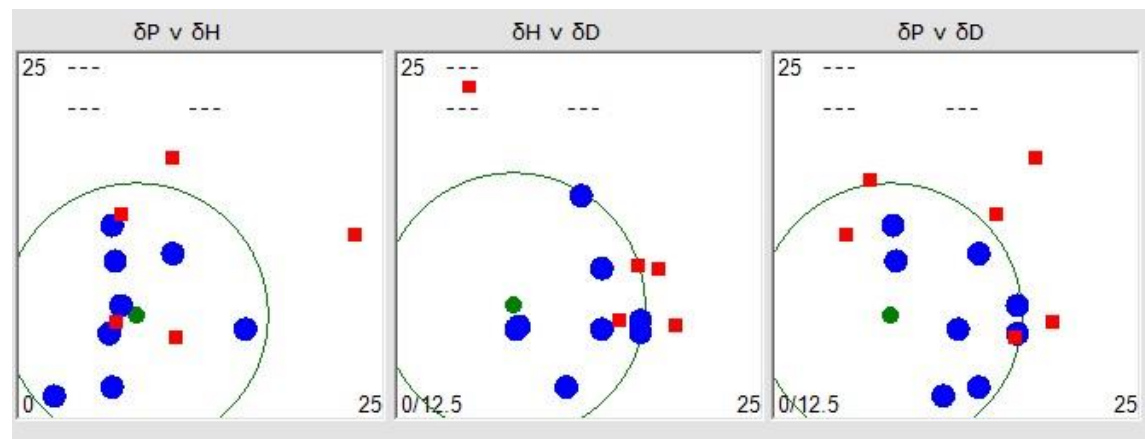
193 Where RED stands for Relative Energy Difference. A RED > 1 implies the molecule is
194 likely insoluble in your main solvent (*n*-dodecane in this case), whereas a RED < 1 implies
195 the molecule is soluble. Our calculated sphere was composed of 13 lab grade compounds
196 known for their presence in fuel and gave a fit of 1 according to HSPIP software. The
197 results for these tests are presented in Table 2.1 . Here it is important to acknowledge that
198 the solubility of the deposit precursors in pure *n*-dodecane this study will likely be different
199 to a conventional fuel due to the presence of aromatic compounds and minor components.
200 Nevertheless, these parameters are useful to understand insoluble formation our surrogate
201 fuel, and to improve the HSP method for future studies.



202

203

Figure 2.1: HSPIP Sphere



204

205

Figure 2.2: HSPIP Sphere parameter fits

206

207

208

209 Table 2.1: Hansen Solubility test solvents and their Associated HSPs. The sphere gave a fit
210 of 1.000

Solvent	Database/Calculated HSP	D	P	H	Score	RED
Indigo	Calculated	21.10	17.4	10.0	0	1.639
Carbazole	Database	21.7	6.4	6.2	0	1.243
p-Benzoquinone	Database	19.8	13.7	6.5	0	1.121
Water	Database	15.5	16.0	42.3	0	4.042
2-Naphthol	Database	20.4	5.4	10.2	0	1.000
Methanol	Database	14.7	12.3	22.3	0	1.800
Di- <i>n</i> -Butyl Sulfoxide	Database	16.4	10.5	6.1	1	0.443
Naphthalene	Database	19.2	2.0	5.9	1	0.884
Pyrrole	Database	19.2	11.0	10.0	1	0.863
Dipropyl Sulfone	Database	16.3	12.9	5.9	1	0.705
Toluene	Database	18.0	1.4	2.0	1	0.961
Indole	Database	20.5	7.5	6.5	1	0.973
Phenol	Database	18.5	5.9	14.9	1	0.979
Quinoline	Database	20.5	5.6	5.7	1	0.995

211

212

213 2.4 Pseudo-Detailed Mechanism in Fuels

214 In order to compare the total insolubles to the number of dimers predicted by DFT, several
215 new reaction steps were proposed which will be elucidated in the results and discussion. To

216 capture the autoxidation reactions in the bulk, the basic autoxidation scheme (BAS) was used
217 which gave good agreement with oxygen and hydroperoxide depletion with experiment. The
218 BAS scheme was optimized for a range of C10-C14 hydrocarbons, whereby the
219 thermochemical and kinetic parameters were obtained using *n*-dodecane as the model fuel.
220 Further details of the BAS scheme can be found in reference.[22] To construct the
221 mechanism, the Eyring equation was used, with A being formed from the calculated entropy
222 barrier and E_a formed from the calculated enthalpy barrier. All the forward and reverse
223 barriers were calculated from a stable pre-reaction and post-reaction complex.

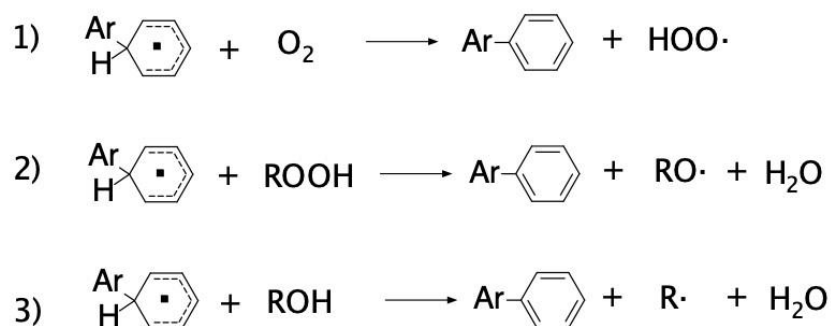
224 For each surrogate fuel, different mechanisms were constructed to study oxygen depletion
225 and deposit formation. For oxygen depletion, the level of oxygen was fixed at 1.8 mmol l⁻¹.
226 [37] For the deposition mechanism, oxygen was removed as a limiting reagent (kept
227 constant at 1.8 mmol l⁻¹) to reflect the continuous supply of oxygen in our deposit forming
228 rig. The mechanism was integrated in MATLAB using the **ode45** solver. The mechanism
229 gave a molar concentration of a dimer, which was then related to a mass via the molecular
230 weight of the proposed dimer.

231 3 Results and Discussion

232 3.1 Homolytic Aromatic Substitution Mechanism

233 The key bottleneck in any HAS reaction is the re-aromatization and liberation of hydrogen
234 from the σ -intermediate. The loss of H \cdot in this step is not well understood. Nevertheless, one
235 paper exploring HAS reactions between aryl iodides and arenes using oxygen as an oxidant,
236 proposed a re-aromatization step involving oxygen this is shown as reaction 1) in Figure 3.1
237 Because hydroperoxides (ROOH) and oxygenated species like alcohols (ROH) form under

238 oxidative conditions in fuels, these were also considered as possible reagents to remove
 239 hydrogen from the σ -intermediate. ROOH reacting with the σ -intermediate is proposed to
 240 form $\text{RO}\cdot$ and H_2O , is shown as reaction 2) in Figure 3.1. ROH reacting with the σ -
 241 intermediate is proposed to form $\text{R}\cdot$ and H_2O , is shown as reaction 3) in Figure 3.1.



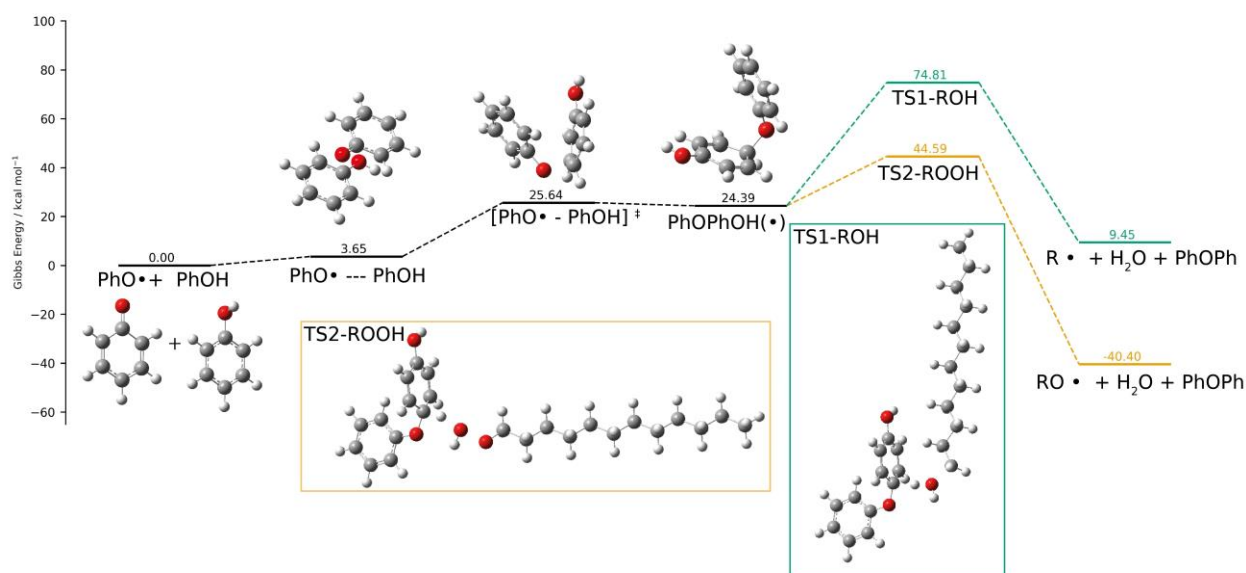
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243 Figure 3.1: HAS reactions considered for fuel coupling reactions. Each step
 244 shows the σ -intermediate formed from an $\text{Ar}\cdot + \text{ArH}$ reaction, and the species
 245 chosen to re-aromatize the intermediate.

246 Considering the mechanisms presented in Figure 3.1, we explored the possibility of these
 247 reactions in phenolic coupling. Phenols have widely been recognized as being detrimental
 248 to fuel thermal stability.[8] HAS mechanisms have previously been considered as a possible
 249 pathway the oxidative coupling of phenols.[14] Nevertheless, it should be noted that in a real
 250 fuel, direct phenol-phenol coupling is not likely to be dominant to the concentration of
 251 phenolic compounds. However, the main of this section is to understand the possible re-
 252 aromatization step available to fuel species. The findings here will be used as a template for
 253 other fuel HAS reactions.

254 The calculated HAS pathways for phenol are presented in Figure 3.2. First, the formation of
 255 the σ -intermediate is endergonic and has a free-energy barrier of $\ddagger G = +25.64 \text{ kcal mol}^{-1}$
 256 leading to an intermediate $\text{PhOPhO}\cdot$. The para- position of the phenol was chosen as the site

257 of oxidative coupling of another phenoxy radical given that this is the generally the more
 258 favorable site.[38] The first mechanism in Figure 3.1, involving the re-aromatization with
 259 oxygen, could not be identified for phenol. A key challenge with the oxygen transition state
 260 is the choice of spin multiplicity. Given that oxygen is in the triplet state, and the system σ -
 261 intermediate is in the doublet state, an open-shell doublet or a quartet surface can be chosen.
 262 The other two mechanisms presented in Figure 3.1 involve ROH and ROOH. The ROOH
 263 pathway in Figure 3.2 shows a lower barrier to re-aromatization of the intermediate
 264 compared to the ROH by 30.22 kcal mol⁻¹. Additionally, the ROOH is thermodynamically
 265 favored, namely due to the enhanced stability of the RO \cdot radical compared to R \cdot . The IRCs
 266 for both these pathways are presented in Figures S.1 and S.2 in the SI. The ROOH and ROH
 267 re-aromatization transition states are characterized by a rotation of the terminal OH moiety
 268 towards an available hydrogen at the para-coupling site.



269

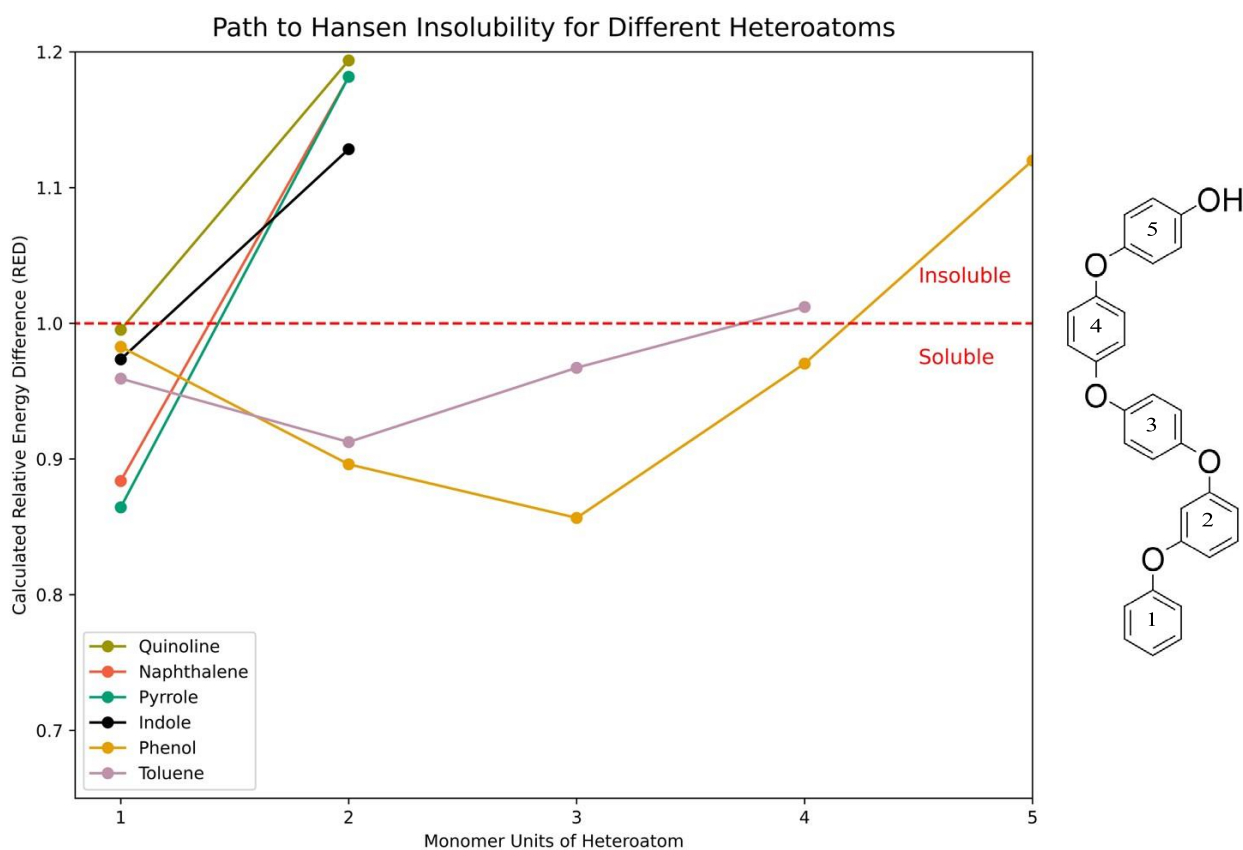
270 Figure 3.2: Comparison of different HAS pathways at the B3LYP-D3//cc-pVTZ level of
 271 theory using *n*-dodecane (PCM) as a solvent. The first step of the process in black shows
 272 the Ar \cdot + ArH---ArHAr \cdot reaction of a phenol and a phenoxy radical, leading to the σ -

273 intermediate. The subsequent levels in green shows the re-aromatization step with ROH
274 and the level in orange shows the re-aromatization step with an ROOH species.

275 3.2 Comparison of Antioxidant Oligomer Solubility and Pathway to 276 Deposit

277 To justify the assumption that the formation of insolubles results from the coupling of
278 ArH species, we calculated Hansen solubility parameters for oligomers for our chosen
279 heterotoms of increasing size. Previous research has hypothesized that aromatic
280 compounds in fuel rapidly become insoluble as they grow in size.[43] Figure 3.3 shows
281 the change in RED score as the oligomer chain grows, where relative energy difference
282 (RED) > 1 indicates an oligomer that has become insoluble in *n*-dodecane. For real fuels,
283 these results will vary, particularly as the aromatic content will increase the 'likeness' of
284 the solvent to other extended aromatic structures.[39] Nevertheless, because our model
285 fuels in this study contain *n*-dodecane as the base solvent, the Hansen plots here are a
286 useful tool to explore deposition tendency in our model fuels. Oligomer structures were
287 chosen based on the favored coupling site for each heteratom based on literature data and
288 our calculations.[38, 40, 41, 42] The phenol chain growth is shown as an example. What
289 is clear is that in general as the oligomer grows, the solubility in *n*-dodecane decreases.
290 However, different oligomers reach the insolubility threshold in fewer units, where a
291 single unit is the monomer, 2 units is a dimer and so on. For example, comparing toluene
292 and naphthalene, naphthalene reaches the insolubility threshold after 2 units have coupled.
293 This is consistent with previous observations that di-aromatics form deposit more rapidly
294 because they 'require fewer consecutive reaction steps to produce high-molecular-
295 weight'.[43]

296 Interestingly, heteroatom size does not influence the solubility of the resultant oligomers.
 297 Instead, the lower solubility is related to the dD parameter in the HAS framework,
 298 representing Van Der Waals forces between the solvent and heteroatom. As the oligomers
 299 grow, the difference in polarity and hydrogen bonding begins to decrease (indicated by the
 300 decreasing dP and dH parameters), but the difference in dispersion forces dD increases.



301

302 Figure 3.3: Effect of oligomer unit size on solubility calculated using the HSPiP software. It
 303 is clear some heteroatoms reach insoluble threshold in fewer units than others. Phenol and
 304 toluene is particularly interesting, becoming initially more soluble in *n*-dodecane before
 305 reaching the threshold. For phenol this is due to the growth of oligomer leading to a lower
 306 proportion of the molecule containing the *H*-bonding –OH group, but as the molecule grows
 307 the Van Der Waals dD difference grows eventually leading to an insoluble.

308 3.3 Predicting Deposition formation using DFT

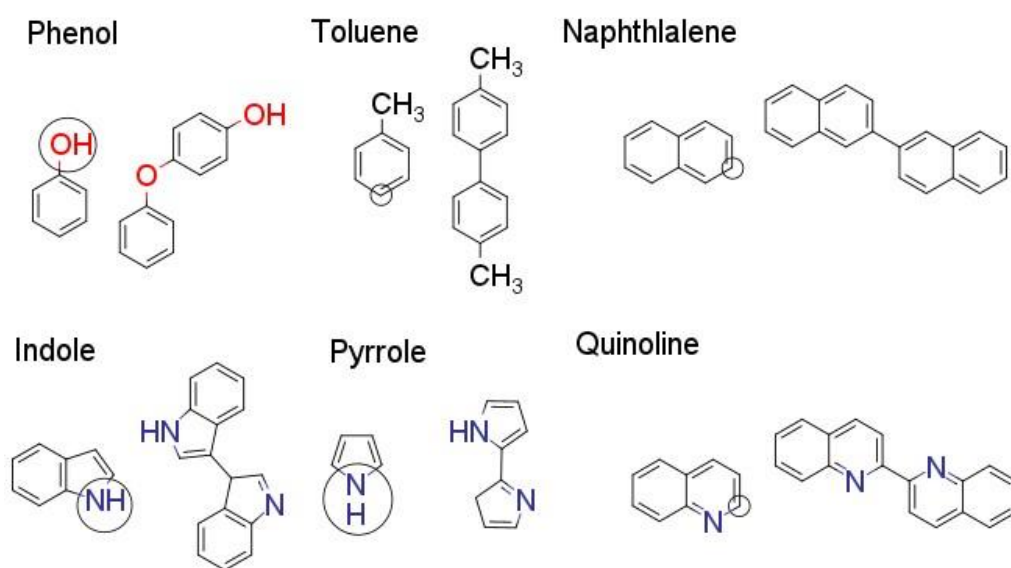
309 3.3.1 H-abstraction and Coupling Mechanisms for Each Heteratom

310 Based on the solubility modelling presented in Figure 3.3, it was clear that the coupling of
311 fuel heteratoms would lead to insoluble formation in our *n*-dodecane surrogate. Following
312 the proposed HAS pathway, we calculated the H-abstraction and subsequent barriers to form
313 dimers via the HAS pathway. The barriers for these reactions are presented in detail in Table
314 S.1 of the appendix. The termination reaction was barrierless for all the species, and the pre-
315 exponential factor was kept constant for each of the species at 3×10^9 . [5]

316 The H-abstraction site and the coupling site for each species was selected based on literature
317 and our own testing, and is summarized in Figure 3.4. For phenol, H-abstraction occurs at
318 the O-site, with coupling between the subsequent phenoxy radical and the para-carbon site
319 of a phenol. [38] For naphthalene, the C3 site was favored over the C2 position in terms of
320 both abstraction and coupling barrier heights. For quinoline, the C2 site is the most favored
321 site for coupling and H-abstraction, and the barriers for abstraction were lower at the C2 site
322 compared to the C3 site. [44] For toluene, the para position was selected for coupling and H-
323 abstraction based on our own testing and literature data. [45]

324 For indole and pyrrole, the favored coupling and H-abstraction site were found to be
325 different. For indole, the N1 site was found to be the most favorable site for H-abstraction,
326 but the C3 site is the most favored for coupling. Nevertheless, C–N linkages are detected
327 very rarely and are found to be thermodynamically prohibited for indole oligomers. [46, 47]
328 As a consequence, we compared the overall pathway to dimers at the C3 position via H-
329 abstraction at the N1 and C3 positions. The results for the indole dimer formation
330 calculations are found in Figure S.4 of the SI. Overall, the C3 H-abstraction pathway shows

331 the highest barriers. Therefore, the N1 H-abstraction pathway for indole was chosen.
 332 Similarly, for pyrrole, H-abstraction at the N1 position is favored, yet polypyrrole is formed
 333 of C2-C2 linkages.[40] Comparing both pyrrole coupling C2 coupling pathways with H-
 334 abstraction at the N1 or C2 position, presented in Figure S.3, both pathways have similar
 335 barrier heights. Nevertheless, the initial H-abstraction reaction at the N1 position is more
 336 favorable and leads to an intermediate I1b G 24.49 kcal mol⁻¹ lower in energy than the C2
 337 pathway. As a consequence, following the N1 pathway, pyrrole would have antiox-



338

339 Figure 3.4: H-abstraction Sites and Dimers Selected for the Pseudo-Detailed Mechanisms.
 340 The selected H-abstraction site is circled, and resultant dimer is shown for each species.

341 idant properties, which is reflected in the petroOxy measurements (Figure 3.6b). Therefore,
 342 the N1 abstraction pathway for pyrrole was chosen.

343 Regarding the different coupling and H-abstraction sites for indoles and pyrroles, it should
 344 be underlined that this difference may only be relevant to self-reactions. Indeed, for indole

345 and pyrrole functionalization reactions under oxidative conditions, the N- group is pre-
346 protected prior to arylation and alkylation reactions. [52,40]

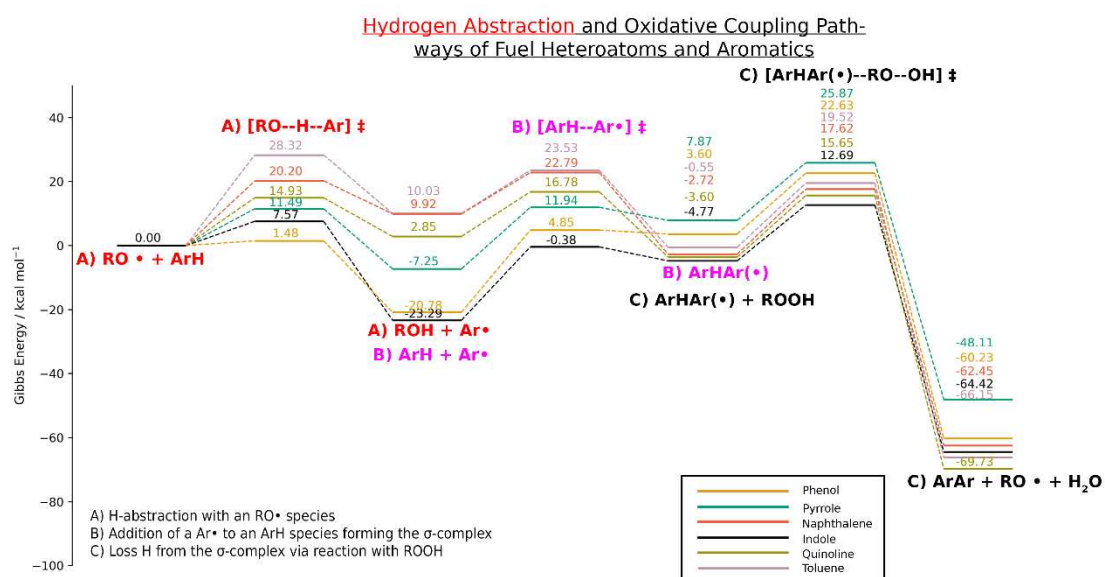
347 Based on the above proposed coupling and H-abstraction sites, we computed the barriers for
348 ArH species reacting with *n*-dodecane R·, RO·, and ROO· radicals and subsequently forming
349 dimers via a HAS process. The Gibbs potential energy surfaces for our chosen heteroatoms
350 undergoing H-abstraction to the formation of dimers are presented in Figure 3.3 for RO·.
351 The values for the reactions with the other radicals are presented in Table S.1 of the SI.

352 The first section (reaction A) of Figure 3.5, showing the abstraction of hydrogen from our
353 selected ArH species. Here, we can see there is a clear difference in the reactivity and
354 thermochemistry. To begin with, phenol shows the lowest barriers for hydrogen abstraction
355 out of all the species tested. Phenol has long been known as a powerful antioxidant in
356 fuels.[5] By contrast, toluene exhibits the highest barrier and the overall Gibbs energy
357 abstraction reaction is endergonic at +28.32kcalmol⁻¹. The overall order of the Gibbs energy
358 barrier to hydrogen abstraction (section A) is, in descending order: toluene > naphthalene >
359 quinoline > pyrrole > indole > phenol.

360 The resultant radicals formed indicate that phenol, pyrrole, and indole all exhibit
361 antioxidant properties, by undergoing an exergonic H-abstraction reactions. By contrast,
362 naphthalene, toluene, and quinoline undergo endergonic H-abstraction reactions showing
363 no antioxidant qualities. At this point in the reaction process, two Ar· radicals can terminate
364 to form a dimer. Nevertheless, this termination process is a rare occurrence due to the low-
365 concentration of Ar· species in fuel (for example, for pyrrole the peak concentration in our
366 mechanism was 5.17E-13 mol l⁻¹).

367 The HAS reaction between an Ar· and ArH first proceeds with an attack of the radical. The
368 radical attack is shown as pathway B) in Figure 3.5. For this step, the antioxidant species
369 formation is endergonic and proceeds with high Gibbs energy barriers for phenol and
370 indole of $\ddagger G$ 25.63 kcal mol⁻¹ and $\ddagger G$ =24.36 kcal mol⁻¹ respectively. By contrast, pyrrole
371 proceeds with a lower barrier of $\ddagger G$ =19.20 kcal mol⁻¹. On the other hand, the non-
372 antioxidant species show lower barriers for pathway B). In fact, naphthalene and toluene
373 show the highest barriers for the H-abstraction step, but lowest barriers out of all the species
374 for step B) at $\ddagger G$ =12.87 kcal mol⁻¹ and $\ddagger G$ =13.50 kcal mol⁻¹ respectively. Additionally, the
375 formation of the intermediate is the most exergonic for naphthalene and toluene. The
376 relationship between the antioxidant tendency and the ease of coupling is likely related to
377 the aromatic structure. Species with more antioxidant qualities will also have higher levels
378 of aromaticity to stabilize radicals, but also will have higher barriers to aromaticity-
379 breaking radical attack.

380 The final step in the dimer forming process is the re-aromatization step *via* loss of hydrogen
381 from the intermediate. Interestingly, the barriers for this step are similar for our aromatics
382 tested, in the range of 23.87-17.47 kcal mol⁻¹. This step is clearly less related to the
383 structure of the ArH compound. Nevertheless, the concentration of ROOH available to
384 complete this step, is related to the antioxidant qualities of the ArH species in fuels. For
385 example, for phenols, due to their antioxidant properties, the concentration of ROOH is
386 expected to be low.[24] As a consequence, termination reactions likely provide a higher
387 source of C–C/C–O coupling. To explore how these interrelated pathways yield deposits
388 for different fuel components, we created different pseudo-detailed mechanisms to
389 compare each fuel.



390

391 Figure 3.5: Growth to a deposit dimer for our chosen heteroatoms, calculated at the B3LYP-
 392 D3/cc-pVTZ *n*-dodecane PCM level of theory. The barriers were calculated from stable pre-
 393 reaction complexes. The R species was *n*-dodecane. The antioxidant species (phenol, indole
 394 and pyrrole) show exergonic H-abstraction in step Ar.

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398 3.3.2 Comparison of Experimental Results and Psuedo-Detailed Models

399 Antioxidant Behavior

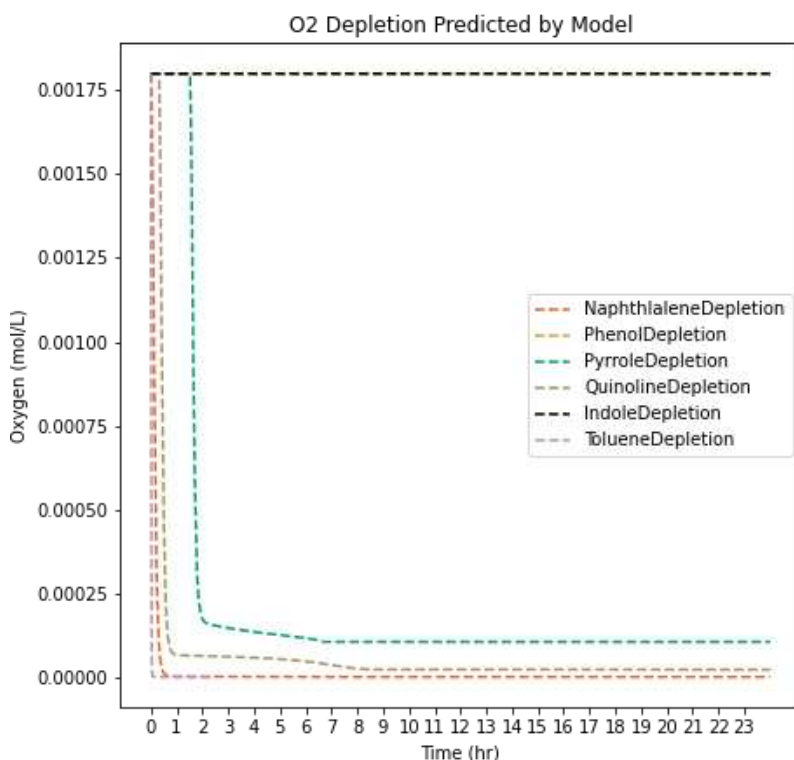
400 First, the antioxidant behavior of our surrogate fuels was explored in relation to our models.
 401 The O₂ depletion predicted by our model alongside the petroOxy depletion curves are
 402 presented in Figure 3.6. Although the petroOxy device cannot measure the O₂ depletion in
 403 the bulk, the device can be used to assess the antioxidant behavior of different fuels.[76] Our

404 model successfully predicts that pyrrole, indole, and phenol are all antioxidant species, as
405 shown by the increased induction period in the petroOxy curves. In addition, the petroOxy
406 device indicates that indole and phenols are stronger antioxidants than pyrrole, which is also
407 reflected in the O₂ depletion curves in our mechanism. However, the difference between
408 indole and phenol in the petroOxy curves is not reflected in the mechanism-

409 **Deposition Behavior**

410 The amount of insoluble dimers predicted by our model compared with the total insolubles
411 measured is presented in Figure 3.7. It should be noted that the comparison here is focused
412 on the *correlation* between amount of dimers predicted and total deposit produced by
413 experiment. As a consequence, the correlation produced will reflect how well the model
414 predicts deposition behavior. Indeed, the difference between correlated and measured
415 deposits by a factor of ~300. This is due to the fact our mechanism only focuses on the
416 formation of dimers. Dimers are likely only to form a small proportion of the total deposit
417 structure, hence the large different in mass. Instead, the results here intend to explore how
418 well the model predicts couple propensity between different species which we hypothesize
419 is related to the ease of forming dimers. The model predicts the insoluble formation behavior
420 between our different surrogates well, with pyrrole producing the largest amounts of
421 insolubles. Interestingly, phenol and indole are shown to produce the lowest amount of
422 deposit in both our experiments and model. By contrast, in real fuels, indoles, and
423 particularly phenol concentration are shown to correlate well with final insoluble mass.[8]
424 A key difference between our simplified surrogates and real fuels are the synergistic effects
425 between fuel classes, which are not captured in our two-component surrogates. In particular,
426 sulfur is shown to interact strongly with 5-membered nitrogen heterocycles, and phenols
427 with other nitrogen compounds.[7, 48] For example, in a simplified surrogate, previous work

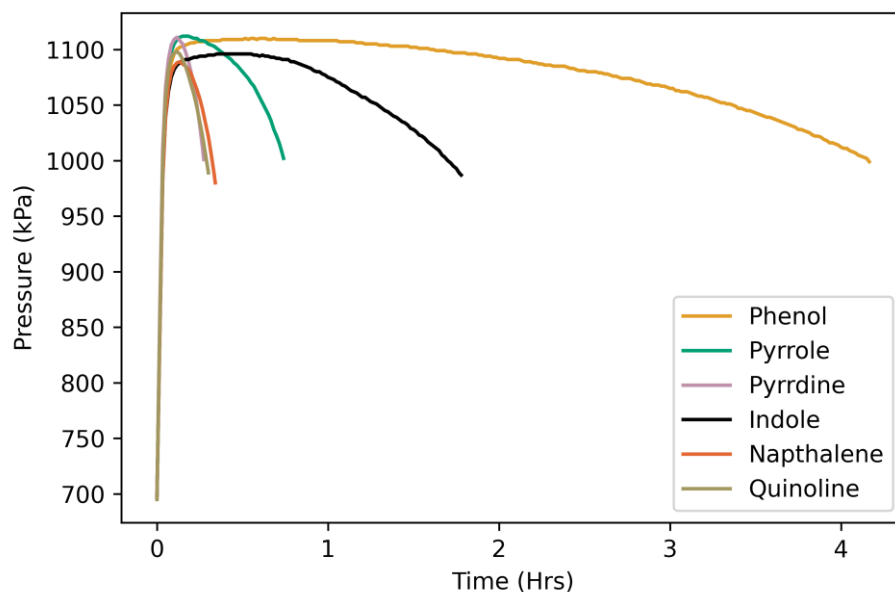
428 has shown trends between deposition propensity of 5- and 6-membered heterocycles break
429 down, where quinoline-like compounds have shown to produce more deposit than indole
430 compounds.[7] Nevertheless, the use of surrogates is still important to understand the
431 chemical interactions within species classes.



432

433

(a) O₂ Depletion Predicted by our model



434

435

(b) Petroxy depletion behavior

436 Figure 3.6: O₂ depletion behavior of our surrogate- comparison between model and
 437 experiment. The model shows the change in O₂ concentration over time. The petroOxy
 438 depletion curves show the change in headspace pressure, and although they are not a direct
 439 measure of O₂ depletion, they can differentiate between antioxidant qualities of different
 440 species.

441 Interestingly, in our experiment and models, toluene and naphthalene produced more
 442 insolubles than phenol and indole. This is interesting as fuel thermal degradation is often
 443 viewed as solely driven by heteroatoms.[25] Exploring the barriers for toluene and
 444 naphthalene in detail in Table S.1, we see that lower barriers to the ArH + Ar· → ArHAr·
 445 reaction are found with the aromatic species. Sensitivity analysis (Figure 3.9) of our models
 446 suggests this coupling step is strongly related to the final insoluble mass. However, in a 2-
 447 component fuel, combining an antioxidant heteroatom and aromatic, the formation of
 448 aromatic insolubles will be significantly reduced due to the size of the H-abstraction barrier
 449 in comparison to the other heteroatoms used in this study (Figure 3.5). Instead, the

450 heteroatom antioxidant class will form the majority of the Ar· radicals going on to form
451 deposit. To strengthen this hypothesis, using our calculated values, a fuel model was built
452 containing both phenol and toluene.

453 The effect of heteroatoms suppressing deposition from non-antioxidant species is
454 demonstrated in Figure 3.8, where insolubles are generated from pseudo-detail model fuels
455 containing different ratios of toluene and phenol is tested. The model was built using the
456 same BAS scheme base described in the section 2.4, with the addition of both toluene and
457 phenol pathways. In this simplified model, toluene-derived insolubles are suppressed upon
458 introduction of phenol. This effect can help explain why fuel deposits/insolubles often have
459 an elemental composition of heteroatoms higher than conventional fuels also containing
460 aromatic hydrocarbons.[49] Another interesting effect of blending is the peak in phenol
461 insolubles at 25:75 phenol:toluene ratios above a 100% phenol mix, which implies that above
462 a certain concentration, phenols will prevent the formation of insolubles. The peak
463 concentration of hydroperoxide steadily drops at different % phenol concentrations, which
464 is related to the extent the autoxidation chain is suppressed. The peak of phenol deposition
465 could be related to the ROOH concentration, allowing more σ -intermediates to be re-
466 aromatized. This shows our model can replicate the effect of changing concentrations of
467 antioxidant on total insolubles.

468 For some of the fuels the pseudo-detailed mechanisms reflect the behavior of 'peak'
469 deposition temperature. The effect of temperature on the concentration of deposits for each
470 mechanism is shown in Figures S.6-10 of the SI. For quinoline, a peak deposition level is
471 reached at 460K. Whereas for toluene, as the temperature increases the level of deposit
472 decreases. All the other fuel models show an increase in concentration of deposit as the
473 temperature rises. This demonstrates these deposit mechanisms can reflect the complex

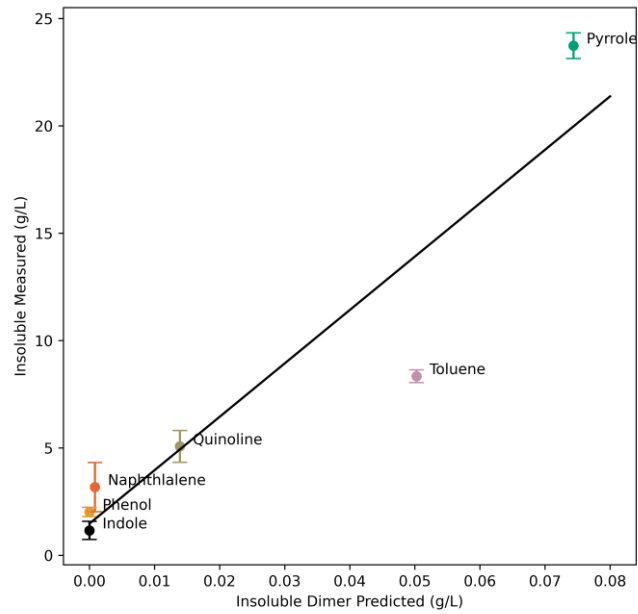
474 behavior of observed in real fuels of increasing and decreasing levels of deposit depending
475 on fuel temperature.[50]

476 Finally, our results here lend credence to a HAS pathway leading to deposit. When the HAS
477 pathway is removed from the mechanism in Figure 3.7b, no discernable trend is found
478 between the formation of dimers and insolubles measured. In fact, the HAS pathway appears
479 particularly important for species with low/no antioxidant tendency, but with a tendency to
480 still form insolubles.

481 Sensitivity analysis of our bespoke mechanisms is presented in Figure 3.9. The reaction
482 numbers cited here correspond to those given in Table S.1. For our mechanisms, the reaction
483 29, $\text{Ar}\cdot + \text{ArH} \rightarrow \text{ArHAr}\cdot$, has the largest influence on the level of deposit with the exception
484 of phenol. Increasing the rate of reaction 29 leads to more $\text{ArHAr}\cdot$ species which can readily
485 form deposit. Reaction 32, $\text{Ar}\cdot + \text{ROOH} \rightarrow \text{ArH} + \text{ROO}\cdot$, removing hydroperoxides from
486 the system also has an influence on the level of deposit. As the rate of reaction 32 increases,
487 hydroperoxides are removed from the system leading to fewer $\text{ArHAr}\cdot + \text{ROOH}$ re-
488 aromatization reactions leading to deposit dimers. The change of ROOH and insoluble
489 concentration presented in Figure 3.10 demonstrates that as insolubles are produced ROOH
490 is depleted. For all the species tested, the $\text{RO}\cdot$ (reaction 26) and $\text{R}\cdot$ (reaction 27) hydrogen
491 abstraction steps have a large influence on the level of deposit, with faster rates leading to
492 more $\text{Ar}\cdot$ species able to undergo coupling reactions. By contrast, the rate of the $\text{ROO}\cdot$
493 abstraction barrier (reaction 16) has a negligible influence on deposition for most species
494 because this reaction in general has high barriers already. Finally, for phenol, reaction 26,
495 $\text{ArH} + \text{R}\cdot \rightarrow \text{Ar}\cdot + \text{RH}$ also influences the formation of deposit more than the other species,
496 and is more important than the coupling step (reaction 29). This is likely because the

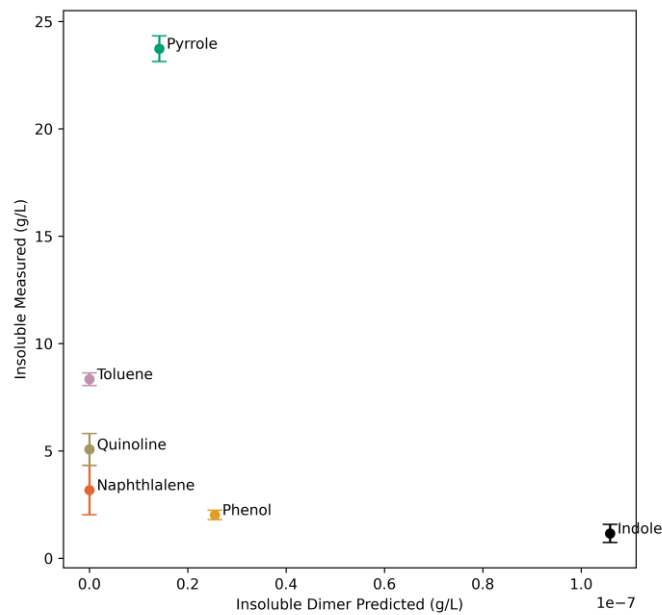
497 termination pathway dominates the formation of deposits here, thus leading to a direct

498 correlation between the concentration of $\text{Ar}\cdot$ and the amount of deposit dimer.



499

500 (a) Correlation between mass of dimer predicted by our model and insolubles measured.

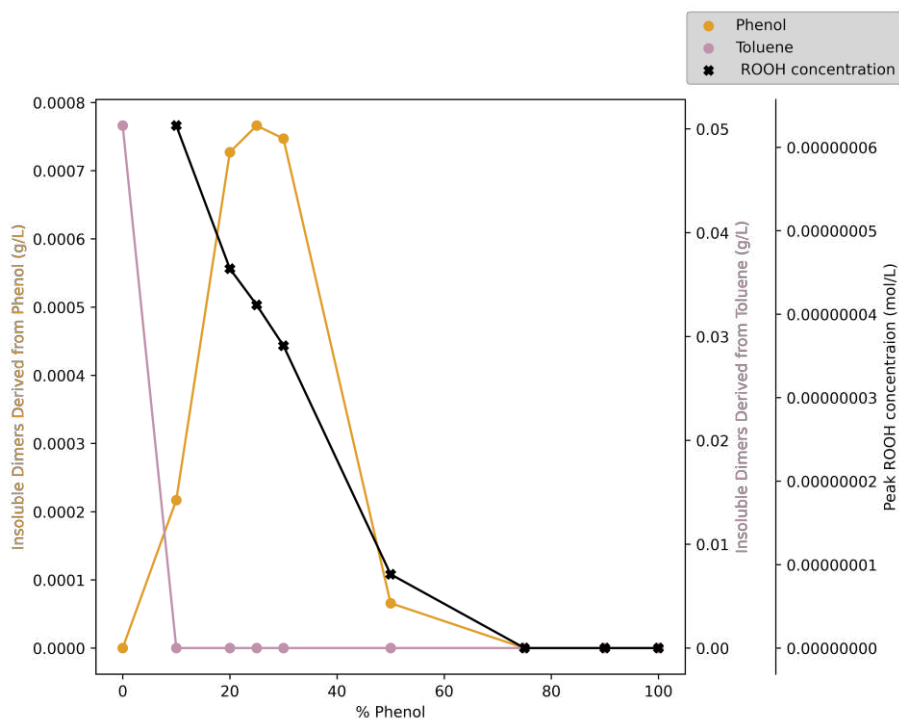


501

502 (b) Correlation between mass of dimer predicted by our model and insolubles measured when the

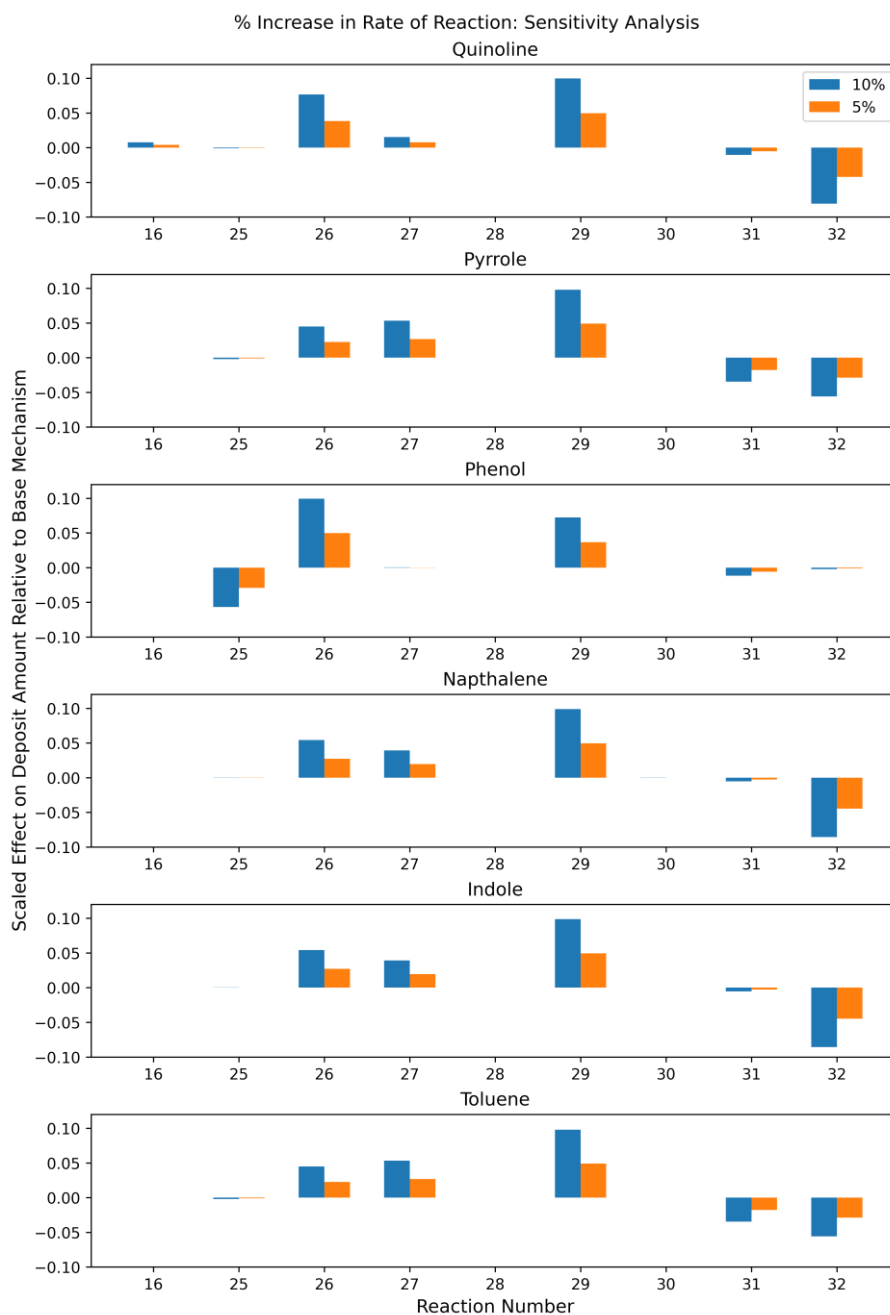
503 HAS pathway is excluded.

504 Figure 3.7: Insoluble formation behavior- comparisons between model and experiment.
505 Temperature of the experiment and psuedo-detailed *n*-dodecane chemical mechanism
506 containing the A and E_a values shown in Table S.1. The temperature was set at 431 K both
507 the model and the experiment.



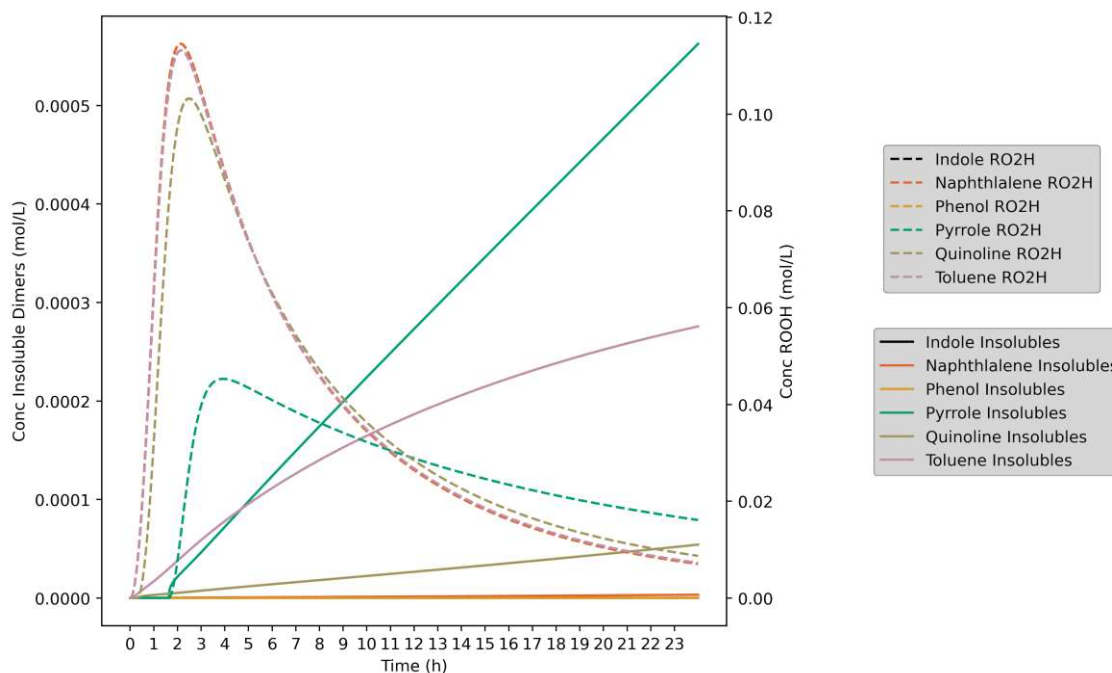
508

509 Figure 3.8: Effect of phenol % in a phenol toluene aromatic total of 0.1 mol L⁻¹ on the
510 insolubles derived from phenol and toluene.



511

512 Figure 3.9: Sensitivity analysis of the bespoke insoluble pseudo-detailed mechanisms. For
 513 the sensitivity analysis, the rate of reaction is increased by a factor of 10% (blue) and 5%
 514 (orange) and the resultant increase in insolubles is shown relative to the base pseudo-
 515 detailed mechanism. The reaction number corresponds to Table S.1 in the SI



516

517 Figure 3.10: Change in the concentration of insolubles and ROOH over the course of the
 518 24h pseudo-detailed models. The thick lines show the change in insoluble dimer
 519 concentration, whereas the dotted lines show the change in ROOH concentration. The
 520 results clearly show that for each species, as ROOH is depleted, the level insolubles begin
 521 to increase.

522 3.4 Implication for Fuels

523 A key novel finding of this study is the role that HAS reactions can play in deposit
 524 formation. Additionally, the work here represents the first study to apply DFT
 525 calculations to deposition reactions to attempt to predict deposition tendency from first
 526 principles.

527 One weakness of this study is that it looked solely into aromatic self-reactions via the
 528 HAS process, whereas side reactions between ArH and RH species will be dominant in a

529 real fuel scenario due to the low concentration of ArH in real-fuels. To briefly explore
530 side reactions, we calculated the initial step of a HAS pathway between propanal, and
531 various nitrogen compounds which is presented in Figure S.5 of the SI. In this pathway,
532 propanal readily forms a σ -intermediate with the nitrogen heteroatoms. Future studies
533 should explore the HAS pathway for fuel-aromatic side reactions, particularly as no
534 mechanism is currently proposed in the fuel literature which does not rely on a
535 termination step to form the C-C bond or without unrealistic EAS steps forming charged
536 intermediates.[52]

537 The formation of fuel insolubles is influenced by both the H-abstraction and coupling
538 propensity of the heteroatoms/aromatics present in fuel. By simplifying the insoluble
539 formation process into the formation of dimers, we were able to show clear differences
540 between the insoluble formation and antioxidant tendency between surrogate fuels.
541 Nevertheless, the formation of dimers represents a small subsection of the
542 insoluble/deposit structure. To expand the mechanism to reach an insolubles formation
543 model which can provide a quantitatively accurate description, additional pathways need
544 to be considered. This is a challenge, particularly as there are likely thousands of possible
545 side reactions between and within species classes.[2] Even in our surrogate fuels the
546 oxidation of *n*-dodecane is not significantly repressed.

547 To address the challenge of building a branching deposition mechanism with thousands
548 of reactions, several approaches using techniques benchmarked in this study can be used.
549 The first approach involves scaling the deposit forming dimer steps to experimental
550 deposit measurements. This would lead to a semi-empirical mechanism, which moves
551 away from the first-principles approach using DFT. Nevertheless, the DFT

552 thermochemical and kinetic parameters will allow the gross differences between species
553 class and structure to be explored. This approach relies on the assumption that the
554 formation of deposit dimers relates to a general property of 'coupling propensity'. Some
555 preliminary calculations imply this assumption is generally correct, where a propanal
556 doublet attacking various nitrogen compounds give barrier sizes (presented in Figure S.5
557 in the SI) in the same order of magnitude as the dimerization barriers for step B) in Figure
558 3.5.

559 A second, more computationally intensive approach, would be a set of high throughput
560 calculations on additional deposit forming pathways. This approach would use HAS and
561 termination reactions to calculate the pathways to various oligomers. These reactions
562 could be constructed following chemical graph theory, as employed in recent work with
563 phenols.[53] Hansen solubility parameters will guide a 'cut-off' point for energetic
564 pathways to oligomers to form insolubles. Nevertheless, insoluble species are still likely
565 to react to form larger molecular weight species, which adds an additional challenge to
566 this approach.

567 Declaration of Interest

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569 Engineering, PhD Scholarship Scheme, and the Powerplant Integration of Novel Engine
570 Systems (PINES) grant number 113263.

571 4.5 Conclusions

572 The formation of insolubles in fuel is driven by coupling reactions between aromatics. In
573 this work we have shown the importance of HAS in explaining the formation of these

574 insolubles. DFT calculations revealed that the hydroperoxides play a key role in
575 facilitating the HAS pathway. As a result of these findings, we showed that kinetic values
576 calculated for a simplified two-component (dodecane and aromatic) surrogate can reveal
577 differences in antioxidant and deposition tendency of different aromatics compared to the
578 experiment. In addition, when the HAS pathway is excluded, the predicted deposition
579 trends break down. Exploring the behavior of the mechanism further, we show that the
580 addition of antioxidant to an antioxidant+aromatic model leads the suppression of
581 insolubles composed of the aromatic. Instead, the antioxidant+aromatic model leads to
582 insolubles only composed of the antioxidant. Finally, sensitivity analysis reveals that the
583 formation of hydroperoxides ($\text{ArH} + \text{ROO} \rightarrow \text{Ar}\cdot + \text{ROOH}$) and the homolytic coupling
584 ($\text{ArH} + \text{Ar}\cdot \rightarrow \text{ArHAr}\cdot$) have a strong influence on the final deposit mass.

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772

1
2 **EXPLORING HOMOLYTIC AROMATIC SUBSTITUTION AS A**
3 **DRIVER FOR FUEL DEPOSITION WITH QUANTUM CHEMISTRY**
4 **AND EXPERIMENTS**

5
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12
13 **Abstract**

14 Liquid phase insoluble formation in fuels can cause performance and safety issues. To
15 understand the formation of insolubles in fuels from first principles, a series of density
16 functional theory (DFT) calculations were run to calculate the energetic barriers of the
17 autoxidation and coupling reactions for several common fuel aromatics/heteroatoms. The six
18 compounds chosen were phenol, toluene, naphthalene, pyrrole, quinoline, and indole. Using
19 a combination of DFT calculations and gravimetric and petroxy experimental work, a novel
20 homolytic aromatic substitution (HAS) coupling pathway was identified for each compound.
21 While previous studies have treated deposition steps implicitly, our detailed calculations of
22 HAS reactions and bulk fuel (RH) oxidation reaction barriers afforded the development of

23 bespoke pseudo-detailed mechanisms for each aromatic compound with explicit reaction
24 steps. These mechanisms were then used to predict trends in deposition behavior of the
25 compounds tested in a simple n-dodecane surrogate. The novel HAS mechanism suggested
26 for fuels was proposed to start with the reaction of an aromatic radical ($\text{Ar}\cdot$) to an aromatic
27 (ArH), which then formed a radical ($\text{ArHAr}\cdot$) σ -intermediate. It was then found that
28 hydroperoxides (ROOH) could re-aromatize the radical intermediate ($\text{ArHA}\cdot$), forming a
29 deposit dimer (ArAr). Although our sensitivity analysis revealed that alkyl fuel radical and
30 fuel alkoxy radical abstraction steps influenced the final mass of the deposit, the $\text{Ar}\cdot + \text{ArH}$
31 HAS coupling step was found to have the largest influence. Finally, an aromatic/heteroatom
32 model containing phenol and toluene was built, which showed that phenol suppressed
33 deposition from toluene, and peaked in deposit mass at a phenol:toluene ratio of 25:75.
34 Although our study was limited to Ar self-reactions, we hypothesize that bulk fuel – aromatic
35 coupling could also be governed by HAS reactions, allowing researchers to move towards a
36 more first-principles based deposition model.

37
38 Keywords: Density Functional Theory, Homolytic Aromatic Substitution, Thermal
39 Stability, Jet Fuel, Pseudo-detailed Mechanism

40 41 42 1. Introduction

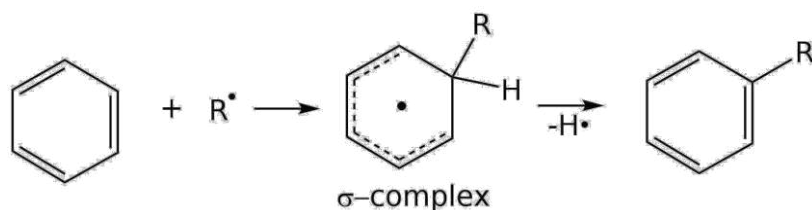
43 The formation of insolubles in the liquid-phase of jet fuels is mainly driven by the formation
44 of oligomers from fuel components.[1, 2] Oligomers successively grow starting from dimers,
45 trimers, tetramers and so on. Each oligomer growth step is predominantly characterized by
46 the formation of C–C and C–O bonds. Previous research has emphasized the termination of
47 antioxidant and/or fuel components ($\text{Ar}\cdot + \text{Ar}\cdot \rightarrow \text{Ar}_2$) as a key source of fuel insolubles,
48 and by that extension C–C/C–O bond formation.[3, 4, 5] This has led Heneghan and

49 Zabarnick to highlight an inverse correlation between the ease of oxidation and the formation
50 of deposits. In other words, a fuel with a lower oxidation rate arises from the higher
51 concentration of chain-breaking $\text{Ar}\cdot$ radicals, and therefore have a higher concentration of
52 $\text{Ar}\cdot$ to undergo termination steps producing deposit.[3] However, in some instances, this
53 relation does not always hold. Notably, some nitrogen compounds like pyrroles and indoles
54 tend to show low/no effects on autoxidation rates yet are severe deposit promoters.[6, 7, 8]
55 To explain these exceptions, Heneghan and Zabarnick propose that some fuels produce
56 termination $\text{Ar}-\text{Ar}$ products with a higher solubility.[3] Nevertheless, there may be other
57 chemical factors that need to be explored.

58 The formation of $\text{Ar}-\text{Ar}$ via the termination of two free-radicals $\text{Ar}\cdot$ in solution is part of an
59 oxidative coupling process. However, it is possible to form $\text{Ar}-\text{Ar}$ without a termination step
60 under oxidative conditions. Focusing on transition metal free processes, homolytic aromatic
61 substitution (HAS) has received considerable attention as a method for cross-coupling
62 aromatic compounds under free-radical conditions.[9, 10, 11, 12] Additionally, HAS
63 mechanisms have been used as a way to understand the rate of radical reactions.[13, 14] The
64 general mechanism of HAS is shown in Figure 1.1. First, an attack of an aryl radical to an
65 arene compound generates a σ -intermediate. The σ -intermediate is then re-aromatized via
66 elimination of a leaving group forming a dimer. In this sense, HAS reactions are analogous
67 to electrophilic aromatic substitution (EAS) reactions, except that the σ -intermediate is not
68 charged. EAS reactions have been proposed as a mechanism in the formation of jet fuel
69 deposits.[15] However, in aprotic non-polar jet fuel, the stabilization of charged EAS σ -
70 intermediates is precluded.[16] By contrast, HAS reactions have been shown to readily occur
71 in non-polar aprotic solvents between arenes under molecular oxygen.[17] In general HAS
72 reactions have presented a challenge to organic chemists due to poor selectivity, leading to
73 intractable mixtures.[11] Nevertheless, in the context of jet fuel fouling, fuel deposits and

74 gums are characterized by highly disordered coupled products composed of mainly aromatic
75 groups.[18, 19] Overall, the HAS reactions between aromatic fuel species should be
76 investigated as possible route to deposits. Particularly as HAS offers a route to form C–C
77 bonds without terminating the free-radical chain mechanism, and can instead be considered
78 a propagation step.

79



80

81 Figure 1.1: Generalized HAS mechanism, where an Ar^\bullet radical attacks a generic aromatic
82 species. This attack subsequently forms a sigma-complex, which is in a doublet state. The
83 sigma complex is re-aromatized by the loss of a hydrogen *via* an unspecified mechanism.

84

85 Several reactions for the formation of insolubles/deposits are represented in pseudo-detailed
86 mechanisms in the public literature.[5, 20] However, at present, they are implicit. As a result,
87 they do not represent specific chemical transformations, but are composed of 'pseudo'
88 species with parameters fitted to experiments. In the future, a wider range of fuel chemistries
89 and blends will require predictive mechanisms with greater sensitivity to the starting
90 components, without relying too heavily on fitting parameters. However, due to complexity
91 and range of insoluble structures, a compromise needs to be met between the range of
92 reactions and products represented.

93 In recent years, density functional theory (DFT) has become a popular tool to build pseudo-
94 detailed mechanisms jet fuel deposition from 'first-principles'. [21, 22] DFT allows direct
95 calculations of thermochemical and kinetic data, and evaluation of competing chemical
96 reaction pathways. By contrast, previous pseudo-detailed mechanisms have been produced
97 by producing activation energies from fitted experimental data. [5, 20] However, this leads
98 to mechanisms which are only suitable for specific types of fuel.

99 It is the aim of this paper to: 1) explore the possibility of HAS as a route to insolubles
100 formation and 2) attempt to predict insoluble formation tendencies using DFT methods. First,
101 several two-component fuels containing bulk and heteroatoms will be stressed to produce an
102 insoluble mass. Then, the energetic pathways from fuel heteroatoms and bulk species to
103 dimers are calculated and compared to insolubles generated by the surrogate fuels. As a
104 means of understanding the deposition process further, the solubility of oligomers will be
105 considered too.

106 2 Methods and Materials

107 2.1 Surrogate Fuels for this Study

108 Six surrogate fuels were built with a range of compounds designed to represent the different
109 heteroatom and aromatic compounds found in fuels. Out of the nitrogen class of compounds
110 pyrrole (Sigma Aldrich, >98% purity), quinoline (Oakwood chemicals, >98% purity), and
111 indole (Sigma Aldrich, >99% purity) were selected.

112 Pyrrole and indole are two 5-membered nitrogen heteroatom compounds known to promote
113 insoluble formation, with pyrrole being a particularly problematic insoluble promoter. [8, 23]
114 Quinoline has been shown to also promote insolubles, but to a lesser degree than pyrrole and

115 indole.[8, 7] Next, phenol (ACROS Organics, >99%) was chosen to represent the phenolic
116 class of compounds, again shown to promote insolubles in a variety of real and surrogate
117 fuels.[8, 24, 25, 26] Finally, two aromatic components, naphthalene (Fluorochem, >99%)
118 and toluene (SLS, 99.5%) were chosen for their presence in the mono-aromatic and di-
119 aromatic class in fuels.[27] Each of the above six components were added as 0.1 mol l⁻¹ to
120 *n*-dodecane (ACROS Organics, >99%).

121 The authors acknowledge that the chosen concentration of 0.1 mol l⁻¹, equivalent to
122 approximately 20,000 ppm of aromatics, is significantly higher than the heteroatom levels
123 typically found in real fuels, which generally range from 100 to 1000 ppm.[51] However,
124 even at this high concentration, the amount of deposit generated from 5 ml of surrogate fuel
125 is relatively low. Therefore, the fuel needed to be spiked with this level of deposit for the
126 study given the sensitivity of the deposit measurement equipment. Furthermore, the primary
127 focus of this study was to investigate the coupling between aromatics in the presence of
128 hydrogen abstraction and addition reactions, hence the requirement for a high concentration
129 of aromatic species to ensure dominant Ar-Ar reactions. Nevertheless, in a real fuel scenario,
130 fuel-aromatic reactions would likely be more prevalent. While homolytic aromatic
131 substitutions would still be relevant (including for fuel-Ar reactions), their impact on the
132 coupling reactions between different species would be more challenging to examine due to
133 the increased complexity of coupling pathways.[14]

134 Another aspect of the design of the surrogate fuels in this study which differ from real fuels
135 was the selection of unsubstituted aromatics. Real fuel aromatics have multiple alkyl-
136 substitutions round the ring aromatic ring. We chose to investigate unsubstituted compounds
137 as a 'base-case' for the coupling reactions here. This base-case was chosen here such that
138 gross differences in aromatic classes could be explored. Future studies adding substituted

139 groups would add another dimension to the work, where the effect of substitutions *within*
140 *and between* each compound class could be explored. Moving beyond the base-case towards
141 a more realistic fuel molecule, additional alkyl- substitutions would likely have two effects
142 based on EAS and HAS theory: 1) block reactive sites where alkyl- substitutions are present
143 and 2) act as weak directing groups.[11] This is also the possibility that alkyl-substitutions
144 would affect the solubility, which can be explored in future work via the methods detailed
145 in section 2.2.

146 2.2 Method of Thermal Stressing and Deposit Measurement

147 To produce the insoluble masses, 5 ml of fuel was added to a 50 ml borosilicate round bottom
148 pressurized flask. The flask was heated to 140°C for 24 h under 1 bar *constant oxygen supply*.
149 *The flask was sealed to all gases aside from the supplied oxygen*. After heating, the flask
150 was allowed to cool and insolubles were then filtered through a 0.1 µm glass fibre filter to
151 give the total weight of insolubles in the bulk. The flask was then washed with trisolvant and
152 then washed into a flask. The flask was then dried in a vacuum oven to remove any liquid
153 residue, weighed, and then compared with the weight of the clean flask- giving the total
154 weight of adherent insolubles left in the flask.[28] The sum of the insolubles weights on the
155 filter and in the flask gave a mass total insolubles per surrogate. The deposit experiments
156 were repeated at least 3 times for each surrogate to improve the accuracy of the total
157 insolubles measurement.

158 A petroOxy device was used to produce oxygen depletion curves for each surrogate fuel.
159 The petroOxy device is a sealed gold-lined chamber in which 5 ml of fuel is thermally

160 stressed at 140°C. The headspace above the heated fuel is depleted as the fuel is stressed,
161 giving a measure of the rate of oxygen consumption in the bulk fuel.

162 2.3 Hansen Solubility Parameters and Computational Details

163 All calculations were performed in Gaussian09 (E.01) using the B3LYP
164 functional.[29][30] Grimme's DFT-D3(BJ) dispersion correction was applied to all the
165 calculations to account for long-range effects.[31] A PCM solvation model, with n-
166 dodecane as the chosen solvent, was selected to replicate the hydrocarbon bulk.[32] The
167 basis set chosen was cc-pVTZ on an ultrafine grid. This basis set adds polarization
168 functions, allowing orbital hybridization to be taken into account.[33] Transition states
169 were optimized using the QST1/3 method depending on the reaction studied. All transitions
170 states were verified by the presence of one imaginary frequency corresponding to the
171 saddle point. Additionally, intrinsic reaction coordinate (IRC) calculations were performed
172 to verify the transition state corresponded to the expected reactants and products.
173 Unrestricted (broken symmetry) calculations were performed on open-shell systems, where
174 the HOMO and LUMO were mixed (guess=mix option). Entropy values were corrected
175 using the GoodVibes script, which employs a quasi-harmonic correction corrected at
176 298K.[34, 35, 36]

177 In Hansen solubility theory, three Hansen solubility parameters (HSPs) are assigned to
178 each molecule: D for dispersion, P for polarity, and H for hydrogen bonding. As a
179 consequence, each solvent exists in a 3-dimensional space of HSPs. The HSP distance
180 between two molecules in the 3d HSP space is given by:

181
$$Ra^2 = 4(D_1 - D_2)^2 + (P_1 - P_2)^2 + (H_1 - H_2)^2 \quad (1.1)$$

182 Where R_a is the Hansen distance.

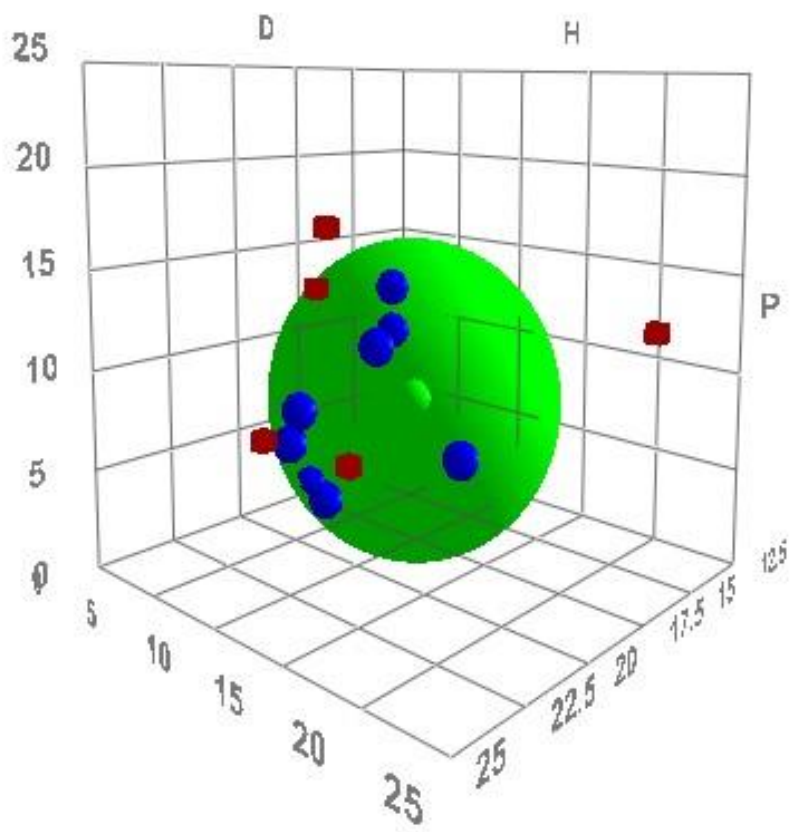
183 The HSP parameters for the test solvents were either obtained from the HSPIP dataset or
184 calculated using the software. The HSPIP software requires a series of test solvents/solutes,
185 tested for their solubility in the *n*-dodecane. A score 0 is assigned to insoluble solvents and
186 a score of 1 is assigned to soluble solvents.

187

188 In each case, 0.1 mol l⁻¹ of each test compound was added to 5ml of *n*-dodecane. Resulting
189 from the series of tests is a 'sphere' in 3d HSP space, whose dimensions are determined by
190 the solubility of the sphere (Figures 2.1 and 2.2). The radius of sphere R_0 is then used to
191 assess the solubility of a proposed solvent, where R_a of the test molecule is used in the
192 following equation:

193
$$RED = R_a/R_0. \quad (10.2)$$

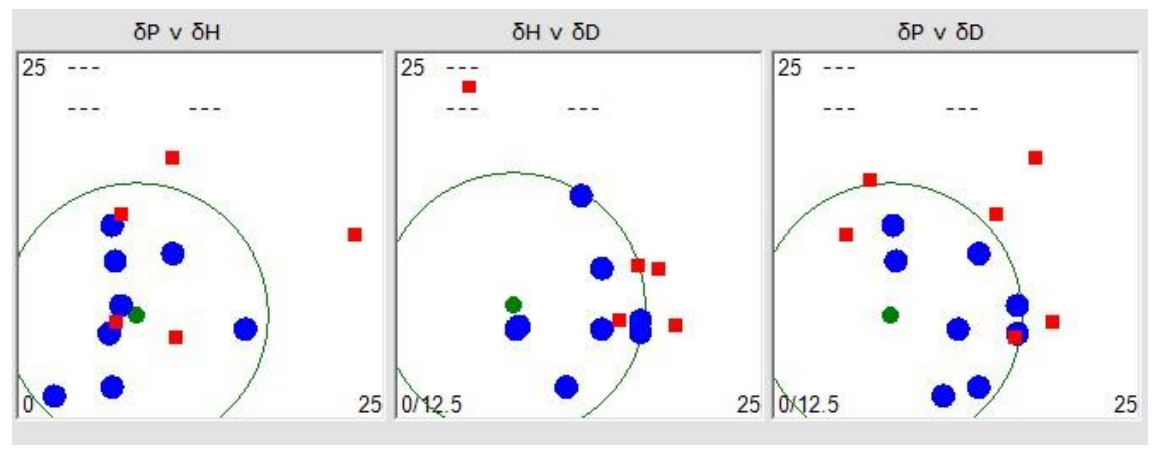
194 Where RED stands for Relative Energy Difference. A RED > 1 implies the molecule is
195 likely insoluble in your main solvent (*n*-dodecane in this case), whereas a RED < 1 implies
196 the molecule is soluble. Our calculated sphere was composed of 13 lab grade compounds
197 known for their presence in fuel and gave a fit of 1 according to HSPIP software. The
198 results for these tests are presented in Table 2.1 . Here it is important to acknowledge that
199 the solubility of the deposit precursors in pure *n*-dodecane this study will likely be different
200 to a conventional fuel due to the presence of aromatic compounds and minor components.
201 Nevertheless, these parameters are useful to understand insoluble formation our surrogate
202 fuel, and to improve the HSP method for future studies.



203

204

Figure 2.1: HSPIP Sphere



205

206

Figure 2.2: HSPIP Sphere parameter fits

207

208

209

210 Table 2.1: Hansen Solubility test solvents and their Associated HSPs. The sphere gave a fit
211 of 1.000

Solvent	Database/Calculated HSP	D	P	H	Score	RED
Indigo	Calculated	21.10	17.4	10.0	0	1.639
Carbazole	Database	21.7	6.4	6.2	0	1.243
p-Benzoquinone	Database	19.8	13.7	6.5	0	1.121
Water	Database	15.5	16.0	42.3	0	4.042
2-Naphthol	Database	20.4	5.4	10.2	0	1.000
Methanol	Database	14.7	12.3	22.3	0	1.800
Di- <i>n</i> -Butyl Sulfoxide	Database	16.4	10.5	6.1	1	0.443
Naphthalene	Database	19.2	2.0	5.9	1	0.884
Pyrrole	Database	19.2	11.0	10.0	1	0.863
Dipropyl Sulfone	Database	16.3	12.9	5.9	1	0.705
Toluene	Database	18.0	1.4	2.0	1	0.961
Indole	Database	20.5	7.5	6.5	1	0.973
Phenol	Database	18.5	5.9	14.9	1	0.979
Quinoline	Database	20.5	5.6	5.7	1	0.995

212

213

214 2.4 Pseudo-Detailed Mechanism in Fuels

215 In order to compare the total insolubles to the number of dimers predicted by DFT, several
216 new reaction steps were proposed which will be elucidated in the results and discussion. To

217 capture the autoxidation reactions in the bulk, the basic autoxidation scheme (BAS) was used
218 which gave good agreement with oxygen and hydroperoxide depletion with experiment. The
219 BAS scheme was optimized for a range of C10-C14 hydrocarbons, whereby the
220 thermochemical and kinetic parameters were obtained using *n*-dodecane as the model fuel.
221 Further details of the BAS scheme can be found in reference.[22] To construct the
222 mechanism, the Eyring equation was used, with A being formed from the **calculated** entropy
223 barrier and E_a formed from the **calculated** enthalpy barrier. All the forward and reverse
224 barriers were calculated from a stable pre-reaction and post-reaction complex.

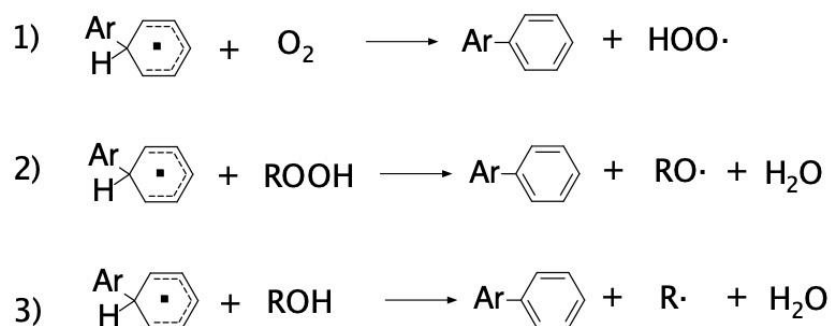
225 For each surrogate fuel, different mechanisms were constructed to study oxygen depletion
226 and deposit formation. For oxygen depletion, the level of oxygen was fixed at 1.8 mmol l⁻¹.
227 [37] For the deposition mechanism, oxygen was removed as a limiting reagent (kept
228 constant at 1.8 mmol l⁻¹) to reflect the continuous supply of oxygen in our deposit forming
229 rig. The mechanism was integrated in MATLAB using the **ode45** solver. The mechanism
230 gave a molar concentration of a dimer, which was then related to a mass via the molecular
231 weight of the proposed dimer.

232 3 Results and Discussion

233 3.1 Homolytic Aromatic Substitution Mechanism

234 The key bottleneck in any HAS reaction is the re-aromatization and liberation of hydrogen
235 from the σ -intermediate. The loss of H \cdot in this step is not well understood. Nevertheless, one
236 paper exploring HAS reactions between aryl iodides and arenes using oxygen as an oxidant,
237 proposed a re-aromatization step involving oxygen this is shown as reaction 1) in Figure 3.1
238 Because hydroperoxides (ROOH) and oxygenated species like alcohols (ROH) form under

239 oxidative conditions in fuels, these were also considered as possible reagents to remove
 240 hydrogen from the σ -intermediate. ROOH reacting with the σ -intermediate is proposed to
 241 form $\text{RO}\cdot$ and H_2O , is shown as reaction 2) in Figure 3.1. ROH reacting with the σ -
 242 intermediate is proposed to form $\text{R}\cdot$ and H_2O , is shown as reaction 3) in Figure 3.1.



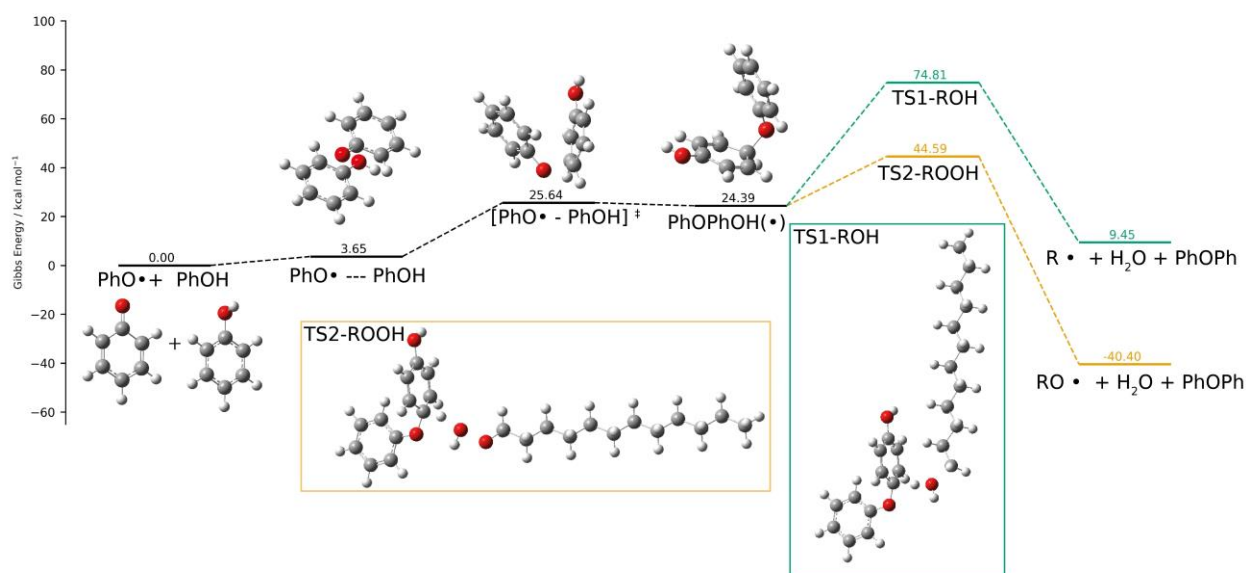
243

244 Figure 3.1: HAS reactions considered for fuel coupling reactions. Each step
 245 shows the σ -intermediate formed from an $\text{Ar}\cdot + \text{ArH}$ reaction, and the species
 246 chosen to re-aromatize the intermediate.

247 Considering the mechanisms presented in Figure 3.1, we explored the possibility of these
 248 reactions in phenolic coupling. Phenols have widely been recognized as being detrimental
 249 to fuel thermal stability.[8] HAS mechanisms have previously been considered as a possible
 250 pathway the oxidative coupling of phenols.[14] *Nevertheless, it should be noted that in a real
 251 fuel, direct phenol-phenol coupling is not likely due to the concentration of phenolic
 252 compounds. However, the main of this section is to understand the possible re-aromatization
 253 step available to fuel species. The findings here will be used as a template for other fuel HAS
 254 reactions.*

255 The calculated HAS pathways for phenol are presented in Figure 3.2. First, the formation of
 256 the σ -intermediate is endergonic and has a free-energy barrier of $\ddagger G = +25.64 \text{ kcal mol}^{-1}$
 257 leading to an intermediate $\text{PhOPhO}\cdot$. The para- position of the phenol was chosen as the site

258 of oxidative coupling of another phenoxy radical given that this is the generally the more
 259 favorable site.[38] The first mechanism in Figure 3.1, involving the re-aromatization with
 260 oxygen, could not be identified for phenol. A key challenge with the oxygen transition state
 261 is the choice of spin multiplicity. Given that oxygen is in the triplet state, and the system σ -
 262 intermediate is in the doublet state, an open-shell doublet or a quartet surface can be chosen.
 263 The other two mechanisms presented in Figure 3.1 involve ROH and ROOH. The ROOH
 264 pathway in Figure 3.2 shows a lower barrier to re-aromatization of the intermediate
 265 compared to the ROH by 30.22 kcal mol⁻¹. Additionally, the ROOH is thermodynamically
 266 favored, namely due to the enhanced stability of the RO \cdot radical compared to R \cdot . The IRCs
 267 for both these pathways are presented in Figures S.1 and S.2 in the SI. The ROOH and ROH
 268 re-aromatization transition states are characterized by a rotation of the terminal OH moiety
 269 towards an available hydrogen at the para-coupling site.



270

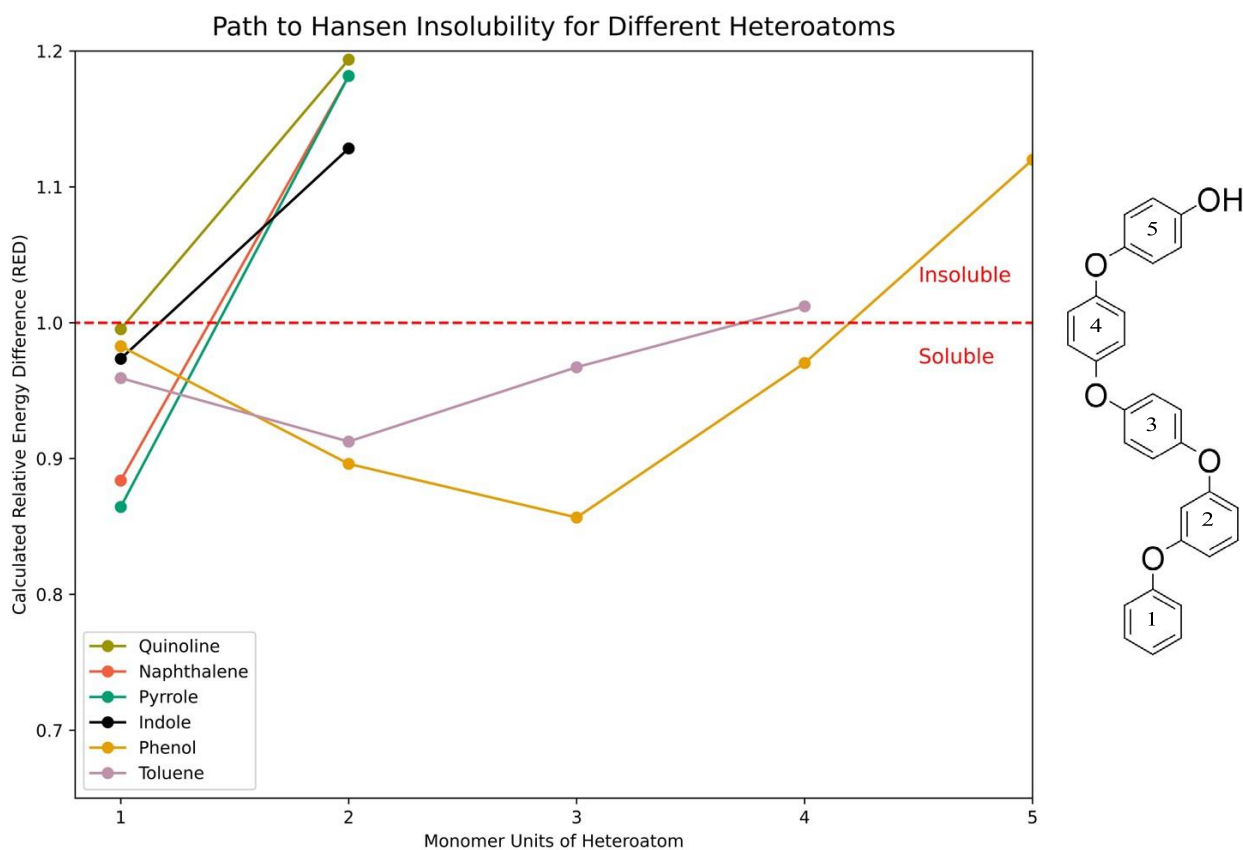
271 Figure 3.2: Comparison of different HAS pathways at the B3LYP-D3//cc-pVTZ level of
 272 theory using *n*-dodecane (PCM) as a solvent. The first step of the process in black shows
 273 the $\text{Ar}\cdot + \text{ArH} \rightarrow \text{ArHAr}\cdot$ reaction of a phenol and a phenoxy radical, leading to the σ -

274 intermediate. The subsequent levels in green shows the re-aromatization step with ROH
275 and the level in orange shows the re-aromatization step with an ROOH species.

276 3.2 Comparison of Antioxidant Oligomer Solubility and Pathway to 277 Deposit

278 To justify the assumption that the formation of insolubles results from the coupling of
279 ArH species, we calculated Hansen solubility parameters for oligomers for our chosen
280 heterotoms of increasing size. Previous research has hypothesized that aromatic
281 compounds in fuel rapidly become insoluble as they grow in size.[43] Figure 3.3 shows
282 the change in RED score as the oligomer chain grows, where relative energy difference
283 (RED) > 1 indicates an oligomer that has become insoluble in *n*-dodecane. For real fuels,
284 these results will vary, particularly as the aromatic content will increase the 'likeness' of
285 the solvent to other extended aromatic structures.[39] Nevertheless, because our model
286 fuels in this study contain *n*-dodecane as the base solvent, the Hansen plots here are a
287 useful tool to explore deposition tendency in our model fuels. Oligomer structures were
288 chosen based on the favored coupling site for each heteratom based on literature data and
289 our calculations.[38, 40, 41, 42] The phenol chain growth is shown as an example. What
290 is clear is that in general as the oligomer grows, the solubility in *n*-dodecane decreases.
291 However, different oligomers reach the insolubility threshold in fewer units, where a
292 single unit is the monomer, 2 units is a dimer and so on. For example, comparing toluene
293 and naphthalene, naphthalene reaches the insolubility threshold after 2 units have coupled.
294 This is consistent with previous observations that di-aromatics form deposit more rapidly
295 because they 'require fewer consecutive reaction steps to produce high-molecular-
296 weight'.[43]

297 Interestingly, heteroatom size does not influence the solubility of the resultant oligomers.
 298 Instead, the lower solubility is related to the dD parameter in the HAS framework,
 299 representing Van Der Waals forces between the solvent and heteroatom. As the oligomers
 300 grow, the difference in polarity and hydrogen bonding begins to decrease (indicated by the
 301 decreasing dP and dH parameters), but the difference in dispersion forces dD increases.



302

303 Figure 3.3: Effect of oligomer unit size on solubility calculated using the HSPiP software. It
 304 is clear some heteroatoms reach insoluble threshold in fewer units than others. Phenol and
 305 toluene is particularly interesting, becoming initially more soluble in *n*-dodecane before
 306 reaching the threshold. For phenol this is due to the growth of oligomer leading to a lower
 307 proportion of the molecule containing the *H*-bonding –OH group, but as the molecule grows
 308 the Van Der Waals dD difference grows eventually leading to an insoluble.

309 3.3 Predicting Deposition formation using DFT

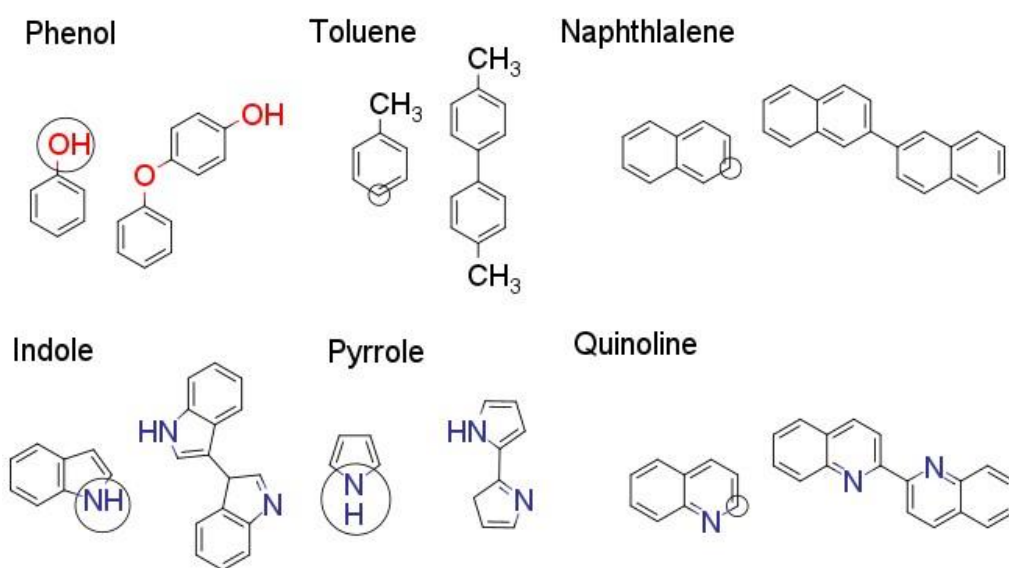
310 3.3.1 H-abstraction and Coupling Mechanisms for Each Heteratom

311 Based on the solubility modelling presented in Figure 3.3, it was clear that the coupling of
312 fuel heteratoms would lead to insoluble formation in our *n*-dodecane surrogate. Following
313 the proposed HAS pathway, we calculated the H-abstraction and subsequent barriers to form
314 dimers via the HAS pathway. The barriers for these reactions are presented in detail in Table
315 S.1 of the appendix. The termination reaction was barrierless for all the species, and the pre-
316 exponential factor was kept constant for each of the species at 3×10^9 . [5]

317 The H-abstraction site and the coupling site for each species was selected based on literature
318 and our own testing, and is summarized in Figure 3.4. For phenol, H-abstraction occurs at
319 the O-site, with coupling between the subsequent phenoxy radical and the para-carbon site
320 of a phenol. [38] For naphthalene, the C3 site was favored over the C2 position in terms of
321 both abstraction and coupling barrier heights. For quinoline, the C2 site is the most favored
322 site for coupling and H-abstraction, and the barriers for abstraction were lower at the C2 site
323 compared to the C3 site. [44] For toluene, the para position was selected for coupling and H-
324 abstraction based on our own testing and literature data. [45]

325 For indole and pyrrole, the favored coupling and H-abstraction site [were found to be](#)
326 [different](#). For indole, the N1 site was found to be the most favorable site for H-abstraction,
327 but the C3 site is the most favored for coupling. Nevertheless, C–N linkages are detected
328 very rarely and are found to be thermodynamically prohibited for indole oligomers. [46, 47]
329 As a consequence, we compared the overall pathway to dimers at the C3 position via H-
330 abstraction at the N1 and C3 positions. The results for the indole dimer formation
331 calculations are found in Figure S.4 of the SI. Overall, the C3 H-abstraction pathway shows

332 the highest barriers. Therefore, the N1 H-abstraction pathway for indole was chosen.
 333 Similarly, for pyrrole, H-abstraction at the N1 position is favored, yet polypyrrole is formed
 334 of C2-C2 linkages.[40] Comparing both pyrrole coupling C2 coupling pathways with H-
 335 abstraction at the N1 or C2 position, presented in Figure S.3, both pathways have similar
 336 barrier heights. Nevertheless, the initial H-abstraction reaction at the N1 position is more
 337 favorable and leads to an intermediate I1b G 24.49 kcal mol⁻¹ lower in energy than the C2
 338 pathway. As a consequence, following the N1 pathway, pyrrole would have antiox-



339

340 Figure 3.4: H-abstraction Sites and Dimers Selected for the Pseudo-Detailed Mechanisms.
 341 The selected H-abstraction site is circled, and resultant dimer is shown for each species.

342 idant properties, which is reflected in the petroOxy measurements (Figure 3.6b). Therefore
 343 the N1 abstraction pathway for pyrrole was chosen.

344 Regarding the different coupling and H-abstraction sites for indoles and pyrroles, it should
 345 be underlined that this difference may only be relevant to self-reactions. Indeed, for indole

346 and pyrrole functionalization reactions under oxidative conditions, the N- group is pre-
347 protected prior to arylation and alkylation reactions. [52,40]

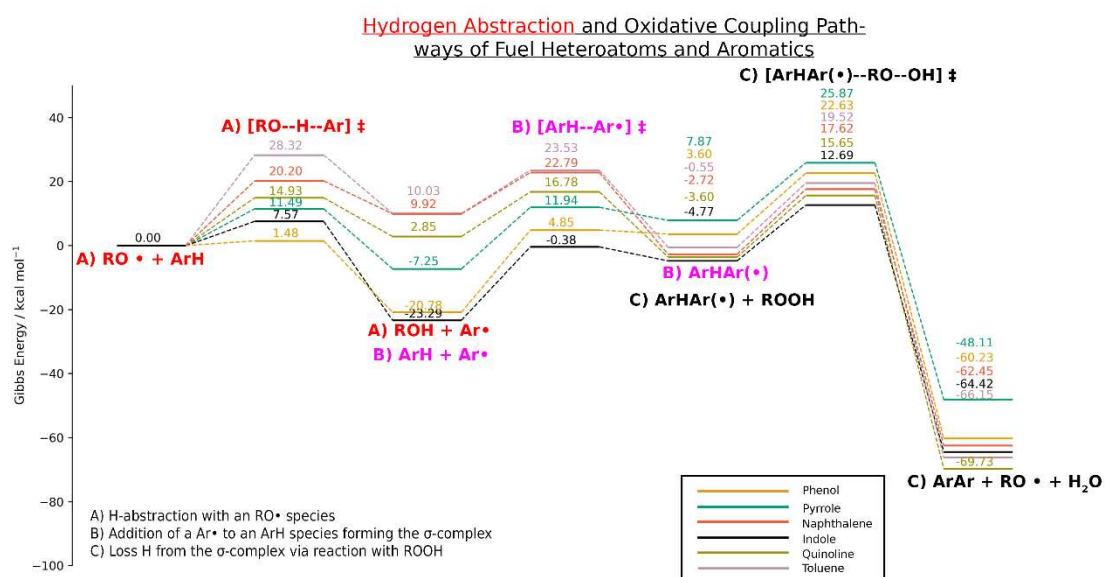
348 Based on the above proposed coupling and H-abstraction sites, we computed the barriers for
349 ArH species reacting with *n*-dodecane R·, RO·, and ROO· radicals and subsequently forming
350 dimers via a HAS process. The Gibbs potential energy surfaces for our chosen heteroatoms
351 undergoing H-abstraction to the formation of dimers are presented in Figure 3.3 for RO·.
352 The values for the reactions with the other radicals are presented in Table S.1 of the SI.

353 The first section (reaction A) of Figure 3.5, showing the abstraction of hydrogen from our
354 selected ArH species. Here, we can see there is a clear difference in the reactivity and
355 thermochemistry. To begin with, phenol shows the lowest barriers for hydrogen abstraction
356 out of all the species tested. Phenol has long been known as a powerful antioxidant in
357 fuels.[5] By contrast, toluene exhibits the highest barrier and the overall Gibbs energy
358 abstraction reaction is endergonic at +28.32kcalmol⁻¹. The overall order of the Gibbs energy
359 barrier to hydrogen abstraction (section A) is, in descending order: toluene > naphthalene >
360 quinoline > pyrrole > indole > phenol.

361 The resultant radicals formed indicate that phenol, pyrrole, and indole all exhibit
362 antioxidant properties, by undergoing an exergonic H-abstraction reactions. By contrast,
363 naphthalene, toluene, and quinoline undergo endergonic H-abstraction reactions showing
364 no antioxidant qualities. At this point in the reaction process, two Ar· radicals can terminate
365 to form a dimer. Nevertheless, this termination process is a rare occurrence due to the low-
366 concentration of Ar· species in fuel (for example, for pyrrole the peak concentration in our
367 mechanism was 5.17E-13 mol l⁻¹).

368 The HAS reaction between an $\text{Ar}\cdot$ and ArH first proceeds with an attack of the radical. The
369 radical attack is shown as pathway B) in Figure 3.5. For this step, the antioxidant species
370 formation is endergonic and proceeds with high Gibbs energy barriers for phenol and
371 indole of $\ddagger G = 25.63 \text{ kcal mol}^{-1}$ and $\ddagger G = 24.36 \text{ kcal mol}^{-1}$ respectively. By contrast, pyrrole
372 proceeds with a lower barrier of $\ddagger G = 19.20 \text{ kcal mol}^{-1}$. On the other hand, the non-
373 antioxidant species show lower barriers for pathway B). In fact, naphthalene and toluene
374 show the highest barriers for the H-abstraction step, but lowest barriers out of all the species
375 for step B) at $\ddagger G = 12.87 \text{ kcal mol}^{-1}$ and $\ddagger G = 13.50 \text{ kcal mol}^{-1}$ respectively. Additionally, the
376 formation of the intermediate is the most exergonic for naphthalene and toluene. The
377 relationship between the antioxidant tendency and the ease of coupling is likely related to
378 the aromatic structure. Species with more antioxidant qualities will also have higher levels
379 of aromaticity to stabilize radicals, but also will have higher barriers to aromaticity-
380 breaking radical attack.

381 The final step in the dimer forming process is the re-aromatization step *via* loss of hydrogen
382 from the intermediate. Interestingly, the barriers for this step are similar for our aromatics
383 tested, in the range of 23.87-17.47 kcal mol^{-1} . This step is clearly less related to the
384 structure of the ArH compound. Nevertheless, the concentration of ROOH available to
385 complete this step, is related to the antioxidant qualities of the ArH species in fuels. For
386 example, for phenols, due to their antioxidant properties, the concentration of ROOH is
387 expected to be low.[24] As a consequence, termination reactions likely provide a higher
388 source of C–C/C–O coupling. To explore how these interrelated pathways yield deposits
389 for different fuel components, we created different pseudo-detailed mechanisms to
390 compare each fuel.



391

392 Figure 3.5: Growth to a deposit dimer for our chosen heteroatoms, calculated at the B3LYP-
 393 D3/cc-pVTZ *n*-dodecane PCM level of theory. The barriers were calculated from stable pre-
 394 reaction complexes. The R species was *n*-dodecane. The antioxidant species (phenol, indole
 395 and pyrrole) show exergonic H-abstraction in step Ar.

396

397

398

399 3.3.2 Comparison of Experimental Results and Pseudo-Detailed Models

400 Antioxidant Behavior

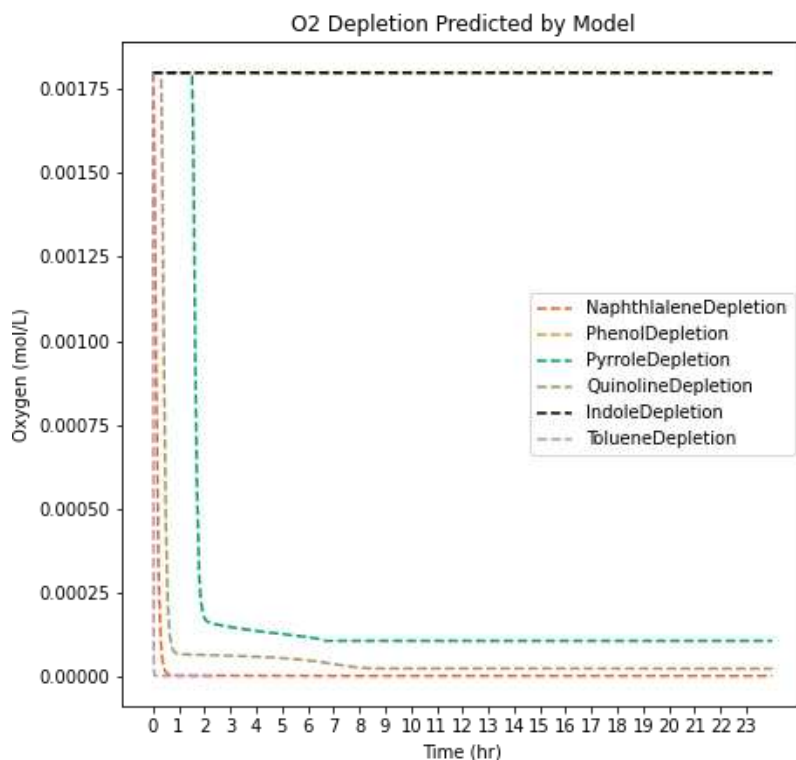
401 First, the antioxidant behavior of our surrogate fuels was explored in relation to our models.
 402 The O₂ depletion predicted by our model alongside the petroOxy depletion curves are
 403 presented in Figure 3.6. Although the petroOxy device cannot measure the O₂ depletion in
 404 the bulk, the device can be used to assess the antioxidant behavior of different fuels.[76] Our

405 model successfully predicts that pyrrole, indole, and phenol are all antioxidant species, as
406 shown by the increased induction period in the petroOxy curves. In addition, the petroOxy
407 device indicates that indole and phenols are stronger antioxidants than pyrrole, which is also
408 reflected in the O₂ depletion curves in our mechanism. However, the difference between
409 indole and phenol in the petroOxy curves is not reflected in the mechanism. ~~Nevertheless,~~
410 ~~this difference between the surrogates is better reflected in the ArH + RO abstraction barrier~~
411 ~~in Figure 3.5. Exploring the GCMS results for indole in our previous study, in Figure 10.22,~~
412 ~~no n-dodecane autoxidation products are observed after 8h. By contrast, pyrrole and~~
413 ~~quinoline both show lesser antioxidant qualities and lead to n-dodecane autoxidation~~
414 ~~products in Figure 5.7. Similarly, for our model, no oxygen is consumed leading to no~~
415 ~~autoxidation products.~~

416 Deposition Behavior

417 The amount of insoluble dimers predicted by our model compared with the total insolubles
418 measured is presented in Figure 3.7. It should be noted that the comparison here is focused
419 on the *correlation* between amount of dimers predicted and total deposit produced by
420 experiment. As a consequence, the correlation produced will reflect how well the model
421 predicts deposition behavior. ~~Indeed, the difference between correlated and measured~~
422 ~~deposits by a factor of ~300. This is due to the fact our mechanism only focuses on the~~
423 ~~formation of dimers. Dimers are likely only to form a small proportion of the total deposit~~
424 ~~structure, hence the large different in mass. Instead, the results here intend to explore how~~
425 ~~well the model predicts couple propensity between different species which we hypothesize~~
426 ~~is related to the ease of forming dimers.~~ The model predicts the insoluble formation behavior
427 between our different surrogates well, with pyrrole producing the largest amounts of
428 insolubles. Interestingly, phenol and indole are shown to produce the lowest amount of

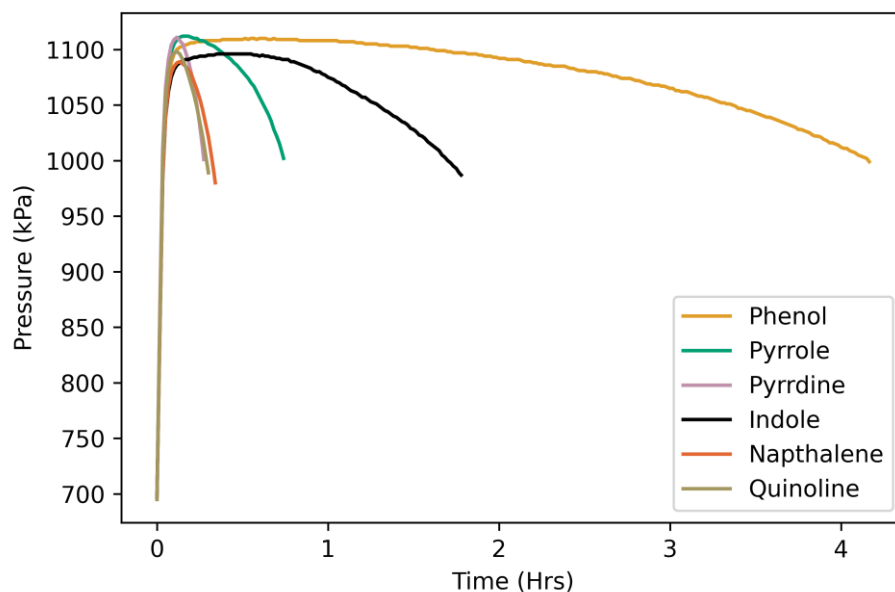
429 deposit in both our experiments and model. By contrast, in real fuels, indoles, and
430 particularly phenol concentration are shown to correlate well with final insoluble mass.[8]
431 A key difference between our simplified surrogates and real fuels are the synergistic effects
432 between fuel classes, which are not captured in our two-component surrogates. In particular,
433 sulfur is shown to interact strongly with 5-membered nitrogen heterocycles, and phenols
434 with other nitrogen compounds.[7, 48] For example, in a simplified surrogate, previous work
435 has shown trends between deposition propensity of 5- and 6-membered heterocycles break
436 down, where quinoline-like compounds have shown to produce more deposit than indole
437 compounds.[7] Nevertheless, the use of surrogates is still important to understand the
438 chemical interactions within species classes.



439

440

(a) O₂ Depletion Predicted by our model



441

442

(b) Petroxy depletion behavior

443 Figure 3.6: O₂ depletion behavior of our surrogate- comparison between model and
 444 experiment. The model shows the change in O₂ concentration over time. The petroOxy
 445 depletion curves show the change in headspace pressure, and although they are not a direct
 446 measure of O₂ depletion, they can differentiate between antioxidant qualities of different
 447 species.

448 Interestingly, in our experiment and models, toluene and naphthalene produced more
 449 insolubles than phenol and indole. This is interesting as fuel thermal degradation is often
 450 viewed as solely driven by heteroatoms.[25] Exploring the barriers for toluene and
 451 naphthalene in detail in Table S.1, we see that lower barriers to the $ArH + Ar \cdot \rightarrow ArHAr \cdot$
 452 reaction are found with the aromatic species. Sensitivity analysis (Figure 3.9) of our models
 453 suggests this coupling step is strongly related to the final insoluble mass. However, in a 2-
 454 component fuel, combining an antioxidant heteroatom and aromatic, the formation of
 455 aromatic insolubles will be significantly reduced due to the size of the H-abstraction barrier
 456 in comparison to the other heteroatoms used in this study (Figure 3.5). Instead, the

457 heteroatom antioxidant class will form the majority of the $\text{Ar}\cdot$ radicals going on to form
458 deposit. To strengthen this hypothesis, using our calculated values, a fuel model was built
459 containing both phenol and toluene.

460 The effect of heteroatoms suppressing deposition from non-antioxidant species is
461 demonstrated in Figure 3.8, where insolubles are generated from pseudo-detail model fuels
462 containing different ratios of toluene and phenol is tested. The model was built using the
463 same BAS scheme base described in the section 2.4, with the addition of both toluene and
464 phenol pathways. In this simplified model, toluene-derived insolubles are suppressed upon
465 introduction of phenol. This effect can help explain why fuel deposits/insolubles often have
466 an elemental composition of heteroatoms higher than conventional fuels also containing
467 aromatic hydrocarbons.[49] Another interesting effect of blending is the peak in phenol
468 insolubles at 25:75 phenol:toluene ratios above a 100% phenol mix, which implies that above
469 a certain concentration, phenols will prevent the formation of insolubles. The peak
470 concentration of hydroperoxide steadily drops at different % phenol concentrations, which
471 is related to the extent the autoxidation chain is suppressed. The peak of phenol deposition
472 could be related to the ROOH concentration, allowing more σ -intermediates to be re-
473 aromatized. This shows our model can replicate the effect of changing concentrations of
474 antioxidant on total insolubles.

475 For some of the fuels the pseudo-detailed mechanisms reflect the behavior of 'peak'
476 deposition temperature. The effect of temperature on the concentration of deposits for each
477 mechanism is shown in Figures S.6-10 of the SI. For quinoline, a peak deposition level is
478 reached at 460K. Whereas for toluene, as the temperature increases the level of deposit
479 decreases. All the other fuel models show an increase in concentration of deposit as the
480 temperature rises. This demonstrates these deposit mechanisms can reflect the complex

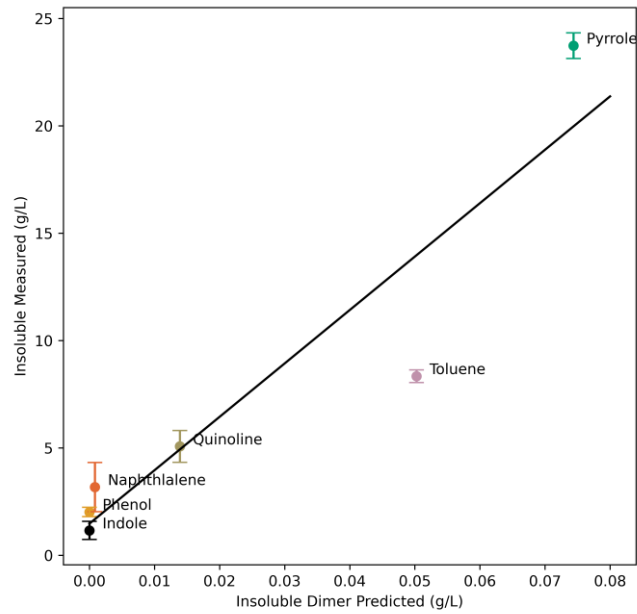
481 behavior of observed in real fuels of increasing and decreasing levels of deposit depending
482 on fuel temperature.[50]

483 Finally, our results here lend credence to a HAS pathway leading to deposit. When the HAS
484 pathway is removed from the mechanism in Figure 3.7b, no discernable trend is found
485 between the formation of dimers and insolubles measured. In fact, the HAS pathway appears
486 particularly important for species with low/no antioxidant tendency, but with a tendency to
487 still form insolubles.

488 Sensitivity analysis of our bespoke mechanisms is presented in Figure 3.9. The reaction
489 numbers cited here correspond to those given in Table S.1. For our mechanisms, the reaction
490 29, $\text{Ar}\cdot + \text{ArH} \rightarrow \text{ArHAr}\cdot$, has the largest influence on the level of deposit with the exception
491 of phenol. Increasing the rate of reaction 29 leads to more $\text{ArHAr}\cdot$ species which can readily
492 form deposit. Reaction 32, $\text{Ar}\cdot + \text{ROOH} \rightarrow \text{ArH} + \text{ROO}\cdot$, removing hydroperoxides from
493 the system also has an influence on the level of deposit. As the rate of reaction 32 increases,
494 hydroperoxides are removed from the system leading to fewer $\text{ArHAr}\cdot + \text{ROOH}$ re-
495 aromatization reactions leading to deposit dimers. The change of ROOH and insoluble
496 concentration presented in Figure 3.10 demonstrates that as insolubles are produced ROOH
497 is depleted. For all the species tested, the $\text{RO}\cdot$ (reaction 26) and $\text{R}\cdot$ (reaction 27) hydrogen
498 abstraction steps have a large influence on the level of deposit, with faster rates leading to
499 more $\text{Ar}\cdot$ species able to undergo coupling reactions. By contrast, the rate of the $\text{ROO}\cdot$
500 abstraction barrier (reaction 16) has a negligible influence on deposition for most species
501 because this reaction in general has high barriers already. Finally, for phenol, reaction 26,
502 $\text{ArH} + \text{R} \rightarrow \text{Ar}\cdot + \text{RH}$ also influences the formation of deposit more than the other species,
503 and is more important than the coupling step (reaction 29). This is likely because the

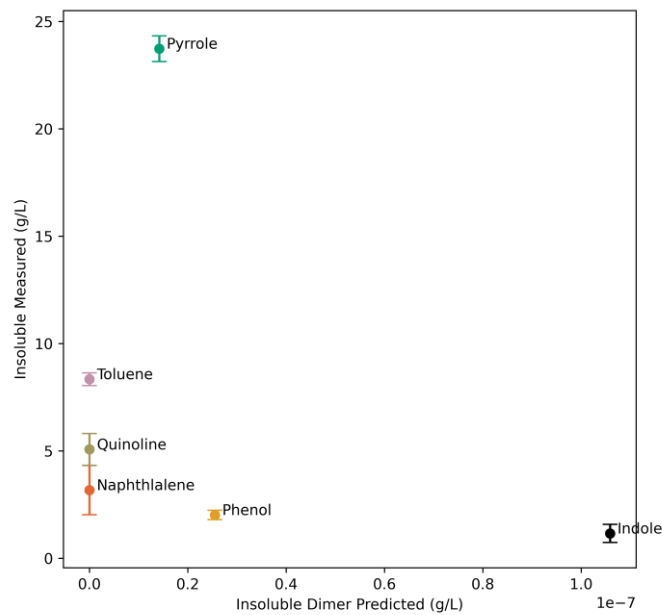
504 termination pathway dominates the formation of deposits here, thus leading to a direct

505 correlation between the concentration of $\text{Ar}\cdot$ and the amount of deposit dimer.



506

507 (a) Correlation between mass of dimer predicted by our model and insolubles measured.

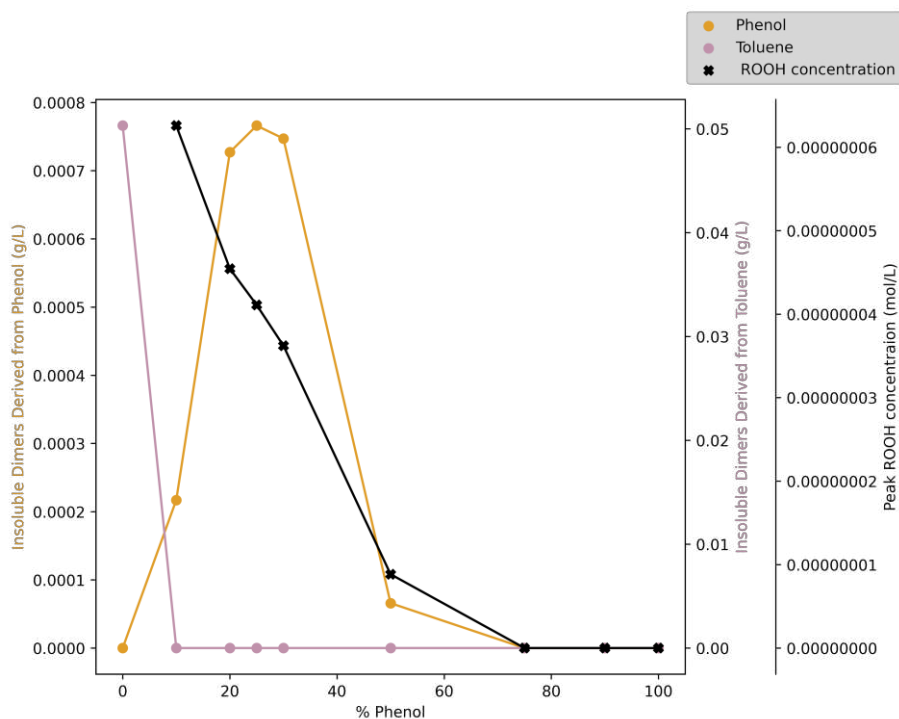


508

509 (b) Correlation between mass of dimer predicted by our model and insolubles measured when the

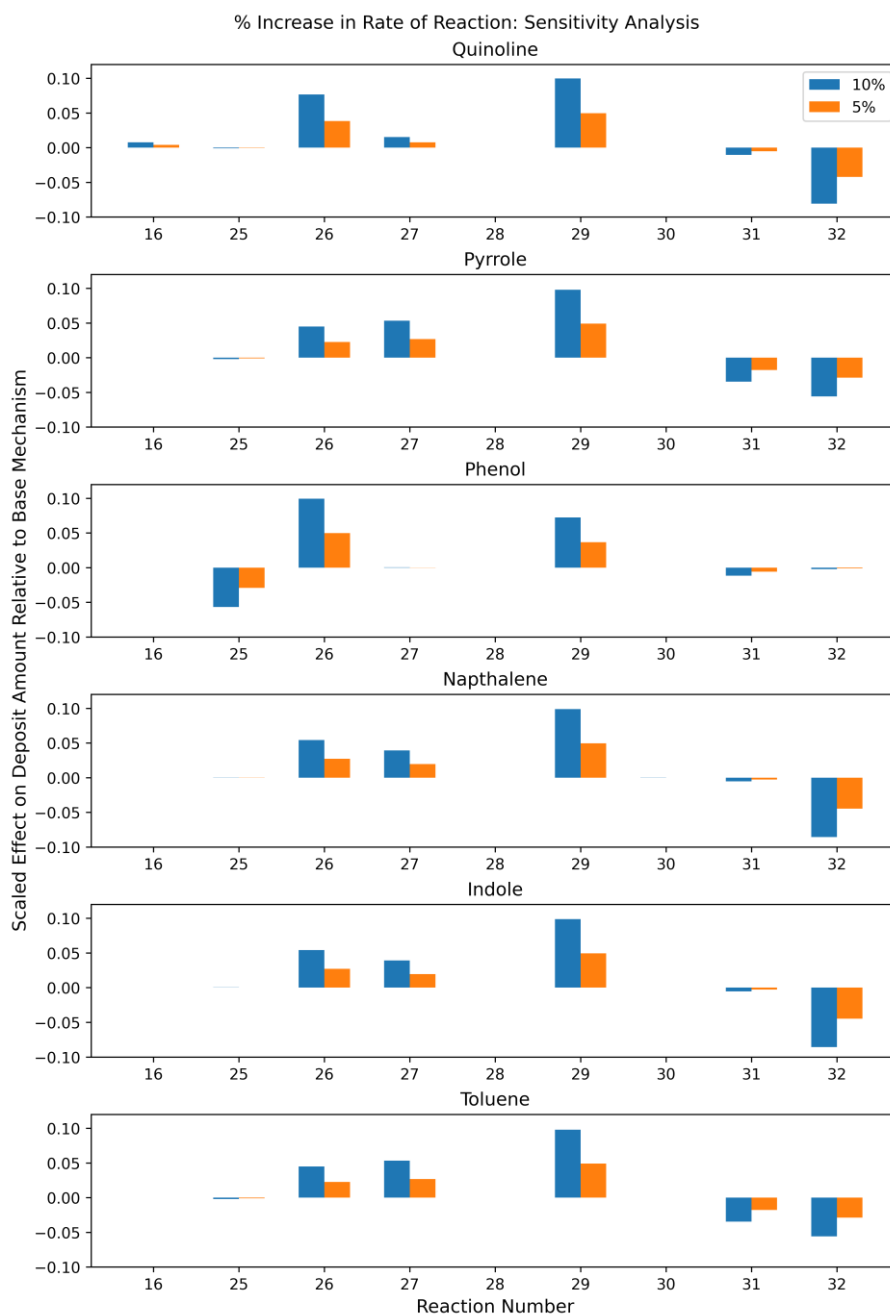
510 HAS pathway is excluded.

511 Figure 3.7: Insoluble formation behavior- comparisons between model and experiment.
512 Temperature of the experiment and psuedo-detailed *n*-dodecane chemical mechanism
513 containing the A and E_a values shown in Table S.1. The temperature was set at 431 K both
514 the model and the experiment.



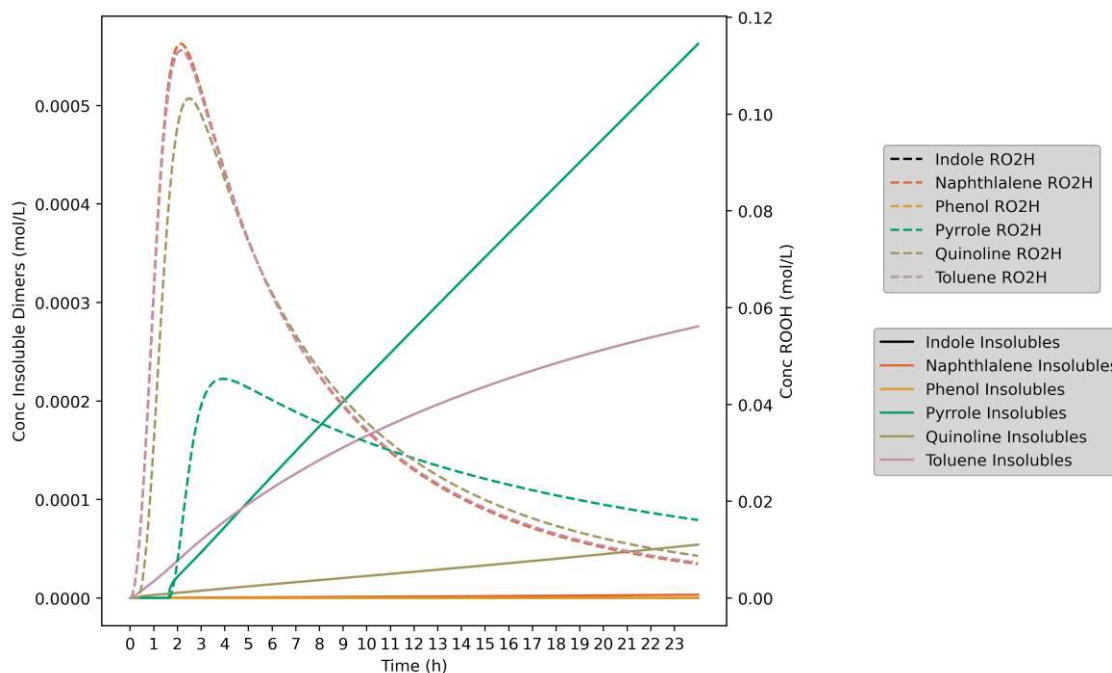
515

516 Figure 3.8: Effect of phenol % in a phenol toluene aromatic total of 0.1 mol L⁻¹ on the
517 insolubles derived from phenol and toluene.



518

519 Figure 3.9: Sensitivity analysis of the bespoke insoluble pseudo-detailed mechanisms. For
 520 the sensitivity analysis, the rate of reaction is increased by a factor of 10% (blue) and 5%
 521 (orange) and the resultant increase in insolubles is shown relative to the base pseudo-
 522 detailed mechanism. The reaction number corresponds to Table S.1 in the SI



523

524 Figure 3.10: Change in the concentration of insolubles and ROOH over the course of the
 525 24h pseudo-detailed models. The thick lines show the change in insoluble dimer
 526 concentration, whereas the dotted lines show the change in ROOH concentration. The
 527 results clearly show that for each species, as ROOH is depleted, the level insolubles begin
 528 to increase.

529 3.4 Implication for Fuels

530 A key novel finding of this study is the role that HAS reactions can play in deposit
 531 formation. Additionally, the work here represents the first study to apply DFT
 532 calculations to deposition reactions to attempt to predict deposition tendency from first
 533 principles.

534 One weakness of this study is that it looked solely into aromatic self-reactions via the
 535 HAS process, whereas side reactions between ArH and RH species will be dominant in a

536 real fuel scenario due to the low concentration of ArH in real-fuels. To briefly explore
537 side reactions, we calculated the initial step of a HAS pathway between propanal, and
538 various nitrogen compounds which is presented in Figure S.5 of the SI. In this pathway,
539 propanal readily forms a σ -intermediate with the nitrogen heteroatoms. Future studies
540 should explore the HAS pathway for fuel-aromatic side reactions, particularly as no
541 mechanism is currently proposed in the fuel literature which does not rely on a
542 termination step to form the C-C bond or without unrealistic EAS steps forming charged
543 intermediates.[52]

544

545 The formation of fuel insolubles is influenced by both the H-abstraction and coupling
546 propensity of the heteroatoms/aromatics present in fuel. By simplifying the insoluble
547 formation process into the formation of dimers, we were able to show clear differences
548 between the insoluble formation and antioxidant tendency between surrogate fuels.
549 Nevertheless, the formation of dimers represents a small subsection of the
550 insoluble/deposit structure. To expand the mechanism to reach an insolubles formation
551 model which can provide a quantitatively accurate description, additional pathways need
552 to be considered. This is a challenge, particularly as there are likely thousands of possible
553 side reactions between and within species classes.[2] Even in our surrogate fuels the
554 oxidation of *n*-dodecane is not significantly repressed.

555 To address the challenge of building a **branching deposition mechanism with thousands**
556 **of reactions**, several approaches using techniques benchmarked in this study can be used.
557 The first approach involves scaling the deposit forming dimer steps to experimental
558 deposit measurements. This would lead to a semi-empirical mechanism, which moves

559 away from the first-principles approach using DFT. Nevertheless, the DFT
560 thermochemical and kinetic parameters will allow the gross differences between species
561 class and structure to be explored. This approach relies on the assumption that the
562 formation of deposit dimers relates to a general property of 'coupling propensity'. Some
563 preliminary calculations imply this assumption is generally correct, where a propanal
564 doublet attacking various nitrogen compounds give barrier sizes (presented in Figure S.5
565 in the SI) in the same order of magnitude as the dimerization barriers for step B) in Figure
566 3.5.

567 A second, more computationally intensive approach, would be a set of high throughput
568 calculations on additional deposit forming pathways. This approach would use HAS and
569 termination reactions to calculate the pathways to various oligomers. [These reactions](#)
570 [could be constructed following chemical graph theory, as employed in recent work with](#)
571 [phenols.\[53\]](#) Hansen solubility parameters will guide a 'cut-off' point for energetic
572 pathways to oligomers to form insolubles. Nevertheless, insoluble species are still likely
573 to react to form larger molecular weight species, which adds an additional challenge to
574 this approach.

575 Declaration of Interest

576 This research was partly funded by the University of Sheffield Department of Mechanical
577 Engineering, PhD Scholarship Scheme, and the Powerplant Integration of Novel Engine
578 Systems (PINES) grant number 113263.

579 4.5 Conclusions

580 The formation of insolubles in fuel is driven by coupling reactions between aromatics. In
581 this work we have shown the importance of HAS in explaining the formation of these
582 insolubles. DFT calculations revealed that the hydroperoxides play a key role in
583 facilitating the HAS pathway. As a result of these findings, we showed that kinetic values
584 calculated for a simplified two-component (dodecane and aromatic) surrogate can reveal
585 differences in antioxidant and deposition tendency of different aromatics compared to the
586 experiment. In addition, when the HAS pathway is excluded, the predicted deposition
587 trends break down. Exploring the behavior of the mechanism further, we show that the
588 addition of antioxidant to an antioxidant+aromatic model leads the suppression of
589 insolubles composed of the aromatic. Instead, the antioxidant+aromatic model leads to
590 insolubles only composed of the antioxidant. Finally, sensitivity analysis reveals that the
591 formation of hydroperoxides ($\text{ArH} + \text{ROO} \rightarrow \text{Ar}\cdot + \text{ROOH}$) and the homolytic coupling
592 ($\text{ArH} + \text{Ar}\cdot \rightarrow \text{ArHAr}\cdot$) have a strong influence on the final deposit mass.

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