Bull. Chem. Soc. Ethiop. **2010**, 24(3), 461-466.
Printed in Ethiopia

ISSN 1011-3924

SHORT COMMUNICATION

ALIPHATIC AND POLYCYCLIC AROMATIC HYDROCARBONS PROFILES OF PHOTOMODIFIED NATURAL BITUMEN OF AGBABU, SOUTHWESTERN NIGERIA

O.M. Olabemiwo[1*], G.O. Adediran[2], F.A. Adekola[3] and A.A. Olajire[1]

[1]Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology,
Ogbomoso, Nigeria
[2]Department of Chemical Sciences, Ajayi Crowther University, Oyo, Nigeria
[3]Department of Chemistry, University of Ilorin, Ilorin, Nigeria

(Received August 10, 2009; revised May 13, 2010)

ABSTRACT. The impact of sunlight on aliphatic and polycyclic aromatic hydrocarbons profiles of Agbabu natural bitumen in Nigeria was investigated. The raw flow type of the bitumen was purified and exposed to sunlight for six consecutive months. Different portions of the bitumen were withdrawn at an interval of one month and were separated into aliphatic and polycyclic aromatic hydrocarbon fractions by column chromatography, followed by the GC analyses of various fractions. The total aliphatic hydrocarbon content was found to be 485, 424, 416 and 392 g/kg for control, one, three and six months solar-irradiated bitumen samples, respectively; while the total polycyclic aromatic hydrocarbons content found in the control, one, three and six months solar-irradiated bitumen samples were 708, 733, 609 and 638 µg/g, respectively. The effects of sunlight on the compositional patterns of bitumen were discussed.

KEY WORDS: Agbabu, Bitumen, Sunlight, GC, Aliphatic hydrocarbon, Polycyclic aromatic hydrocarbon

INTRODUCTION

Bitumen is a very important engineering material; it is used in road construction, roofing of residential and industrial buildings, construction of dams, and airways tarmac [1]. Bitumen like any other materials is prone to structural modification which can lead to the emission of greenhouse and some carcinogenic gases [2]. Service bitumens are known to be in constant touch with some of the environmental factors, thus making them to be more vulnerable to structural modification. Water [3], light [4, 5] and heat [6, 7] are some of the environmental factors which have been established to alter the chemical composition of crude oil and allied materials such as bitumen. Depreciation in quality of bitumen and all materials in general leads to huge financial loss arising from replacements or system failure. Consequently, there is the need to investigate the extent of the depreciation of bitumen arising from its interaction with the environment. This becomes more important in this era of global climate change [2]. The results of such investigations will be useful in determining the appropriate measures needed for the prevention or attenuation of system failures that might occur due to such depreciation.

Research activities on the vast deposit of Agbabu natural bitumen in Nigeria have largely been concentrated on the physico-chemical characterization [8, 9], geological mapping and examination [10] and effect of future exploitation of this important material on the soil and water samples of this area [11, 12]. Very little investigation has been carried out on the effects of environmental factors on this bitumen. However, our previous study [13] on this showed that the infrared spectrum of the bitumen was greatly altered when the bitumen was exposed to sunlight. As part of our efforts in getting detailed information on interaction of sunlight with the Agbabu natural bitumen, we had, in this work examined the effects of sunlight on the aliphatic

---

*Corresponding author. E-mail: olabemiwo@yahoo.com and polycyclic aromatic hydrocarbon profiles of Agbabu bitumen using gas chromatographic technique.

EXPERIMENTAL

Purification of the bitumen. 100 g of the bitumen was weighed and purified using the modified method of Rubinstein and Strausz [14]. The weighed bitumen was dissolved in 1 L of chloroform and filtered. The bitumen in the filtrate was recovered by vacuum evaporation of the solvent. The recovered bitumen was used for solar irradiation experiment.

Solar irradiation of the bitumen. Solar irradiation of the bitumen is as described in our previous study [13]. Approximately 5 g of the purified bitumen was weighed into a dried and pre-weighed petridish (Pyrex). The sample was spread to form a thin layer of about 0.1cm thickness. The petridish was covered with a very thin transparent glass. This was then placed on top of one storey building (about 18 m tall) at the back of works department, Ladoke Akintola University of Technology, Ogbomoso, Nigeria, between November 2006 and April 2007. This arrangement allowed unhindered penetration of rays of sunlight on to the sample in the petridish.

While the irradiation was in progress, 0.4 g of the bitumen was withdrawn at intervals of one, three and six months. The withdrawn samples were each fractionated into aliphatic and aromatic fractions using standard analytical procedures. Asphaltene was precipitated from the bitumen by dissolving the sample withdrawn (0.4 g) in 25 mL of isooctane (2,2,4-trimethylpentane) and filtered. Fractions of saturated hydrocarbons, aromatic hydrocarbons and polar compounds were separated from maltene fraction by elution with *n*-hexane, dichloromethane/*n*-hexane (95/5) and dichloromethane, respectively (50 mL of each eluent). The separated fractions were each concentrated using rotatory evaporator.

Gas chromatographic analysis. The gas chromatographic analyses (GC) were carried out on a 5890 series 11 Hewlet Packard gas chromatograph equipped with flame ionization detector (FID). A fused-silica capillary column (30 m × 0.25 μm i.d.) stationary phase coated with 0.25 m film of HP-5 stationary phase was used.

For saturated hydrocarbons, 2 μL of sample was injected. The column temperature started at 60 ^{o}C, held isothermally for 2 min and then increased to 200 ^{o}C at the heating rate of 10 ^{o}C/min for 20 min. It was held at this temperature for 2 min, thereafter increased to 320 ^{0}C at the heating rate of 12 ^{o}C/min for 5 min and held at this temperature for 2 min. Nitrogen was used as carrier gas at a pressure of 30 psi. Hydrogen and air were at pressures of 22 and 28 psi, respectively. Injector and detector temperatures were 300 and 320 ^{o}C, respectively.

The column temperature for the aromatic hydrocarbon started at 68 ^{o}C and was held at this temperature for 2 min, thereafter, the temperature increased to 260 ^{o}C at heating rate of 12 ^{o}C/min for 16 min. It was held isothermally at 260 ^{o}C for 4 min and thereafter increased to 320 ^{o}C at heating rate of 15 ^{o}C/min for 4 min and held at this temperature for 8 min. The carrier gas was nitrogen at a pressure of 35 psi. Hydrogen and air were at pressures of 25 and 30 psi, respectively. The injector and detector temperatures were 300 and 320 ^{o}C, respectively and the volume of sample injected was 2 μL. Calibration curves for the saturated and aromatic hydrocarbons were prepared using the standards supplied by the GC equipment manufacturer.

RESULTS AND DISCUSSION

The concentration of each aliphatic hydrocarbon found in the natural bitumen at various period of its exposure to sunlight is as presented in Table 1. It is clearly seen from Table 1 that the composition of the bitumen was altered as a result of its exposure to sunlight. The non-irradiated sample which served as the control showed the predominance of even-numbered carbon atoms (CPI < 1). The reverse was the case for samples of the bitumen irradiated with sunlight for one, three and six months (CPI > 1). Thus, the overall consequence of interaction of sunlight with the bitumen is re-distribution of carbon type in the bitumen. These re-distributions suggest that the even numbered carbon atoms in the Agbabu bitumen are more vulnerable to photo modification than the odd-numbered carbon atoms.

In the control and the sample which were solar irradiated for six months, C_{24} was the most abundant carbon atom, whereas C_{11} was the most abundant in the samples of the bitumen irradiated with sunlight for one and three months. Also, C_{29} was present in detectable amount in the samples irradiated for six months and the control sample. The C_{30} occurred below the detection limit of the instrument in all the samples except in the six months-irradiated sample. It is apparent from Table 1, that there is a surge in concentration of C_{11} in all samples of the bitumen exposed to sunlight.

Table 1. Aliphatic hydrocarbons profile of Agbabu natural bitumen at different period of exposure to sunlight.

	Period (months) of exposure of the bitumen to sunlight			
Compound	0	1	3	6
C_{11} (g/kg)	37.1	105	192	119
C_{12}	0.49	1.80	1.64	0.14
C_{13}	25.1	90.9	63.1	9.11
C_{14}	1.66	3.73	2.05	2.31
C_{15}	61.2	90.3	33.4	54.4
C_{16}	2.86	4.83	1.87	5.35
C_{17}	5.85	6.07	3.17	3.22
C_{18}	3.99	3.46	4.31	2.89
C_{19}	4.35	3.28	3.91	6.62
C_{20}	11.4	8.75	4.01	3.95
C_{21}	25.1	5.32	8.04	4.19
C_{22}	15.5	9.84	4.80	9.05
C_{23}	3.06	1.95	0.90	4.65
C_{24}	210	55.5	79.4	158
C_{25}	8.76	5.36	2.26	2.57
C_{26}	49.0	19.5	9.50	3.38
C_{27}	10.8	5.30	1.06	0.41
C_{28}	8.00	2.90	0.56	1.97
C_{29}	0.10	$< 10^{-5}$	$< 10^{-5}$	0.10
C_{30}	$<10^{-5}$	$< 10^{-5}$	$< 10^{-5}$	2.5×10^{-5}
TOCA	181	313	308	205
TECA	303	110	108	187
CPI	0.60	2.84	2.85	1.09
TALPH	485	424	416	392

TALPH: total aliphatic hydrocarbons, CPI: carbon preference index = TOCA/TECA, TECA: total even-numbered carbon atoms, TOCA: total odd-numbered carbon atoms.

The observed changes in the compositions of the bitumen may be attributed to cracking and recombination of cracked products. The photolysis of the bitumen probably brought about the cracking of some higher molecular mass hydrocarbons to medium and lower molecular mass radicals. Alkyl radicals are known to be by-products of photo-oxidation of hydrocarbons [15]. The homolytic cleavage of the typical pi (π) and sigma (σ) bonds found in the saturated hydrocarbons of the bitumen was made possible because sunlight has enough quantum of energy to achieve this [16]. The very low molecular mass radicals probably recombined to form the excess C_{11} molecule detected in the irradiated samples of the bitumen. The trace quantities of C_{29} and C_{30} found in the six months irradiated bitumen sample might be due to recombination of medium and low molecular mass radicals earlier formed in sample of the bitumen irradiated for one and three months. The compositional pattern of the photo-modified bitumen samples suggests that there was initial cracking of large molecular mass hydrocarbons in the bitumen, followed by recombination after long periods of exposure to sunlight.

The polycyclic aromatic hydrocarbon profile of the Agbabu natural bitumen as a function of the period of irradiation with sunlight is as given in Table 2. The total concentration of polycyclic aromatic hydrocarbons (TPAH) in one month irradiated sample of the bitumen increased compared to the concentration of TPAH in the non-irradiated sample (control). However, the reverse was the case for the samples of the bitumen irradiated for three and six months (Table 2). This suggests that aromatization might have occurred at the early stage (one month) of photolysis, while at longer period of exposure (3 and 6 months), the aromatic moiety was broken and/or volatilized and this led to a decrease in the total concentration of polycyclic aromatic hydrocarbons.

The distribution of individual polycyclic aromatic hydrocarbons (PAHs) in the samples of bitumen irradiated with sunlight was also found to be at variance with the distribution of PAHs in the control sample. The distribution of the PAHs in the irradiated samples was found to vary with the period of irradiation. For instance, the concentration of naphthalene (433 μg/g) in one month irradiated bitumen sample is greater than the concentration of naphthalene (394 μg/g) in the control sample. However, the concentration of this compound (naphthalene) in the bitumen samples irradiated for three and six months is below detection limit (10^{-5} μg/kg). The non-irradiated samples of the bitumen and sample irradiated for one month are dominated by 2- and 3-rings PAHs. Whereas the bitumen sample irradiated for three and six months are dominated by 3-rings PAHs and some quantities of 4- and 5-rings PAHs (Figure 1).

Table 2. Profile of polycyclic aromatic hydrocarbons of Agbabu natural bitumen at different period of exposure to sunlight.

S/N	Compound (μg/g)	Period (months) of exposure of PFB to sunlight			
		0	1	3	6
1	Naphtalene	394	433	< 10^{-5}	< 10^{-5}
2	Acenaphthylene	< 10^{-5}	< 10^{-5}	< 10^{-5}	< 10^{-5}
3	Acephthene	15.8	24.1	40.4	< 10^{-5}
4	Fluorene	134	95.6	158	418
5	Phenanathrene	117	125	216	172
6	Anthracene	8.29	32.0	26.3	24.8
7	Fluoranthene	27.0	13.4	25.7	8.60
8	Pyrene	< 10^{-5}	10.56	20.05	< 10^{-5}
9	Benzo (a) anthracene	< 10^{-5}	< 10^{-5}	30.3	14.6
10	Chrysene	11.8	< 10^{-5}	26.93	< 10^{-5}
11	Benzo (k) fluoranthene	< 10^{-5}	< 10^{-5}	20.04	< 10^{-5}
12	Benzo (b) fluoranthene	< 10^{-5}	< 10^{-5}	29.09	< 10^{-5}
13	Benzo (a) pyrene	< 10^{-5}	< 10^{-5}	16.18	< 10^{-5}
14	Indeno (1, 2, 3-cd) pyrene	< 10^{-5}	< 10^{-5}	< 10^{-5}	< 10^{-5}
15	Dibenzo (a, h) anthracene	< 10^{-5}	< 10^{-5}	< 10^{-5}	< 10^{-5}
16	Benzo (g, h, i) perylene	< 10^{-5}	< 10^{-5}	< 10^{-5}	< 10^{-5}
	TPAH	708	733	609	638

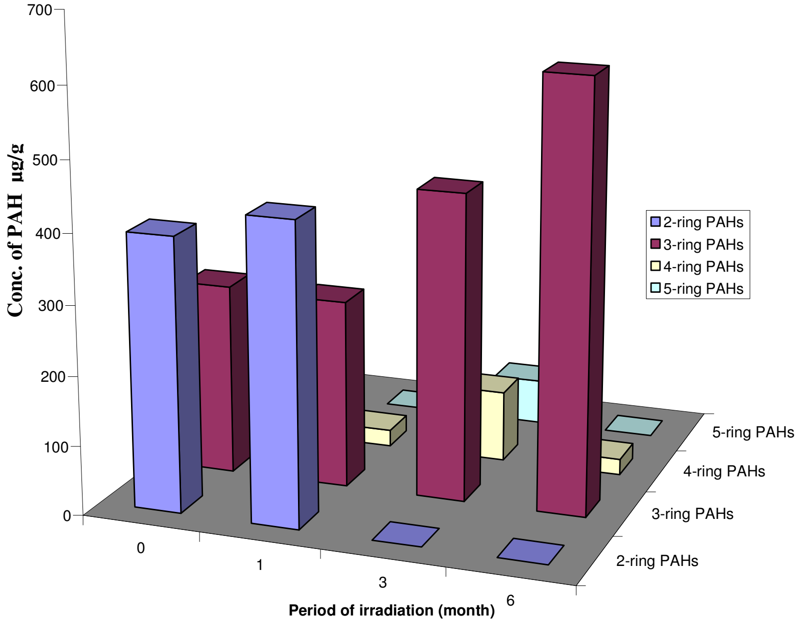

Figure 1. Distribution pattern of different groups of PAHs in control and solar irradiated Agbabu bitumen.

The non-detection of naphthalene in the three and six months irradiated samples may be due to volatilization and/ or decomposition. Some lower members of the PAHs are capable of being volatilized or decomposed by sunlight [17]. As the ambient maximum temperature of the experimental site was 35 °C coupled with an average monthly daily global solar irradiation of 4.97 kwh/m^2/day [18], the volatilization and/or decomposition of some of the PAHs in the bitumen is a possibility.

The relatively high concentration of TPAH found in one-month irradiated sample might be due to aromatization of some saturated hydrocarbons in the bitumen and by inference, this might account for the reduction of the total saturated hydrocarbons as previously observed (Table 1). Some of the PAHs found in the irradiated samples but not found in the control sample, might be products of re-arrangement of some saturated hydrocarbons (such as naphthene) to PAHs. Naphthene in petroleum fractions is known to be converted to high octane aromatics through reforming process [19]. It is also possible that some of the new PAHs found in the irradiated samples are products of hydrocarbon fragmentation caused by sunlight. Such fragments are capable of interacting with each other through radical recombination to form higher molecular weight polycyclic aromatic hydrocarbons [20-22].

CONCLUSIONS

Exposure of Agbabu natural bitumen to sunlight caused a decrease in its total aliphatic hydrocarbons. Distribution of individual aliphatic hydrocarbon was also found to vary with extent of irradiation of the bitumen with sunlight. The polycyclic hydrocarbon profile of the bitumen was also found to depend on the period of exposure of sunlight volatilization, cracking and recombination of cracked products. The changes in the composition of the bitumen will, no doubt, reduce its strength. A reduction in strength will definitely increase the rate of ageing of the bitumen.

REFERENCES

1. Arie N. *Am. Ass. Petrol. Geo. Bull.* **1978**, 62, 837.
2. Smart, N.U. *Environmental Management and Protection*, 1st ed., Precision Printers & Publishers: Enugu, Nigeria; **1978**; pp 8-35.
3. Brandt, H.C.A.; Degriot, P.C. *Water. Res.* **2001**, 35, 4200.
4. Sparlin, R. *Proc. Am. Soc. Testing Materials* **1958**, 58, 1316.
5. Montepera. A.; Santugata, E.; Tosi. G. Photochemical degradation of pure bitumen by U.V. radiation. WWW.uniprint/arpa/dipcia/felice-files Articoli/Guilianiad Montepra- minsk **1999**; accessed on May 7, 2007.
6. Kovaleva, O.V.; Golubeo, Ye.A. *Geophysical Research Abstract* **2005**, 7, 01487.
7. Sonibare, O.O.; Egashira, R.; Adedosu, T.A. *Thermochim. Acta* **2003**, 405, 195.
8. Ekweozor, C.M.; Nwachukwu, J.I. *Ass. Petrol. Exp. Bull.* **1989**, 4, 82.
9. Oluwole, F.F.; Adegoke, O.S.; Kehinde, L.O.; Borishade, A.B.; Ako, B.D.; Ajayi, T.R.; Enu, E.L.; Nwachukwu, J.I.; Coke, S.T.L.; Wallace, D.; Asubiojo, O.I.; Ogunsola, O. *Proceedings of 3rd International Conference on Heavy Crude and TarSands*, Long Beach, California; **1985**; p 373.
10. Adegoke, O.S. *Geology and Reserve Estimate*, Unpublished Report, Geological Consultancy Unit, University of Ile-Ife, (Now Obafemi Awolowo University, Ife), Nigeria, **1980**; pp 126.
11. Olajire, A.A.; Alade, A.O.; Adeniyi, A.A.; Olabemiwo, O.M. *J. Environ. Sci. Health Part A* **2007**, 42, 1043.
12. Olajire, A.A.; Olujobade, M.R.; Olabemiwo, O.M. *Int. J. Environ. Studies* **2008**, 65, 769.
13. Olabemiwo, O.M.; Adediran, G.O.; Adekola, F.A.; Olajire, A.A. *Science Focus* 2008, 13, 37.
14. Rubinstein, I.; Strauz, O.P. *Geochim. Cosmochim. Acta* **1979**, 43, 1887.
15. Bahl, B.S.; Tuli, G.D.; Bahl, A. *Essential of Physical Chemistry*, Chand and Company Ltd.: New Delhi; **2004**; pp 835-845.
16. Rohatgi-Mukhorjee, K.K. *Fundamentals of Photochemistry*, New Age International Publishers: New Delhi; **2006**; pp 243-254.
17. Cer Niglia, C.E. *Bidegradation* **1992**, 3, 351.
18. Ojosu, J.O. *Solar Radiation Distribution Maps of Nigeria*, Nigerian Building and Road Research Institute (NBRRT): Lagos, Nigeria; **1988**; Report No 11; p 10.
19. Stern, J.P.; Stern, E.S. *Petrochemical Today: Studies in Chemistry*, No. 5, Edward Arnold Ltd.: London; **1971**; pp 55-66.
20. Sullivan, R.F.; Boduszynski, M.M.; Fetzer, J.C. *Energy and Fuels* **1989**, 3, 603.
21. Guerin, M.R.; Epler, J.L.; Griest, W.H. *Polycyclic Aromatic Hydrocarbons from Fossil Fuels Conversion Processes* in *Carcinogenesis*, James, P.W.; Freudenthal, R.I. (Eds.), Vol. 3, Raven Press: New York; **1978**; pp 21-33.
22. Jian-hua, Y.; Xiao-fang, Y.; Xiao-dong, L.; Ming-jiang, N.; Xue-feng, Y.; Ke-fa, C. *Zhejiang Univ. Sci.* **2004**, 5, 1554.