

**Catalytic oxidation and reduction of polycyclic aromatic hydrocarbons (PAHs)
present as mixtures in hydrothermal media**

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Abstract

The reactivity of fluorene, anthracene and fluoranthene under oxidation and reduction conditions has been investigated in this study. This project looks at catalytic and green approaches of converting PAH to less toxic and/or less stable derivatives that are amenable to further degradation. Hydrothermal reactions have been performed at 300 °C with pure H₂O and Nafion-SiO₂ catalyst for oxidation, and pure H₂O, HCOOH, Pd-C and Nafion-SiO₂ catalysts for reductive hydrogenation. Time series has been performed for both the oxidation and hydrogenation systems. The products of the reaction were identified and quantified by the use of Gas Chromatography-Mass Spectrometry and the NIST Library. The reaction products include oxidised products of anthracene and fluorene; and hydrogenated derivatives of anthracene and fluoranthene. Fluoranthene did not undergo oxidation; and fluorene did not undergo hydrogenation under the conditions of this research.

Keywords: Anthracene, fluorene, fluoranthene, hydrothermal, oxidation, reduction

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) such as fluorene, anthracene and fluoranthene are known hazardous by-products of combustion in the coal, petroleum and metal smelting industry. They are naturally generated from volcanoes and forest fires [1, 2, 3].

PAHs belong to the group of persistent organic pollutants (POPs). These are organic contaminants that are resistant to degradation and can remain in the environment for long periods [4]. The notion that PAHs are inert entities even at high temperatures has been rarely questioned by chemists [5]. PAHs are known to pollute air, soil and water resources (even low concentrations are found to be toxic), exhibiting high thermal stability and persistence in soil and groundwater [6].

The widespread release of PAH is associated with health and environmental hazards [7] and a global treaty, whose main purpose is the total elimination of 12 POPs on a global scale, was signed in May 2001 in the Stockholm Convention for the regulation of POPs [8]. The European Union as well as the USEPA have classified 16 PAHs as priority compounds with specified permissible limits and the list includes fluorene, anthracene and fluoranthene [9, 10].

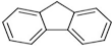
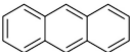
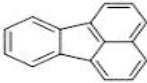
Due to the ever increasing enforcement of regulations on the emission levels of PAH in the environment, remediation technologies have evolved over the years to prevent increased environmental levels of these pollutants. These include landfilling [11], the use of microbes in biodegradation [12, 13, 14], incineration, chemical and or catalytic oxidation [15, 16, 17, 18] to gaseous products predominantly CO₂ and C_xH_y, ozone degradation to various oxidised products [19, 20], ultraviolet (UV) degradation [21, 22] or combination of such methods. Improvements and refinements of these techniques and technologies are continuing. New

catalysts and methods have been tried for oxidation and/or reduction of polycyclic aromatic hydrocarbons in order to produce less toxic and more environmental friendly reaction products.

In this context, Nafion-SiO₂ catalyst has successfully been used in the oxidation as well as reduction of a mixture of PAHs. Nafion-SiO₂ is a perfluorosulfonic acid resin, which is a copolymer of tetrafluoroethene and a perfluorosulfonylether derivative. It is a strong Brønsted acid [23]. The silicate supported Nafion-SiO₂ catalyst; Nafion-SiO₂ has the acid catalyst properties of Nafion-SiO₂ resin with the high surface area characteristic of silica as a porous support [24]. Nafion-SiO₂ catalyst has been used in the hydrodeoxygenation of bio-derived phenols to hydrocarbons [25]. A previous article from our research reports the successful oxidation and reduction of anthracene with the Nafion-SiO₂ catalytic system [26].

In this paper the use of Nafion-SiO₂ catalyst in oxidative (in H₂O) and reductive hydrogenation (with H₂O + HCOOH + Pd-C) reaction systems for degradation of a mixture of polycyclic aromatic hydrocarbons (PAH) as a remediation measure has been explored.

Table 1: Chemical properties of parent PAH in this study

Chemical name	Molecular formular	Molecular weight	Boiling point (°C)	Water solubility 25 oC (mg/l)	Structure
Fluorene	C ₁₃ H ₁₀	166.22	298.0	1.690	
Anthracene	C ₁₄ H ₁₀	178.23	339.9	0.045	
Fluoranthene	C ₁₆ H ₁₀	202.25	375.0	0.265	

2. Experimental

Hydrothermal treatment of a mixture of fluorene, anthracene and fluoranthene under oxidative and reductive conditions at 300 °C has been studied using high pressure reactors. The Nafion-SiO₂ catalyst which is polymeric and environmentally benign has been used to enhance the rate of degradation of PAH under both oxidative and reductive processes.

Gas Chromatography-Mass Spectrometry (GC-MS) was used for analysis of the reaction products. The reactor was tested by filling with 10 ml of water and heating for 24 hours. The volume of water remained constant.

2.1 Standards, solvents and reagents

Formic Acid of 99 % purity was obtained from Riedel-de Haen®, Seelze-Germany.

Anthracene, fluorene and fluoranthene of 98 % purity, ethyl acetate, Nafion-SiO₂ and Pd-C were obtained from Sigma Aldrich, St. Louis, MO 63103-USA.

2.2 Procedure A: Oxidation reaction system

Accurate aliquots of 5.0 mg each of anthracene, fluorene and fluoranthene were transferred into a 20 ml capacity cylindrical stainless steel (SS316) reactor. Nafion-SiO₂ of mass 5.0 mg was added. An aliquot of 5.0 ml of doubly distilled water was added and air was retained as the headspace gas. The weight of the assembled reactor was determined before and after heating to ensure that there was no leakage. The reactor was sealed and tightened with screws. The reactor was then transferred into a pre-heated oven set at 300 °C and heated for a predetermined period. The reactor was then removed from the oven and cooled in an air stream. The weight after opening the reactor to expel any gaseous products was also determined. Batch processes of the above procedure were repeated for different durations of 1 hour increments until the rate of conversion reached a maximum.

2.3 Procedure B: Hydrogenation reaction system

Accurate aliquots of 5.0 mg each of anthracene, fluorene and fluoranthene were transferred into a 20 ml capacity cylindrical stainless steel (SS316) reactor. Nafion-SiO₂ of mass 5.0 mg and Pd-C of mass 1.0 mg were added. Aliquots of 5.0 ml of doubly distilled water and 0.2 ml formic acid were added. The reactor was sealed and tightened with screws. The reactor was then transferred into a pre-heated oven set at 300 °C. The weight of the assembled reactor was determined before and after heating to ensure that there was no leakage. The weight after opening the reactor to expel any gaseous products was also determined. Batch processes of the above procedure were repeated for different durations of 1 hour increments until the rate of conversion reached a maximum.

2.4 Extraction of residue

After each reaction process, the reactor was cooled to room temperature and its content transferred into a separating funnel. The product was extracted with 10 ml (3, 3, 4ml) of analytical grade ethyl acetate. The organic phase was collected into a vial and stored in a refrigerator prior to analysis.

2.5 GC-MS Conditions

GC-MS analysis was performed with the use of Thermo Scientific Trace GC Ultra equipped with (25 m x 0.2 mm, 0.33 μ m) Ultra - 2 HP WCOT fused silica column by Agilent Technologies from J&W Scientific, USA. The GC is coupled with Thermo Scientific DSQ II quadrupole mass spectrometer. Samples were injected at a rate of 1 μ l min⁻¹ by splitless injection mode and helium was used as the carrier gas at a constant flow rate of 1 ml min⁻¹. The oven program was started at 50 °C and held for 1 min, increased at a rate of 8 °C min⁻¹ up to 220 °C and held for 1 min, and then increased at a rate of 10 °C min⁻¹ up to 300 °C and held for 1min. Mass detection was operated in a full scan mode (m/z ratio of range 50 - 400) at 3.86 scans s⁻¹ for product identification. Ionisation was by electron impact at 70 eV. Ion source temperature was 250 °C.

2.6 Quality Assurance

High purity analytical grade chemicals were used in all cases. All glassware was soaked overnight in detergent and thoroughly washed with acetone and dried before use. Doubly distilled water was used for all reactions. Replicate values are reported. Semi-quantification of reaction products was conducted by determining relative percentage of peaks. Reliability of quantification was established by preparation of a calibration curve of solutions of known concentrations.

3. Results and Discussion

The rate of decay of individual PAHs in the mixture are presented in Figures 1 and 2. In Figure 1, the oxidative decay of anthracene and fluorene seem to follow a first order reaction law. The oxidised products are 9 H-Fluorene-9-one and 9, 10 anthracenedione (shown in Figure 6). Fluoranthene did not undergo oxidation under the experimental conditions though it was present in the mixture. Figure 2 shows that hydrogenation of anthracene and fluoranthene increased with time but does not fit a linear pseudo first order reaction. Fluorene however remained stable in the mixture throughout the reaction process. A number of hydrogenated forms of the starting material were formed and these have been presented in Figures 3 and 4. Suggested mechanisms for oxidation and hydrogenation processes have been presented in Figure 5. Figure 6 shows the chemical structures of the reaction products and Table 1 shows some properties of the pure PAHs considered in the study.

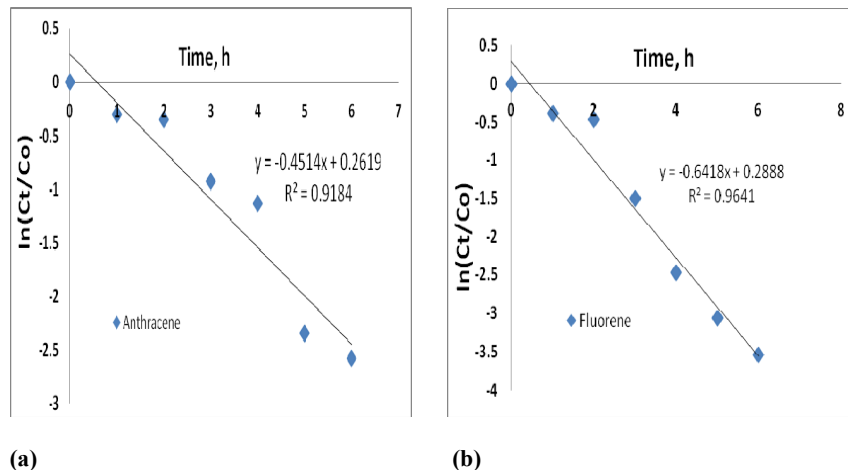
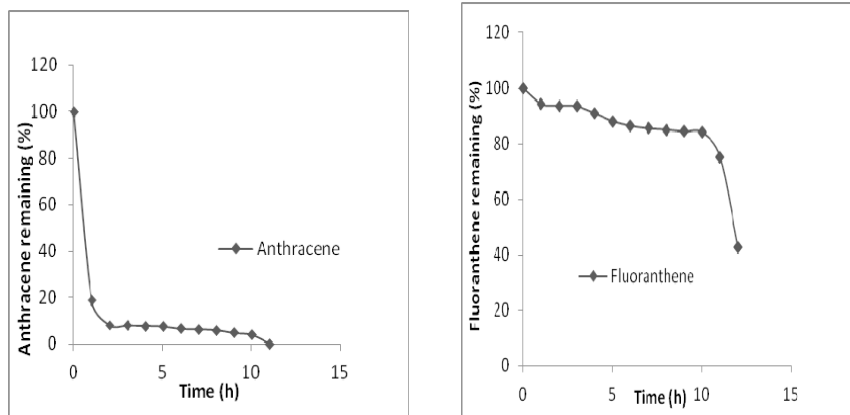


Figure 1: Degradation curves of (Ant: anthracene and Fle: fluorene):

(a) $\ln ([Ant]_t / [Ant]_0)$ versus duration of hydrothermal oxidation (b) $\ln ([Fle]_t / [Fle]_0)$ versus time of hydrothermal oxidation.



(a) (b)
Figure 2: Degradation curves of: (a) Anthracene (%) versus duration of hydrothermal hydrogenation (b) Fluoranthene (%) versus duration of hydrothermal hydrogenation

3.1 Oxidation reaction of fluorene, anthracene and fluoranthene

There was complete oxidation of anthracene and fluorene to 9, 10 - anthracenedione and 9 H-Fluorene-9-one respectively while fluoranthene remained un-reactive after 7 hours (Figure 1).

In the oxidation process, it is assumed that oxygen from air in the reactor head acts as an oxidant.

3.1.1 Anthracene

Anthracene showed 73.82 % degradation within the first 1 hour to 100.00 % degradation in 7 hours (Figure 1(a)) at 300 °C. Anthraquinone was the only product formed from anthracene oxidation at all durations of oxidation reaction. In a previous part of this study where hydrothermal treatment was done with anthracene without other PAH, there was complete oxidation of anthracene in 6 hours in the presence of Nafion-SiO₂ but oxidation started in the second hour and increased steadily until completion. Though, anthracene has been proven to undergo a slow oxidation in the presence of water without Nafion-SiO₂ catalyst, a yield of only 48.4 % degradation was observed for 96 hours at 400 °C, a clear indication that the

Nafion-SiO₂ catalyst enhanced the rate of conversion in this instance. It was also observed that though the same ratio of reactants was used in both cases, the initial rate of degradation of anthracene was enhanced in the mixture relative to experiments with only anthracene. Rate constants *K* of 0.3504 and 0.4514 were obtained for reactions involving anthracene only and anthracene in a mixture respectively [26]. From the results, it seems the mechanism of oxidation is a straight forward oxidation of anthracene as shown in Figure 5. The first step oxidation leads to anthrone. Further oxidation of anthrone leads to 9, 10-anthracenedione, It appears that anthrone functioned as an intermediate in this reaction since it was not detected in any of the reaction products. Oxidation of anthracene to anthraquinone and or with other products has been extensively studied by other authors with different reaction systems such as metachloroperbenzoic acid (*m*-CPBA) as oxidant in the presence of iron and manganese porphyrins (FeF₂₀TPPCL, MnF₂₀TPPCL, FeCl₈TPPCL and MnCl₈TPPCL) as catalysts yielded anthrone, oxanthrone and anthraquinone [27]. Also, anthracene oxidation with cerium (IV) ammonium nitrate in the presence of air yielded 99.6 % anthraquinone precipitate [28].

3.1.2 Fluorene

Complete oxidation of fluorene to 9H-fluorene-9-one was observed in 7 hours but the rate was faster than that of anthracene with 67.43 % degradation in 1 hour to 100.00 % in 7 hours (Figure 1(b)). This could be attributed to the fact that fluorene has a lower molecular weight (166 g/mol) as compared to that of anthracene (178 g/mol) and therefore molecules have a high kinetic energy which leads to more effective collisions and fast formation of products. The mechanism of oxidation is again straight forward as in the case of anthracene (Figure 5). Successful production of fluorenone has been reported by other authors for reaction of fluorene by alkaline hexacyanoferrate (III) [29] and vanadium (V) in aqueous acetic acid containing 1.0 M sulfuric acid at 50 °C [30], an indication that the oxidation of fluorene can be performed at relatively low temperatures in strong acidic medium.

3.1.3 Fluoranthene

Fluoranthene remained stable and did not undergo oxidation throughout the reaction durations of 1 - 7 hours. The use of a stronger oxidising agent other than O₂ from air probably will give a satisfactory result since successful degradation of fluoranthene in soil has been achieved with the use of Fenton's reagent (H₂O₂ +FeSO₄) [31]. Air oxidation of fluoranthene in the presence of minerals such as calcite, clay and silica at 100 °C also resulted in decomposition to CO₂ and other C_XH_Y gaseous products [32]. Most of the research on oxidation of fluoranthene are bacteria induced and includes *Mycobacterium* sp. strain PYR-1 and *P.ostreatus* mycelium degradation to 9H-fluoren-9-one and other products [10, 33], an indication that fluoranthene is more susceptible to bacteria oxidation than chemical oxidation.

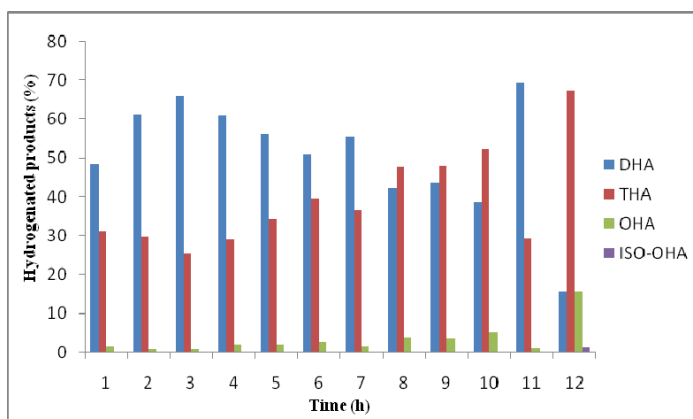


Figure 3: Relative percent composition of hydrogenated products of anthracene versus time (OHA: 1, 2, 3, 4, 5, 6, 7, 8 - Octahydroanthracene, Iso - OHA: 1, 2, 3, 4, 4a, 9, 9a, 10 – Octahydroanthracene)

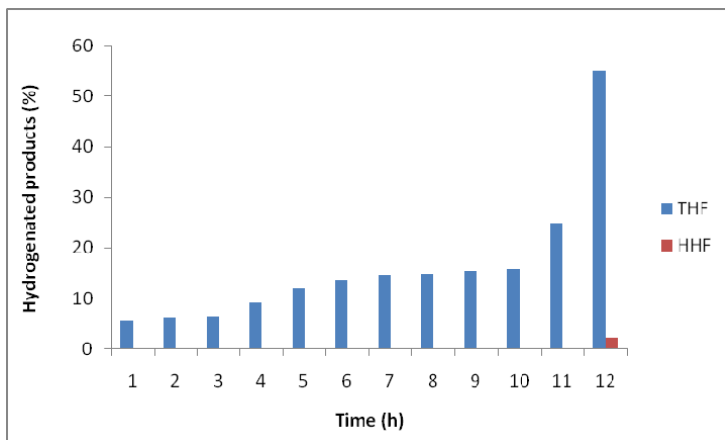


Figure 4: Relative percent composition of hydrogenated products of fluoranthene versus time (THF: 1, 2, 3, 10b -Tetrahydrofluoranthene, HHF: 6b, 7, 8, 9, 10, 10a-Hexahydrofluoranthene)

3.2 Reductive hydrogenation of fluorene, anthracene and fluoranthene

The experimental results indicate that there was 100 %, 55 % and 0.0 % hydrogenation of anthracene, fluoranthene and fluorene respectively. Formic acid, HCOOH acts as hydrogen donor for the hydrogenation processes [34]. The hydrogenation processes are predicted to proceed by a mechanism similar to the Birch reduction of aromatic hydrocarbons. However, the reduction is not selective [35].

3.2.1 Anthracene

Complete degradation of anthracene by hydrogenation was observed in 12 hours starting with 81.14 % degradation in the first hour (Figure 2(a)). The hydrogenated products were identified as 9,10 - dihydroanthracene (DHA) , 1, 2, 3, 10b - tetrahydroanthracene (THA) , 1, 2, 3, 4, 5, 6, 7, 8 - octahydroanthracene (OHA) and 1, 2, 3, 4, 4a, 9, 9a, 10- octahydroanthracene (Iso-OHA). These products were observed in a previous study when hydrothermal oxidation of anthracene alone resulted in complete conversion in 8 hours.

However, it should be noted that the mass of anthracene in the previous study was 1.0 mg as compared to 5.0 mg of individual PAHs in this study. Considering duration of 8 h for 1.0 g anthracene to 12 h for a mixture of 5.0 g each of anthracene, fluorene and phenanthrene, it could be said that the individual PAHs have a synergetic effect on the individual reaction rates [26]. It was observed that though anthracene content decreased with time of reaction, the same cannot be said about the hydrogenated products of anthracene. For reaction time of 1 hour, the distribution was 48.47 % -DHA, 31.10 % -THA and 1.57 %-OHA, however the distribution trend did not have a correlation with time of reaction. In the final product however the percentage of THA was highest at 67.35% with that of the rest being 15.61 % -DHA, 67.35 % -THA, 15.68 % - OHA and 1.36 % of Iso-OHA a new product (Figure 3). This trend could be attributed to isomerisation and continuous hydrogenation. However combination of the Pd-C and Nafion-SiO₂ catalysts together with HCOOH enhances degradation. This is observed when compared to results of anthracene hydrogenation with only HCOOH at 400 °C in the presence of water which yielded only 47.2 % of hydrogenated products in 96 hours [26]. The mechanism follows the Birch type reduction but does not stop after the formation of 9, 10 - dihydroanthracene [34]. This is similar to results reported by Nelkenbaum et al., 2007 [6], where hydrogenation was achieved by the use of TMPyP-Ni catalyst and nano-ZVI as an electron donor. Nelkenbaum et al. achieved complete hydrogenation in 168 hours at ambient temperature and pressure [6].

3.2.2 Fluorene

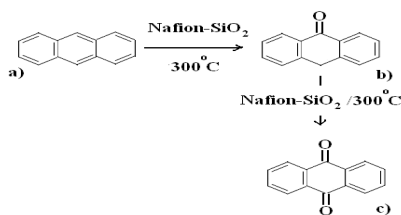
The fluorene used in this experiment had <1.0 % 1, 4-dihydrofluorene as impurity. This figure remained constant throughout all the batch reactions up to 12 hours. Fluorene was un-reactive to the hydrogenation system employed in this work. Thus, hydrothermal reaction at 300 °C was not enough to promote fluorene reactivity. Research done by scientists in the Department of Chemical Engineering, University of Delaware indicates that catalytic hydrogenation and hydrocracking reaction for fluorene is possible at 335-380 °C and 153-atm total pressure

when presulfided NiW/Al₂O₃ catalyst is used for isomerization and hydrogenation to yield 1, 2, 3, 4, 4a, 9a-hexahydrofluorene and ultimately perhydrofluorene [36].

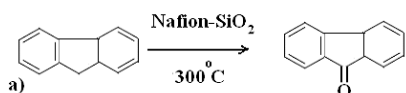
Reaction of a mixture of anthracene, phenanthrene and fluorene NiMo/Al₂O and H₂ at 573 K by Koltai et al., 2002 [37] indicated that the order of hydrogenation of fluorene was several orders of magnitude lower than the other components of the mixture. This confirms that fluorene has a high chemical and thermal stability with regards to reduction [37].

3.2.3 Fluoranthene

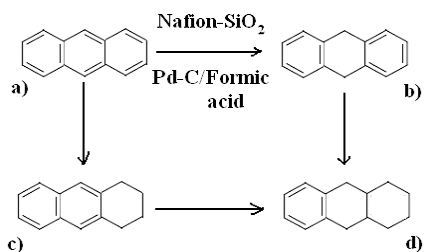
The hydrogenation of fluoranthene started at 5.71 % in the first hour of the reaction and increased steadily to 55.0 % in 12 hours. The hydrogenated product was mainly 1, 2, 3, 10b - tetrahydrofluoranthene (THF), throughout the reaction until 12 hours when 2.26 % of 1, 2, 3, 6b, 7, 8, 9, 10, 10a-Hexahydrofluoranthene (HHF) was formed (Figure 4). A time series on the catalytic reaction for fluoranthene hydrogenation and further hydrocracking has been performed by Lapinas et al., 1987 [38] in the temperature range of 310 to 380 °C and 153 atm. Fluoranthene hydrogenation was catalyzed by a presulfided NiW /Al₂O₃ catalyst, whereas its hydrogenation and subsequent hydrocracking were catalyzed by a presulfided NiMo/zeolite-Y catalyst to yield tetrahydrofluoranthene and finally to perfluoranthene [38]. The temperature range used by Lapinas et al., 1987 is high when compared to the current study at 300 °C.



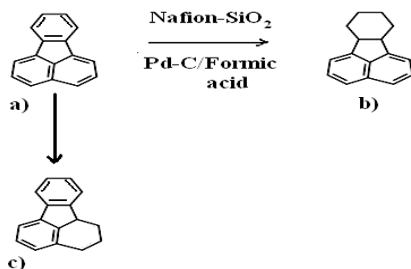
(i)



(ii)

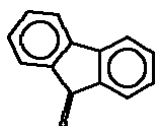


(iii)

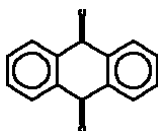


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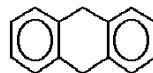
Figure 5: Suggested routes for oxidation and hydrogenation processes
(i) Anthracene oxidation (ii) Fluorene oxidation (iii) Anthracene hydrogenation
(iv) Fluoranthene hydrogenation



(i) 9 H-fluorene-9-one



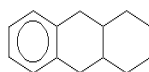
(ii) 9, 10 - anthracenedione



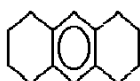
(iii) 9, 10 - dihydroanthracene



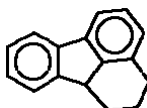
(iv) 1, 2, 3, 4-tetrahydroanthracene



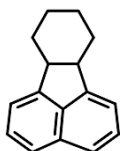
(v) 1, 2, 3, 4, 4a, 9, 9a, 10 - octahydroanthracene



(vi) 1, 2, 3, 4, 5, 6, 7, 8 - octahydroanthracene



(vii) 1, 2, 3, 10b - tetrahydrofluoranthene



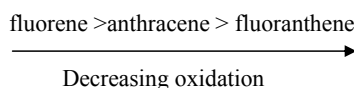
(viii) 6b, 7, 8, 9, 10,10a-Hexahydrofluoranthene

Figure 6: Chemical structures of the identified product compounds in this study (i) - (vi)

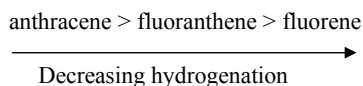
4. Conclusion

The degradation of PAHs remains a global challenge in the quest to limit pollution from these hazardous chemicals. The experimental results from this study confirm that it is possible to use Nafion-SiO₂ and H₂O reaction systems at 300 °C to obtain 100 % oxidisation of anthracene to anthraquinone. It also indicates that fluorene can undergo 100 % conversion to 9 H-Fluorene-9-one under the same chemical conditions. However fluoranthene is stable and not reactive under these conditions. On the other, reductive hydrogenation in the presence of Nafion-SiO₂, H₂O, HCOOH and Pd-C at 300 °C for 12 hours resulted in 100 % and 55.0 % conversion of anthracene and fluoranthene respectively while fluorene remained un-reactive. The presence of other PAHs enhanced the conversion of anthracene.

The order of the extent of the individual PAHs to oxidation is as follows:



The order of the extent of the individual PAHs to hydrogenation is as follows:



Products like anthaquinone and flourenone have industrial and medical applications if isolated.

5. Acknowledgement

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6. References

1. Keith, L.H (Ed.). 1976. Identification and Analysis of Organic Pollutants in Water, Ann Arbor Science, Michigan.
2. Bradley, J.N. Magee, B.H., and S.L. Allen. 1994. Background Levels of Polycyclic Aromatic Hydrocarbons (PAH) and Selected Metals in New England Urban Soils, *J Soil Contamin.* 3(4):349-361.
3. Ochsenkuhn-Petropoulou, M. Staikos, K. Matuschek, G., and A. Kettrup. 2003. On-line determination of polycyclic aromatic hydrocarbons in airborne particulate matter by using pyrolysis/GC-/MS, *J. Anal. Appl. Pyrolysis* 70:73-85.
4. Wild, S.R. and, K.C. Jones. 1995. Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget, *Environ. Pollut.* 88:91.
5. Necula, A., and L.T. Scott. 2000. High temperature behavior of alternant and non-alternant polycyclic aromatic hydrocarbons, *J. Anal. Appl. Pyrolysis* 54:65-87.
6. Nelkenbaum, E. Dror, I., and B. Berkowitz. 2007. Reductive hydrogenation of polycyclic aromatic hydrocarbons catalyzed by metalloporphyrins, *Chemosphere*, 68:210-17.
7. Ntainjua, E.N., and S. H. Taylor. 2009. The catalytic total oxidation of polycyclic aromatic hydrocarbons, *Top Catal.* 52:528-541.
8. Nadala, M. Schuhmachera, M., and J. L. Domingo. 2004. Levels of PAHs in soil and vegetation samples from Tarragona County, Spain, *Environ. Pollut.* 132:1-11.
9. Campro Scientific, Priority PAHs. 2011. [<http://www.campro.eu/PDF/Brochures/Flyer-CHIRON/2009-09-BMF-40-PAHs.pdf>, accessed: 2nd February, 2011)].
10. USEPA, 2008. *Polycyclic aromatic hydrocarbons* (PAHs). United States Office of Solid Waste. Environmental Protection Agency Washington, DC 20460.

11. [11] USEPA, Landfills. 2010.
<http://www.epa.gov/wastes/nonhaz/municipal/landfill.htm>, accessed: 2nd February, 2011)].
12. Kanaly, R.A., and S. Harayama. 2000. Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by Bacteria, *J. Bacteriol.* 182 (8):2059 – 2067.
13. Shuttleworth, K.L., and C.E. Cerniglia. 1995. Environmental aspects of PAH biodegradation, *Appl. Biochem. Biotechnol.* 54:219-302.
14. Lepo, J.E., and C. R. Cripe. 1999. Biodegradation of Polycyclic Aromatic Hydrocarbons (PAH) from crude oil in sandy-beach microcosms, *Bioremediation, Microbial Biosystems: New Frontiers Proceedings of the 8th International Symposium on Microbial Ecology*, Bell CR, Brylinsky M, Johnson-Green P (eds) Atlantic Canada Society for Microbial Ecology, Halifax, Canada.
15. Pollution issues: Incineration [<http://www.pollutionissues.com/Ho-Li/Incineration.html>, (Accessed 4th November, 2010)]
16. Solvay, S. A. 2010. Chemical Oxidation [<http://www.remediation-soil.com/processes/chemicaloxidation/0,,51621-2-0,00.htm>, (Accessed: 28th October, 2010)].
17. Technologies. Chemical oxidation. 2010.
[http://www.arstechnologies.com/chemical_oxidation.html, Accessed: 10th November, 2010], 98 North Ward Street New Brunswick, New Jersey, U.S.A. 08901: 1-732-296-6620.
18. Shie, J.-L. Chang, C.-Y. Chen, J.-H. Tsai, W.-T. Chen, Y.-H. Chiou, C.-S., and C.-F. Chang. 2005. Catalytic oxidation of naphthalene using a Pt/Al₂O₃ Catalyst, *Appl. Catal. A, Environmenta*, 58:289-297.
19. Wu, D. Yong-Jun, X., and W. Jian- Long. 2007. Degradation of acenaphthene by ozone, *Biorem. Sci.* 20:291-294.

20. Ma, J. Lui, Y., and H.He. 2010. Degradation kinetics of anthracene by ozone on mineral oxides, *Atmos. Environ.* 44:4446-4453.
21. Zhang, L. Li, P. Gong, Z., and X.Li. 2008. Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using TiO₂ under UV light, *J. Hazard. Mater.* 158 (2-3):478-484.
22. Guieysse, B.Viklund, G. Toes, A.C., and B. Mattiasson. 2004. Combined UV-biological degradation of PAHs, *Chemosphere*, 55 (11):1493-1499.
23. Olah, G.A. Pradeep, S.I., and G.K.S. Prakash. 1986. *Synthesis*, 513. In Laufer, M.C. Bonrath, W., and W.F. Hoelderich. 2005. Synthesis of (all-rac)- α -tocopherol using Nafion resin/silica nanocomposite materials as catalysts. *Catal. Lett.* 100:1-2.
24. Lim, N.H. Yarmo, M.A. Huang, N.M. Khiew, P.S. and W.S .Chiu. 2009. Synthesis, characterisation and catalytic performance of porous nafion resin/silica anocomposites for esterification of lauric acid and methanol, *J. Phys. Sci.* 20(2):23-36.
25. Zhao, C. Kou, J. Lemonidou, A. A. Xuebing, L., and J. A. Lercher. 2010. Hydrodeoxygenation of bio-derived phenols to hydrocarbons using RANEY® Ni and Nafion/SiO₂, *Chem. Commun.*, 46 (3): 412-414.
26. Nkansah, M.A. Christy, A.A., and T. Barth. 2011. The use of anthracene as a model compound in a comparative study of hydrous pyrolysis method for industrial waste remediation, *Chemosphere*, 84:403-408.
27. Safari, N. Naghavi, S.S., and H.R. Khavasi. 2005. Homogeneous *m*-CPBA-Oxidation of anthracene by electron-withdrawing metalloporphyrins in different reaction conditions, *Appl. Catal., A: General*, 285 (1-2):59-64.
28. Rindone, B., and C. Scolastico.1971. Oxidation of anthracene with cerium (IV) ammonium nitrate, *J. Chem. Soc. B*, 2238-2241.
29. Pillay, M.K., and N. Nagasundaram. 1986. Kinetics of oxidation of fluorene by alkaline hexacyanoferrate (III), *Proc. Indian Acad. Sci. (Chem. Sci.)*, 96 (1-2):13-19.

30. Narasimhan, S., and N. Venkatasubramanian. 1979. Oxidation of fluorenes by ammonium metavanadate: a kinetic study, *Int. J. Chem. Kinet*, 11(8):883-897.
31. Qiang, Z. Chang, J.H. Huang, C.P., and D. Cha. 2000. Oxidation of selected polycyclic aromatic hydrocarbons by the Fenton's Reagent: Effect of major factors including organic solvent, *Nucl. Site Remed.* 187-209.
32. Ghislain, T. Faure, P. Biache, C., and R. Michels. 2010. Low-temperature, mineral-catalyzed air oxidation: A possible new pathway for PAH stabilization in sediments and soils, *Environ. Sci. Technol.* 44:8547-8552.
33. López, Z. Vila, J. Minguillón, C., and M. Grifoll. 2006. Metabolism of fluoranthene by *Mycobacterium* sp. strain AP1. *Appl Microbiol. Biotechnol.*70:747-756.
34. Delgado, O. Bolívar, C. Ovalles, C., and C.E. Scott. 2005. Hamaca Crude Oil Upgrading Using Formic Acid as Hydrogen Precursor under Steam-Injection Conditions, *Heavy Hydrocarbon Resour.* 143-152.
35. Kaiser, E. M. 1972. A Comparison of Methods Using Lithium/Amine and Birch Reduction Systems: *Synthesis*, 391-415.
36. Lapinas, A.T. Klein, M.T., and B.C. Gates. 1991. Catalytic hydrogenation and hydrocracking of fluorene: Reaction pathways, kinetics and mechanisms, *Ind. Eng. Chem. Res.* 30: 42-50.
37. Koltai, T. Macaуда, M. Guevara, A. Schulz, E. Lemaire, M. Bacaud, R., and M. Vrinat. 2002. Comparative inhibiting effect of polycondensed aromatics and nitrogen compounds on the hydrodesulfurization of alkyldibenzothiophenes, *Appl. Catal., A: General*, 231:253-261.
38. Lapinas, A.T. Klein, M.T., and B.C. Gates. 1987. Catalytic hydrogenation and hydrocracking of fluoranthene: Reaction pathways and kinetics, *Ind. Eng. Chem. Res.* 26:1026-1033.