

1 The use of anthracene as a model compound in a
2 comparative study of hydrous pyrolysis methods for
3 industrial waste remediation

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26

27 **Abstract**

28 Polycyclic aromatic hydrocarbons are very stable compounds and tend to bioaccumulate in the
29 environment due to their high degree of conjugation and aromaticity. Hydrous pyrolysis is explored as a
30 technique for the treatment of industrial water containing PAH, using anthracene as a model compound.
31 The reactivity of anthracene under a range of temperatures and durations are studied in this paper.
32 Aliquots of 1.0 - 10.0 mg of anthracene in a range of 1.0 - 5.0 ml of H₂O are subjected to hydrous
33 pyrolysis under varied conditions of temperature, reagents and duration. The conditions include
34 oxidising systems comprising distilled water, hydrogen peroxide and Nafion-SiO₂ solid catalyst in
35 water; and reducing systems of formic acid and formic acid / Nafion-SiO₂ / Pd-C catalysts to assess a
36 range of redox reaction conditions. Oxygen in air played a role in some of the reaction conditions.
37 Pyrolysed products were identified and quantified by the use of Gas Chromatography-Mass
38 Spectrometry (GC-MS). The major products were anthrone, anthraquinone, xanthone from oxidation;
39 and multiple hydro-anthracene derivatives from reductive hydrogenation. The nature of reaction
40 conditions influenced the extent of anthracene degradation. The products formed are more reactive (less
41 stable) as compared to anthracene the starting material and will therefore be less persistent in the
42 environment.

43 **Keywords:** Anthracene, pyrolysis, degradation, oxidation, reduction, GC-MS

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49 **1. Introduction**

50 Anthracene (C₁₄H₁₀) belongs to a class of organic compounds termed polycyclic aromatic hydrocarbons
51 (PAHs). Anthracene can vary in appearance from a colourless to pale yellow crystal-like solid. Like
52 other PAHs, though anthracene can be naturally occurring, it is also formed when products like coal, oil,
53 gas, and garbage undergo incomplete combustion (ATSDR, 2010). In the aluminium industry, PAHs
54 including anthracene are generated at the anode in the Soderberg electrolytic furnace (AFFG, 2005).
55 Anthracene like all PAHs, is stable and persistent in the environment due to its slow response to
56 biodegradation (Cheung et al., 2008). Anthracene tends to bioaccumulate in aquatic life, and is highly
57 toxic to wildlife. In water, anthracene tends to bind fairly strongly to sediments and any other solid
58 matter, but a small proportion can leach to groundwaters (SEPA, 2010) and is thus a potential
59 environmental problem.

60 Several studies have been carried out on the reactivity of anthracene. Anthracene has been reported to
61 undergo selective oxidation at the 9, 10 positions in the presence of V₂O₅/SiO₂ catalyst (Bonfranceschi,
62 et al, 2002). This is a useful intermediate process with a 99% yield of anthraquinone which is applicable
63 in the dye industry and also in the synthesis of hydrogen peroxide (UEIC, 1998). Oxidation of
64 anthracene to anthraquinone has been achieved in the presence of 'air/oxygen/nitric acid', 'nitrogen
65 dioxide in acetic acid' among others (Das, Das, 1982). A number of PAHs including anthracene have
66 also been oxidised to CO₂ and benzene polycarboxylic acid groups with a RuO₄ catalyst (Menendez et
67 al., 2000).

68 Hydrogenation of anthracene has also been investigated in several studies, and a procedure which
69 converts anthracene to 9, 10-dihydroanthracene at a relatively low temperature of 80 °C in the presence
70 of tetralin in SbCl₃ has been published (Buchanan et al., 2010). Catalytic hydrogenation with palladium

71 on several support systems and H₂ has been done on Benzo[a]pyrene (B[a]P) and phenanthrene as
72 models (Yuan, Marshall, 2007). Hydrous pyrolysis of phenanthrene and anthracene with formic acid and
73 different iron minerals was conducted over a period of 3-17 days and various hydrogenated forms of the
74 starting material were obtained afterwards by McCollom et al., (1999). Many articles have been
75 published regarding an attempt at hydrogenating or oxidising PAH as a remediation method due to their
76 stability and persistence.

77 The present study seeks to look at alternative routes of converting anthracene to less toxic and or less
78 persistent derivatives. A novel catalyst in this context is Nafion which has successfully been used in the
79 oxidation as well as reduction of anthracene. Nafion is a perfluorosulfonic acid resin, which is a
80 copolymer of tetrafluoroethene and a perfluorosulfonylether derivative. It is a strong Brønsted acid
81 (Olah et al., 1986 in Laufer et al., 2005). The silicate supported Nafion catalyst; Nafion-SiO₂ has the
82 acid catalyst properties of Nafion resin with the high surface area characteristic of silica as a porous
83 support (Lim et al., 2009). As alternative systems, direct oxidation of PAH with H₂O and O₂ in air and
84 modified forms of peroxide oxidation as well as formic acid reduction are employed in this study.

85

86 **2. Experimental Section**

87 The extent of reactivity of anthracene under different pyrolysis conditions has been studied using
88 stainless steel 316 pyrolysis reactors. The reaction products were analysed by GC-MS. A Thermo
89 Scientific DSQ II Gas Chromatography-Mass Spectrometry (GC-MS) with Trace GC Ultra furnished
90 with a single quadrupole analyser and supporting NIST Library was used for the identification and
91 quantification of peaks. No analyses of gaseous products of hydrous pyrolysis were performed.

92

93 **2.1 Standards, solvents and reagents**

94 Anthracene of 99% purity was obtained from Merck Schuchardt, Darmstadt - Germany; 98-100%
95 Formic Acid from Riedel-de Haen®, Seelze-Germany, 35% Hydrogen peroxide, GC-MS Analytical

96 grade ethyl acetate, Nafion-SiO₂ and Pd-C were all obtained from Sigma Aldrich, St. Louis, MO 63103-
97 USA. Freshly doubly distilled water was used in all cases.

98

99 **2.2 Laboratory Procedures**

100 **2.2.1 Anthracene at 400 °C**

101 A mass of 2.0 ± 0.1 mg ($\sim 1.1 \times 10^{-5}$ moles) of anthracene was weighed with an analytical balance and
102 transferred into a 20 ml capacity cylindrical stainless steel (SS 316) reactor, manufactured by PARR
103 Instrument Company, Illinois, USA. An aliquot of 5.0 ml distilled water was added. The headspace
104 volume of the reactor consisted of air and it contained approximately 1.4×10^{-4} moles of O₂. The reactor
105 was sealed and tightened with screws. The reactor was then transferred into a pre-heated oven set at 400
106 °C. This method was adapted from McCollom et al. (1999). The weight of the assembled reactor was
107 determined before and after heating to ascertain any change in mass due to leakage. After pyrolysis, the
108 reactor was cooled to room temperature and its content transferred into a separating funnel. The process
109 was repeated for durations of 24, 48, 72 and 96 h. The product was extracted with 5.0 ml of GC-MS
110 grade ethyl acetate by shaking for 15-20 minutes to ascertain extraction of products into the organic
111 phase. The mixture was allowed to stand for 30 min and the organic phase was collected into a vial and
112 stored in a refrigerator prior to analysis.

113 **2.2.2 Anthracene with Formic Acid at 400 °C**

114 Anthracene was treated in a similar manner as described above but with the addition of 0.1 ml of 98-
115 100% ($\sim 2.7 \times 10^{-3}$ moles) formic acid to the water phase before pyrolysis at 24, 48, 72 and 96 h
116 respectively.

117 **2.2.3 Anthracene with H₂O₂ 380 °C**

118 Several aliquots of anthracene ranging from 1.0 (± 0.1) - 10.0 (± 0.1) mg were pyrolysed in a 5.0 ml
119 narrow corrosion resistant stainless steel (SS 316) cylindrical tube reactor (manufactured by PARR
120 Instrument Company, Illinois, USA) with 2.5 ml of deionised water and 0.5 ml of 35% (6×10^{-3} moles)
121 H₂O₂. The pyrolysis was done in pre-heated oven at 380 °C. The process was repeated for durations of

122 15 min to 1 h. After pyrolysis, the reactor was cooled to room temperature and its content transferred
123 into a separating funnel. The product was extracted with 3.0 ml of GC-MS grade ethyl acetate. The
124 organic phase was collected into a vial and stored in a refrigerator prior to analysis.

125 **2.2.4 Anthracene with Nafion-SiO₂ at 300 °C**

126 A mass of 1.0 ± 0.1 mg of anthracene was weighed and transferred into a 20 ml capacity cylindrical
127 stainless steel (SS 316) reactor, manufactured by PARR Instrument Company, Illinois, USA. An aliquot
128 of 1.0 ml of distilled water was added together with 1.0 mg of Nafion-SiO₂. The headspace of the
129 reactor contained approximately 19.0 ml of air, which comprised approximately 3.98 ml of oxygen (1.78
130 $\times 10^{-4}$ moles of O₂). The reactor was sealed and transferred into a pre-heated oven at 300 °C for 1 h. The
131 process was repeated with an hourly increment of duration until all anthracene had degraded. The
132 reactor was cooled after duration of each experiment and the content extracted with 5.0 ml GC-MS
133 grade ethyl acetate.

134 **2.2.5 Anthracene with formic acid / Nafion-SiO₂ / Pd-C catalysts at 300 °C**

135 Masses of 5.0 ± 0.1 mg each of anthracene and Nafion-SiO₂ was pyrolysed with 1.0 mg of Pd-C
136 catalyst, 1.0 ml H₂O and 0.1 ml of 98-100% ($\sim 2.7 \times 10^{-3}$ moles) HCOOH (Formic Acid) in a 20 ml
137 capacity cylindrical stainless steel (SS 316) reactor, manufactured by PARR Instrument Company,
138 Illinois, USA. Extraction of products was done with GC-MS grade ethyl acetate. The process was
139 carried out for 1 - 8 h durations at hourly increments. The method is a modification of work done on the
140 hydrogenation of phenols by Zhao et al in the USA (Zhao et al., 2010).

141

142 **2.3 GC-MS Conditions**

143 GC-MS analysis was carried out by the use of a Thermo Scientific Trace GC Ultra equipped with (25
144 m x 0.2 mm, 0.33 μ m) Ultra - 2 HP WCOT fused silica column by Agilent Technologies from J&W
145 Scientific, USA. The GC is coupled with Thermo Scientific DSQ II quadrupole mass spectrometer.
146 Samples were injected at a rate of 1 μ l min⁻¹ by spiltless injection mode and Helium was used as the
147 carrier gas at a constant flow rate of 1 ml min⁻¹. The oven program was started at 50 °C and held for 1

148 min, increased at a rate of $8\text{ }^{\circ}\text{C min}^{-1}$ up to $220\text{ }^{\circ}\text{C}$ and held for 1 min, and then increased at a rate of 10
149 $^{\circ}\text{C min}^{-1}$ up to $300\text{ }^{\circ}\text{C}$ and held for 1 min. Mass detection was operated in a full scan mode (m/z ratio of
150 range 50 - 400) at 3.86 scans s^{-1} for product identification. Ionisation was by electron impact at 70 eV.
151 Ion source temperature was $250\text{ }^{\circ}\text{C}$.

152

153 **2.4 Quality Assurance**

154 High purity analytical grade chemicals were used in all cases. All glassware were soaked overnight in
155 detergent and thoroughly washed with acetone and dried before use. The water used for reactions was
156 doubly distilled. The results presented are the mean of duplicate values. Semi-quantification of reaction
157 products was conducted by determining relative percentage of peaks areas on the assumption that all
158 products would have an approximately equal response. Random injection of standards of anthracene,
159 anthraquinone (representing oxidized products) and 1, 2, 3, 4, 5, 6, 7, 8- octahydroanthracene
160 (representing hydrogenated products) resulted in reproducible results in terms of peak area. The ethyl
161 acetate extraction procedure recovers around 90% of anthracene in tests of un-reacted anthracene with
162 water.

163

164 **2.5 Results and Discussion**

165 The outcomes of the pyrolysis of anthracene under the five different conditions are reported in Tables
166 1, 2, 3 and 4. A summary of the general outcome of the research has been presented in Table 5. Figure 1
167 gives the best fit linear graphical presentations of the rate of decay of anthracene for some of the
168 reaction conditions. In Figure 1 the decay of anthracene can be said to follow Pseudo – First Order
169 kinetics in all the investigated reaction systems, where $\ln [A]_t = -kt + \ln [A]$, (where A is the reactant
170 and the other symbols have their usual meanings). The logarithmic ratio of un-reacted anthracene to
171 initial anthracene and time shows a linear correlation with the R^2 values in all cases being more than
172 0.95. The chemical structures of compounds discussed in this study are presented in Figure 2.

173

175 **2.5.1 Products of hydrous pyrolysis of anthracene (C₁₄H₁₀) at 400 °C**

176 Results for the oxidation of anthracene by water and O₂ at supercritical conditions (400 °C) for
177 different durations are given in Table 1. The percent oxidised anthracene increased from 24.25% at 24 h
178 to 48.4% for 96 h respectively. Different oxidised forms of anthracene including anthraquinone,
179 anthrone and xanthone were observed [Table 1].

180 It was observed that degradation was quite slow so the duration of pyrolysis was critical to the extent of
181 oxidation of anthracene [Figure 1].

182 Supercritical water oxidation (SCWO) of high molecular weight organic compounds is a widely used
183 technique for management of industrial waste (Yermakova et al., 2006; Abeln et al, 2010). SCWO or
184 hydrothermal oxidation (HTO) consists of the homogeneous oxidation of chemical compounds in an
185 aqueous medium using oxygen or hydrogen peroxide as the oxidising agent, at temperatures and
186 pressures above the critical point of water (374 °C and 217.7 atm) (Franck , 1987 in Abeln et al, 2010).
187 At supercritical conditions water is a non-polar solvent which is miscible with organics. The water also
188 offers complete miscibility with oxygen, creating a homogeneous reaction medium, hence a very
189 suitable medium for the oxidation of organics (Freeman, 1989 in Frank, 1984 in Japas, Franck, 1985 in
190 Bermejo, Cocero, 2006). Supercritical water oxidation as applied in the current study occurred without
191 the presence of any deliberately added oxidising agent, an indication that water and gaseous oxygen
192 from air in the reactor head acted as oxidants at supercritical conditions though significant oxidation was
193 observed first only after days of heating at 400 °C.

194 **2.5.2 Products of hydrous pyrolysis of anthracene with formic acid at 400 °C**

195 In this part of the work, formic acid was used as a hydrogen donor at supercritical water conditions.
196 Successful hydrogenation was observed from 9.7 - 47.2% for 24 - 96 h [Table 2]. The major products
197 were 9, 10-dihydroanthracene and 1, 2, 3, 4 - tetrahydroanthracene. Traces of 1, 2, 3, 4, 5, 6 -
198 octahydroanthracene were observed but were found to be less than 2% of the peak area. The reactor
199 made from stainless steel (SS 316), with nickel as a component could have had a catalytic effect on the

200 reactions. Hydrogenation generally requires a hydrogen donor and a catalyst in order to progress
201 effectively since molecular hydrogen does not react readily (Teledyne Isco. Inc., 2010), however formic
202 acid decomposition can generate more reaction hydrogen in situ (Barth , Kleinert, 2008).

203 Hydrogenation of anthracene with formic acid has been successfully conducted by McCollom et al.,
204 1999 within a period of 11 - 14 days at 330 °C after which the starting material was completely
205 converted into different hydrogenated derivatives (McCollom et al., 1999). The relative amount of water
206 used by McCollom et al was low as compared to that used in this research. An increased volume of
207 water seems to have increased the rate of anthracene hydrogenation.

208 **2.5.3 Products of hydrous pyrolysis of anthracene with H₂O₂ at 380 °C**

209 The hydrous pyrolysis of anthracene of varying amounts up to 10 mg with hydrogen peroxide yielded no
210 detectable products (peaks) by GC-MS analysis of the organic extract; an indication of complete
211 degradation of the starting material. A lot of gas evolved after pyrolysis. This was inferred from the
212 sound from the reactor when opened after pyrolysis and from the ~1.0 g loss in mass of reactor before
213 and after opening. The gas produced could be attributed to CO₂ and C_xH_y from anthracene degradation
214 and largely to the decomposition of H₂O₂ according to the reaction: $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2(\text{g})$. However
215 when 10 mg of anthracene was pyrolysed for 1 h, GC-MS analysis of the product gave a single peak
216 which was identified as anthrone [Figure 2 (iii)]. No rate plot could be made due to the rapid
217 degradation.

218 Peroxide oxidation (i.e. supercritical water oxidation) is a very useful technique for remediation of
219 water, soil as well as other industrial waste (Goi et al., 2009). Though peroxide oxidation is possible
220 without the aid of a catalyst and or other oxidants (Zheng et al., 2007), degradation can be enhanced
221 when dealing with large volume of PAH or even at an industrial scale. The use of metal catalyst like iron
222 has successfully been used (Ferrarese et al., 2008). Complete thermal oxidation of hydrocarbons
223 generally yields CO₂ and H₂O; however incomplete combustion can yield CO and other smaller

224 hydrocarbons (US Department of Energy et al., 2008). However, with the primary focus on degradation
225 in this work, gas phase products were not analysed.

226 **2.5.4 Products of hydrous pyrolysis of anthracene with Nafion-SiO₂ at 300 °C**

227 The mass ratio of the reactant and catalyst in this process was 1:1 (Anthracene: Nafion-SiO₂) together
228 with 1 ml of deionised H₂O. Under these conditions, anthracene was completely oxidised with oxygen
229 from air in the presence of Nafion-SiO₂ catalyst in 6 h. Reaction at 1 h duration did not yield any
230 oxidised products but oxidation was observed from 2 h until complete decay of anthracene at 6 h. The
231 only product formed from this reaction was 9, 10 - anthracenedione, thus giving a high level of
232 specificity in the reaction. Anthraquinone is a very useful material in a number of industrial processes
233 such as catalyst for pulp manufacture and raw material for bird and insect repellent (Anthraquinone Fact
234 Sheet, 1998).

235 This method of oxidation of anthracene is novel and there is no record of the procedure in literature. It
236 was discovered during trials of different systems to test the reactivity of anthracene. The only published
237 result involving catalytic oxidation with Nafion-SiO₂ is in the Fe⁺⁺/H₂O₂, Fenton system (Osgerby,
238 2006 in Gryzenia et al., 2009) to oxidise propane into acetone and ethanol (Frusteri, 2002).

239 There are however several routes of selective oxidation of anthracene to anthraquinone which include
240 the use of air over V₂O₅ supported on silica, acetic acid with air in the presence of nitric acid and in the
241 presence of inorganic - organic hybrid materials based on molybdovanadophosphoric acids
242 (Bonfranceschi et al, 2002; Das, Das, 1982; Rodriguez et al., 1989; Do et al., 1990; Bordoloi et al.,
243 2007). The method developed in the current study could be considered for commercial production of
244 anthraquinone considering the fact that there is 100% conversion.

245 **2.5.5 Products of hydrous pyrolysis of anthracene with HCOOH, Nafion-SiO₂ / Pd-C catalysts at** 246 **300 °C**

247 The mass ratio of the reactant and catalyst in this process is 1:1:0.2 (Anthracene: Nafion-SiO₂: Pd-C)
248 together with 1 ml of water and 0.1 ml of formic acid.

249 The slightly modified method used here for anthracene (polycyclic aromatics) hydrogenation resulted in
250 the complete conversion of anthracene into multiple hydrogenated derivatives in 8 h. The catalytic
251 hydrogenation yields ranged from 58.3% within 1 hour to 100% in 8 h. The products were
252 predominantly 9, 10 - dihydoroanthracene and 1, 2, 3, 4 - tetrahydroanthracene with minor quantities of
253 isomers of 1, 2, 3, 4, 5, 6, 7, 8 - octahydroanthracene at 7 and 8 h respectively.

254 This method can also be considered novel since it is the first attempt at using the Nafion-SiO₂ and Pd-C
255 catalyst systems and HCOOH in hydrogenation of polycyclic aromatics.

256 The catalytic hydrogenation of aromatics by Nafion-SiO₂ / Pd-C catalyst system has been successfully
257 used to hydrogenate bio-derived phenols (Zhao et al., 2010). It is however worth mentioning that
258 HCOOH alone has been used in hydrogenation of PAH (McCollom et al., 1999), [Table, 2], and a
259 combination of HCOOH and Pd-C catalyst have been used for the hydrogenation of olefins as well as
260 nitro aromatic hydrocarbons (Bulushev, Ross, 2010; Prasad et al., 2005).

261 **2.6 Conclusion**

262 Anthracene has been successfully reacted under different hydrous pyrolysis conditions. Though all the
263 methods gave some level of reactivity, the rates are very different. Hydrous pyrolysis of anthracene
264 alone at 400 °C and with formic acid respectively yielded results of only 48.4% and 42.57% conversion
265 after 96 h. However hydrous pyrolysis in the presence of H₂O₂ at 380 °C , Nafion-SiO₂ at 300 °C and
266 Pd/C /Formic Acid / Nafion at 300 °C resulted in the complete conversion of anthracene the starting
267 material to easily degradable oxidised and reduced derivatives within 1, 6 and 8 h respectively. The two
268 main catalysts used in the study are recyclable according to literature. Pd-C by filtration (Mori et al.,
269 2008, Zhu, Cai, 2007, Gruber et al., 2004). Nafion-SiO₂ was tested to be re-useable at least 3 times by
270 washing with methanol and dichloromethane. Though the objective of the study is remediation, hydrous
271 oxidation of anthracene by Nafion can be explored for commercial production of anthraquinone which is
272 used as a pesticide (USEPA, 1998). Hydrogenation by Nafion and peroxide oxidation can be considered

273 for industrial remediation purposes but cost of catalyst and oxidant can be a challenge. All the products
274 formed in the various reaction systems results in breaking the aromaticity of anthracene which gives less
275 stable and less persistent forms of the starting material.

276

277 **2.7 Acknowledgement**

278 The authors are grateful to the Agder Fund for financing this research and to the Department of
279 Chemistry of the University of Bergen (UiB) for the use of their facilities for this work.

280 **List of Figure captions**

281 Figure 1: unreacted anthracene ($C_{14}H_{10}$) Vs. duration of pyrolysis (time) for: (a) $C_{14}H_{10} + H_2O$ at 400 °C
282 (b) $C_{14}H_{10} + HCOOH + H_2O$ at 400 °C c) $C_{14}H_{10} + Nafion/SiO_2 + H_2O$ at 300 °C (d) $C_{14}H_{10} +$
283 $Nafion/SiO_2 + HCOOH + H_2O$ at 300 °C

284 Figure 2: Chemical Structure of compounds under consideration (i - viii)

285 **List of Table captions**

286 Table 1: Composition (%) of products of hydrous pyrolysis of anthracene at 400 °C with time

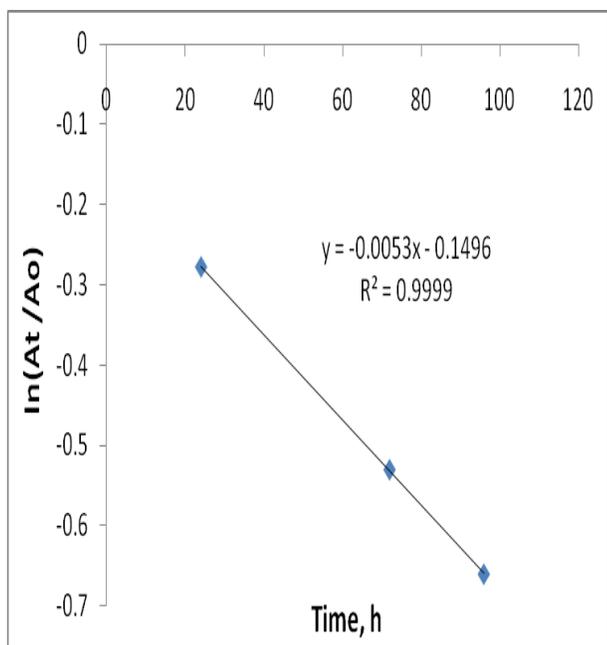
287 Table 2: Composition (%) of products of hydrous pyrolysis of anthracene and H_2CO_2 at 400 °C with
288 time

289 Table 3: Composition (%) of products of hydrous pyrolysis of anthracene and Nafion- SiO_2 at 300 °C
290 with time

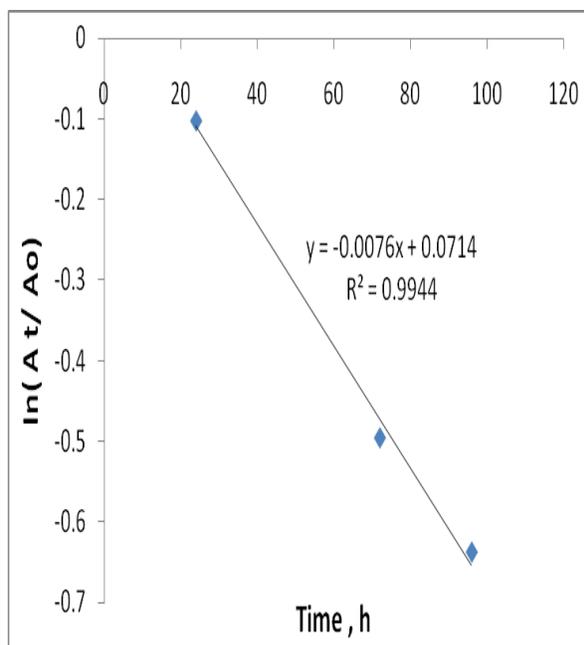
291 Table 4: Composition (%) of products of hydrous pyrolysis of anthracene with formic acid / Nafion-
292 SiO_2 / Pd-C catalysts at 300 °C with time

293 Table 5: Summary of reaction conditions and outcomes

294



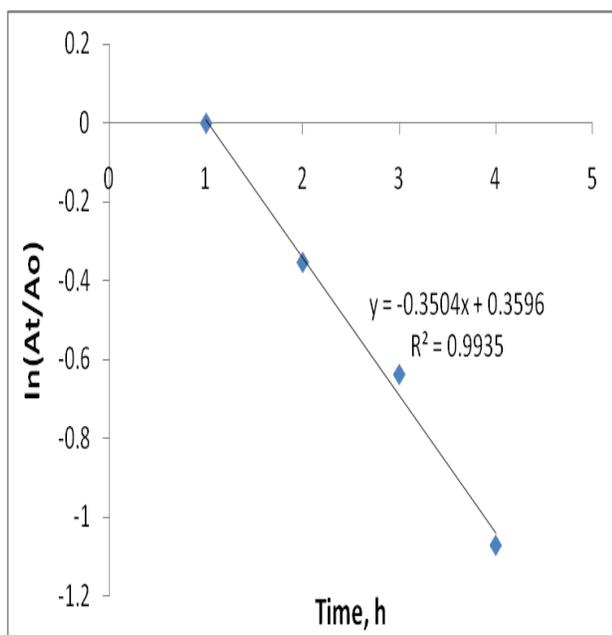
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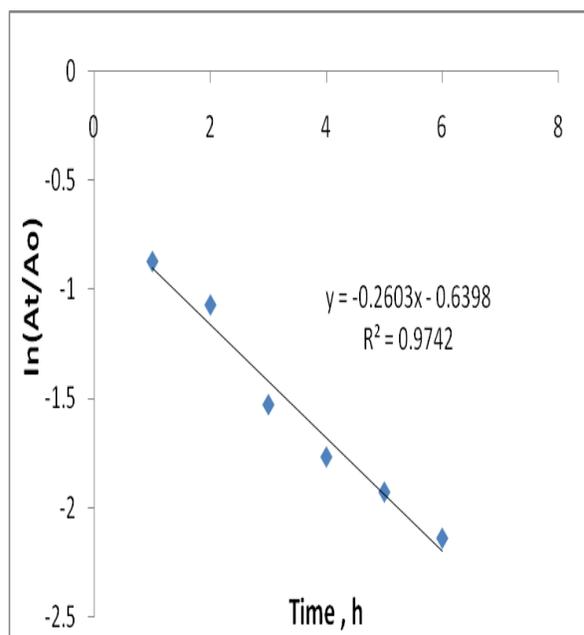
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(a)

(b)



298



299

(c)

(d)

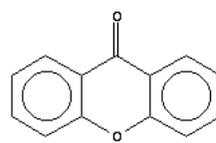
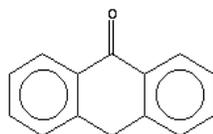
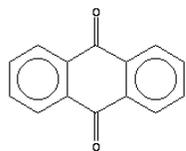
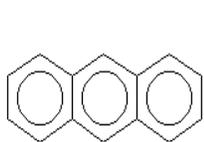
300 **Figure 1 (a - d)**

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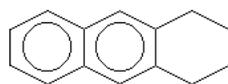
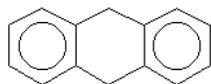
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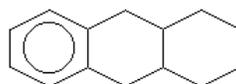
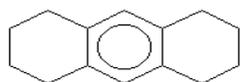
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306

i) *Anthracene*ii) *9, 10 - anthracenedione*iii) *anthrone*iv) *xanthone*

307

308

v) *9, 10-dihydroanthracene*vi) *1, 2, 3, 4-tetrahydroanthracene*

309

310

vii) *1, 2, 3, 4, 5, 6, 7, 8 - octahydroanthracene*viii) *1, 2, 3, 4, 4a, 9, 9a, 10 – octahydroanthracene*

311

Figure 2 (i-viii)

312

TABLES

313

Table 1

Duration, Hour (hr)	un-reacted anthracene (% peak area)	Major products
24	75.75	i) 9, 10-Anthracene-dione
48	71.84	i) 9, 10-Anthracene-dione
72	58.82	i) 9, 10-anthracenedione ii) Anthrone iii) Xanthone
96	51.63	i) 9, 10-anthracenedione ii) Anthrone iii) Xanthone

314

315

316 **Table 2**

Duration , Hour (hr)	un-reacted anthracene (% peak area)	Major products
24	90.30	i) 9, 10-dihydroanthracene
48	69.94	i) 9, 10-dihydroanthracene ii) 1,2,3,4 - tetrahydroanthracene
72	60.90	i) 9, 10-dihydroanthracene ii) 1,2,3,4 - tetrahydroanthracene
96	52.84	i) 9, 10-dihydroanthracene ii) 1,2,3,4- tetrahydroanthracene

317

318

319 **Table 3**

Duration (hours)	un-reacted anthracene (% peak area)	9,10 anthracenedione (% peak area)
1	100.00	0.00
2	70.20	29.80
3	52.80	47.20
4	34.20	65.80
5	6.40	93.60
6	N/D	100.00

320

N/D: None detected

321

322

323

324

325 **Table 4**

Duration (hours)	Anthracene (% peak area)	Major products (% peak area)
1	41.70	(i) 9,10-dihydroanthracene (ii) 1,2,3,4-tetrahydroanthracene
2	34.20	(i) 9,10-dihydroanthracene (ii) 1,2,3,4-tetrahydroanthracene
3	21.70	(i) 9,10-dihydroanthracene (ii) 1,2,3,4 tetrahydroanthracene
4	17.10	(i) 9,10-dihydroanthracene (ii) 1,2,3,4 tetrahydroanthracene
5	14.57	(i) 9,10-dihydroanthracene (ii) 1,2,3,4 tetrahydroanthracene
6	11.80	(i) 9,10-dihydroanthracene (ii) 1,2,3,4 tetrahydroanthracene
7	5.70	(i) 9,10-dihydroanthracene (ii) 1, 2, 3, 4-tetrahydroanthracene (iii) 1, 2,3, 4, 5, 6, 7, 8-octahydroanthracene
8	N/D	(i) 9,10-dihydroanthracene (ii) 1,2,3,4-tetrahydroanthracene (iii) 1,2,3,4,5,6,7,8-octahydroanthracene (iv) cis & trans,1,2,3,4,4a,9,9a,10octahydroanthracene

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- **N/D: None detected**

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331 **Table 5**

Entry	Ox / Red	T (°C)	Time range (h)	K	Comment
1	O ₂ / H ₂ O	400	24 - 96	0.0053	Partial degradation
2	HCOOH	400	24 - 96	0.0076	Partial degradation
3	H ₂ O ₂	380	1	n/a	Complete degradation
4	Nafion-SiO ₂ / Pd-C/HCOOH	300	1-8	0.2603	Complete degradation
5	Nafion-SiO ₂ / O ₂	300	1-6	0.3504	Complete degradation

332 ***Ox: oxidation, Red: reduction, n / a: not applicable**

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342 **2.8 References**

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