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Compositional Changes in Aliphatic and Aromatic Fractions of Agbabu Natural Bitumen under Low Temperature Heating.

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ABSTRACT

The compositions of aliphatic and polycyclic aromatic hydrocarbons in Agbabu natural bitumen (ANB) sample subjected to heating at low temperatures were examined. The raw flow type of ANB was obtained from the observatory well in Agbabu, and subsequently purified. The purified sample was divided and each division heated in an air oven for five hours at a specific temperature. The heated samples were cooled, separated and their aliphatic and polycyclic aromatic hydrocarbons contents were quantified using gas chromatograph coupled with flame ionization detector (GC-FID). The total aliphatic hydrocarbons (TALPH) found in the unheated sample of the bitumen was 484 g/kg, but samples subjected to heating at 50, 70, 90, 100, 110, 120 and 140°C contained 484, 467, 462, 420, 414, 388 and 350 g/kg respectively. Similarly, the total polycyclic aromatic hydrocarbons (TPAHs) in the control sample was 708 µg/g while samples heated at 50, 70, 90, 100, 110, 120, 140 and 160°C contained 600, 523, 387, 307, 245, 213, 168 and 689 µg/g respectively. Distribution of these hydrocarbon compounds in the unheated sample was at variance with what was found in the heated samples. This implies that exposure of ANB to heating at low temperatures is sufficient enough to qualitatively and quantitatively alter the composition of the aliphatic and polycyclic aromatic hydrocarbons of the bitumen.

Keywords: Agbabu natural bitumen, Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, Heating, Low Temperatures

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INTRODUCTION

Bitumen is a mixture of organic liquids that is viscous, black and sticky. It is a complex mixture of high boiling point range of compounds and molecules with a relatively low hydrogen – to-carbon ratio [1]. Basically, bitumen consists of two groups and normally separated to four classes. Applications of bitumen is found in many fields ranging from its use as a refinery feed stock, binder in the construction of highways and runways, production of bituminous roofing sheet, just to mention but a few. Most of these applications is based on the viscoelastic property of the bitumen [2]. This property in turn depends on the constituents of bitumen. Compositionally, bitumen is a complex system made up of a mixture of asphaltenes, saturates, aromatics and resins. In this, there exists a delicate balance of polar to non polar, homogeneous to heterogeneous, small compounds to large compounds and aromatics to paraffin compounds among these constituents [3]. This delicate mixture balance plays a very important role in the stability and hence the viscoelastic property of bitumen. Any alteration in the chemistry of this mixture leads to incompatibility, the consequence of which is poor performances and reduced durability. Heat, sunlight, moisture are some factors which are capable of altering the balance between the constituents of bitumen. It has been reported that exposure of bitumen to sunlight, oxygen, heat and uv light lead to changes in the physical and chemical structure of bitumen [4-6]. These changes are deteriorating and are collectively termed ageing [7]. Temperature has a great influence on the physical state of bitumen as it affects its flow, consistency and brittleness. The semi- solid bitumen gradually changes to liquid as temperature increases. Conventional study of effect of temperature examines the effects of heat on the whole bitumen and its effects on the engineering properties of the bitumen. The rolling thin-film oven (RTFO), ASTM D-2872 test is the internationally and most commonly used laboratory method of investigating the effects of heat on bitumen. The test simulates the changes in properties of bitumen during hot mixing in production, laying and compaction of asphalt mixture [8]. Reports of detailed studies on the effects of heat at low temperature on the constituents of bitumen appears to be scanty. This study however, deals with compositional changes in aliphatic and polycyclic aromatics hydrocarbons constituents of maltene of ANB at temperature range of 50-160°C. Processing of bitumen for asphalt pavement is carried out at temperature range of 45-200°C. Hence this study gives an analytical profile of aliphatic and polycyclic aromatics hydrocarbons in bitumen during the hot mixing.

MATERIALS AND METHODS

Sample collection and Preparation

The bitumen sample (flow type) was obtained in 2007 from one of the observatory wells in Agbabu. Agbabu is a village in Ondo state Nigeria, that lies at Latitude 6°17' 03" and Longitude 4° 49' 12". The sample was immediately transported to laboratory for analysis, where the samples was purified as described in one of our earlier studies on Agbabu bitumen[9].

Heating of the bitumen

The purified bitumen sample (10g) was weighed into 250mL beaker (Borosilicate) and placed in an air-oven which had earlier been set at appropriate temperature of interest. The sample was withdrawn after it had been heated for Five hours, placed in a desiccators, until further analysis.

Seperation of Heated Bitumen

The cooled heated sample was fractionated into maltene and asphaltene and maltene further fractionated into saturated and aromatics as described in our earlier study [10].

Gas Chromatographic Analysis

The gas chromatographic analyses of aliphatic and aromatic fractions were carried out with a 5890 series II Hewlett Packard gas chromatograph equipped with flame ionization detector (FID). A fused silica capillary column (30m × 0.25μm) coated with 0.25μm film of HP-5 was used. The chromatograph was powered with HPCHEM software. The GC instrumentation for the saturate fraction is as follows: the column temperature started at 60°C, held isothermally for 2 minutes and then increased to 260°C at the heating rate of 10°C/min for 20 minutes. The temperature increased to 320°C at a rate of 12°C/min for 5 minutes and held at this temperature for 2 minutes. Nitrogen was used as carrier gas with a flow rate of 30psi. Hydrogen and air flow rates were 22 and 28psi respectively. Injector and detector temperatures were 300 and 320°C respectively. 2μL of sample was injected. For the aromatic components, the column temperature started at 68°C and held at this temperature for 2 minutes. It was then increased to 260°C at a rate of 12°C/min for 16 minutes and held at 260°C for 4 minutes and thereafter increased to 320°C at a rate of 15°C/minutes for 4 minutes. It was held at 320°C for 8 minutes. The carrier gas was nitrogen at flow rate of 35 psi. Hydrogen and air were supplied at 25 and 30 psi respectively. Injector and detector temperatures were 300 and 320°C respectively and the volume of sample injected was 2μL. Identification of the PAHs was based on comparison of the retention times of the peaks from sample with those obtained from the standard mixture of PAHs (supplied by instrument manufacturer) and from spiked samples analysed under the same conditions. Quantification was based on external calibrations curves prepared from standard solutions of each of the PAHs.

RESULTS AND DISCUSSION

The profiles of odd-and even –numbered aliphatic hydrocarbons in the samples of ANB heated for five hours at different temperatures are as presented in Tables 1 and 2. Figure 1 shows the effect of temperature on the sum of all Aliphatic Hydrocarbons, sum of all Odd- Carbon Atoms and sum of all Even- Carbon Atoms in the bitumen. The distributions of odd-and even- carbon atoms in the unheated sample were at variance with what was found in heated samples (Tables 1 and 2). This shows that heat has caused redistribution of these carbon atoms. It can also be seen clearly from Figure 1, that there is a gradual decrease in the total aliphatic hydrocarbons (C₁₁ – C₃₀) in the ANB as the temperature

increases. However, the pattern changes in case of sample of the bitumen heated at 160°C. The decrease in total aliphatic hydrocarbons in the bitumen is expected as increase in temperature will cause the loss of some volatile materials [10]. Decomposition of lower molecular mass aliphatic hydrocarbons of the bitumen to volatile compounds with subsequent loss is another reason which may be adduced for the reduction in total hydrocarbons content as temperature increases.

An earlier study by Olabemiwo et al.[11] showed that the TALPH in bitumen exposed to solar radiation also decreased with time of exposure. However, the rate of degradation of TALPH under heating appears to be faster than when the bitumen was exposed to solar radiation. Exposure of the bitumen to solar radiation for three months reduced TALPH from 485 to 394g/Kg, whereas heating at 120°C for five hours reduced same quantity of TALPH to 350g/Kg. Similarly, exposure of Agbabu bitumen to ultraviolet radiation (365nm) for seven hours caused the TALPH in the bitumen to be reduced from 620 to 403g/kg.[12]

The source of increase in total aliphatic hydrocarbons in sample of ANB heated at 160°C may be from decomposition products. Thermal cracking of high molecular mass hydrocarbons are known to produce lower molecular mass hydrocarbons [3,8]. Since the bitumen contains higher hydrocarbon compounds with more than thirty carbon atoms [13,14]. The increase in the total hydrocarbon in sample of ANB heated at 160°C may therefore be attributable to thermal cracking of some higher molecular mass hydrocarbons in the bitumen. A substantial increase in quantity of C₁₁, C₁₃ and C₂₉ was found in heated samples of ANB compared to the control sample (Table 1). An exception to this was the sample heated at 160°C in which C₂₉ was not detected. Aliphatic hydrocarbon with C₃₀ was not detected in control sample and samples heated at 140 and 160°C. A very relative small quantity of this hydrocarbon (C₃₀) was found in samples of the bitumen heated at 50, 100, 110, and 120°C (Table 2).

The compositions of PAHs in ANB heated at different temperatures for five hours are presented in Table 3. The effect of temperature on the sum of polycyclic aromatic hydrocarbons (PAHs) found in the bitumen samples heated at different temperatures are as presented in Figure 3. The total polycyclic aromatic hydrocarbons (TPAHs) in the samples of ANB decreases as the temperature at which the sample is heated increases. However, the quantity of TPAHs in the sample heated at 160°C is very close to what was observed in the control sample (i.e. sample of the bitumen kept at room temperature 27 ± 2°C). The decrease in the TPAHs in the samples of the bitumen heated at different temperatures is due to the loss of the lowest member of the PAHs (i.e. Naphthalene) as the temperature increases. Incidentally, the proportion of the naphthalene in the TPAHs in the bitumen samples is the highest. Hence, the gradual reduction in the TPAHs as the temperature increases is observed.

At 160°C, in addition to normal loss of the naphthalene and because of the high temperature, there was probably another process which generated naphthalene. The generation of naphthalene at this temperature (160°C) exceeded its loss. This probably accounts for the relatively high quantity of naphthalene found in the sample of ANB heated at 160°C. This inference is supported by the fact that pyrosynthesis of some unsubstituted

PAHs series from organic matter heated at high temperature is possible [15]. Heat did not only affect the total PAHs in ANB, but their distribution was also affected. The distribution of the PAHs in the bitumen as affected by heat at different temperatures is as presented in Tables 3 and 4. Benzo (a) anthracene and Pyrene were not present in the unheated PFB, but were found in various quantities in the samples of the bitumen heated at different temperatures. These compounds are likely to be the products of pyrosynthesis. Low molecular weight PAHs such as naphthalene are capable of undergoing pyrosynthesis via Zizag addition process to form higher molecular mass PAHs [15]. Another notable effect of heat on PAHs in ANB is seen on benzo (b) fluoranthene and benzo (k) fluoranthene. These compounds were not found in samples of the bitumen heated at 70, 120 and 140°C. But none of these compounds was detected in the control and other samples of ANB heated at 90, 100, 110 and 160°C. High molecular weight (5- and 6- ring PAHs) were not detected in the heated samples except B(k)F which was detected in samples heated at 100 and 120 °C. This finding is at variance with our earlier studies [10,11] where exposure of bitumen to solar and ultraviolet(365nm) radiations led to the formation of 5- and 6- ring PAHs. The distribution pattern of various groups/types of PAH in the bitumen samples at different temperatures is shown in Table 4. Only one type of 2-ring (Naphthalene) PAH was detected in the unheated and heated samples. The same trend was observed in case of 3-ring PAH; five different types were detected in both unheated and heated samples. In case of 4-ring PAHs, four different types were found in the all the samples except in unheated and sample heated at 70°C where 2 and 3 types of 4-ring PAHs were detected respectively. 5-ring PAHs were only detected in samples heated at 50, 70, 120 and 140°C respectively.

The above discussions have shown that the ANB samples heated at different temperatures had their compositions affected. The heat affected the hydrocarbon compounds in the ANB in terms of quantity and quality. One can therefore, say that the composition and structure of PAHs in ANB is a function of temperature. It thus required that importance should be attached to temperatur regulation when producing asphalt pavements.

Table 1: The Profile of Odd-Carbon Atoms in the Samples of ANB at different Temperatures

Compound	Concentration of Aliphatic Hydrocarbons ANB g/Kg								
	27°C	50°C	70°C	90°C	100°C	110°C	120°C	140°C	160°C
C ₁₁	37.14	273.00	262.63	261.38	234.77	189.17	172.41	100.95	245.47
C ₁₃	25.08	72.32	75.62	29.47	25.40	78.91	74.59	62.85	78.20
C ₁₅	61.21	28.73	36.55	35.82	34.26	25.52	23.72	28.91	41.40
C ₁₇	5.85	5.76	5.29	5.37	4.93	3.84	3.60	5.63	3.86
C ₁₉	4.35	3.39	3.14	3.17	2.97	2.37	2.17	3.23	4.79
C ₂₁	25.14	3.30	3.06	3.30	2.97	3.90	3.68	7.00	9.80
C ₂₃	3.06	1.87	1.74	1.89	1.73	1.61	1.53	2.50	1.22
C ₂₅	8.76	5.52	4.62	5.60	4.94	5.52	4.09	7.06	2.76
C ₂₇	10.78	6.88	6.56	9.06	8.17	9.00	7.01	14.10	1.28
C ₂₉	0.10	0.63	0.71	0.82	0.66	0.77	0.87	0.63	n.d

n.d.= Not Detected

Table 2: The Profile of Even-Carbon Atoms in the Samples of ANB at different Temperatures

Compound	Concentration of Aliphatic Hydrocarbons ANB g/Kg								
	27°C	50°C	70°C	90°C	100°C	110°C	120°C	140°C	160°C
C ₁₂	0.49	3.12	2.89	2.90	2.51	1.89	1.93	1.19	2.04
C ₁₄	1.66	3.80	3.52	3.49	3.11	2.63	2.46	2.72	2.52
C ₁₆	2.86	3.56	3.28	3.28	3.01	2.35	2.19	2.95	2.30
C ₁₈	3.99	3.47	3.17	3.24	3.00	2.47	2.31	3.62	5.25
C ₂₀	11.45	7.62	6.97	7.24	6.70	6.01	5.67	9.81	4.79
C ₂₂	15.53	9.67	8.99	9.46	8.74	5.85	7.24	11.75	5.89
C ₂₄	210.24	25.29	19.04	38.72	35.33	48.40	48.84	50.92	67.30
C ₂₆	49.04	20.08	17.53	33.30	30.65	18.50	18.83	27.75	11.35
C ₂₈	8.00	5.98	1.72	5.15	6.28	5.40	4.71	6.86	0.15
C ₃₀	n.d	1.4X10 ⁻⁵	n.d	n.d	1.310 ⁻⁵	5.3X10 ⁻⁵	5.3X10 ⁻⁵	n.d	n.d

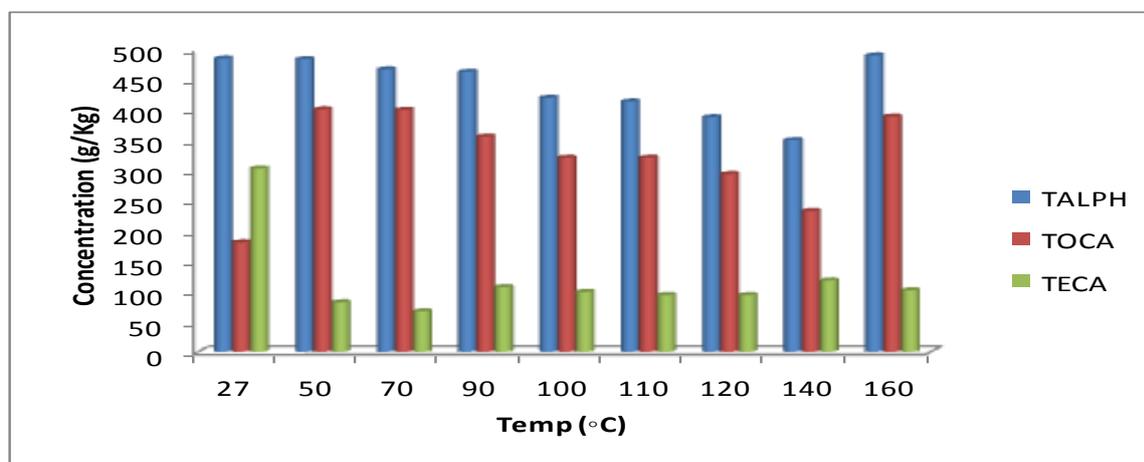


Figure 1: Effect of Temperature on TALPH, TOCA and TECA

TALPH= Total aliphatic hydrocarbon in ANB, TOCA = Total Odd- Carbon Atoms in ANB, TECA= Total Even-Carbon Atoms in ANB

Table 3: Composition of Polycyclic Aromatic Hydrocarbons of ANB at Different Temperatures

Compound	Concentration of PAH (µg/g)								
	27°C	50°C	70°C	90°C	100°C	110°C	120°C	140°C	160°C
Naphthalene	393.77	376.40	323.79	162.87	126.59	117.03	84.11	52.43	303.82
Acenaphthylene	0.00	0.00	0.000	0.00	0.00	0.00	0.00	0.000	13.14
Acephthene	15.79	18.37	18.46	6.73	5.88	6.33	3.02	3.62	26.21
Fluorene	133.50	77.57	66.16	87.93	64.75	45.64	41.55	30.32	119.92
Phenanathrene	117.40	56.35	49.61	82.30	61.96	40.48	39.28	31.48	111.44
Anthracene	8.29	22.24	26.54	14.04	11.80	10.84	7.66	7.59	41.08
Fluoranthene	26.98	7.34	6.13	7.75	6.44	4.35	8.52	13.89	37.19
Pyrene	n.d	21.10	17.16	14.70	12.86	9.47	8.85	11.53	21.27
Benzo(a) anthracene	n.d	8.85	7.56	10.55	8.55	5.82	6.73	6.60	6.40
Chrysene	11.77	7.34	6.12	n.d	8.47	5.12	6.19	6.19	8.50
Benzo(b) fluoranthene	n.d	1.72	1.96	n.d	n.d	n.d	4.10	1.66	n.d
Benzo(k) fluoranthene	n.d	2.68	n.d	n.d	n.d	n.d	2.91	2.59	n.d

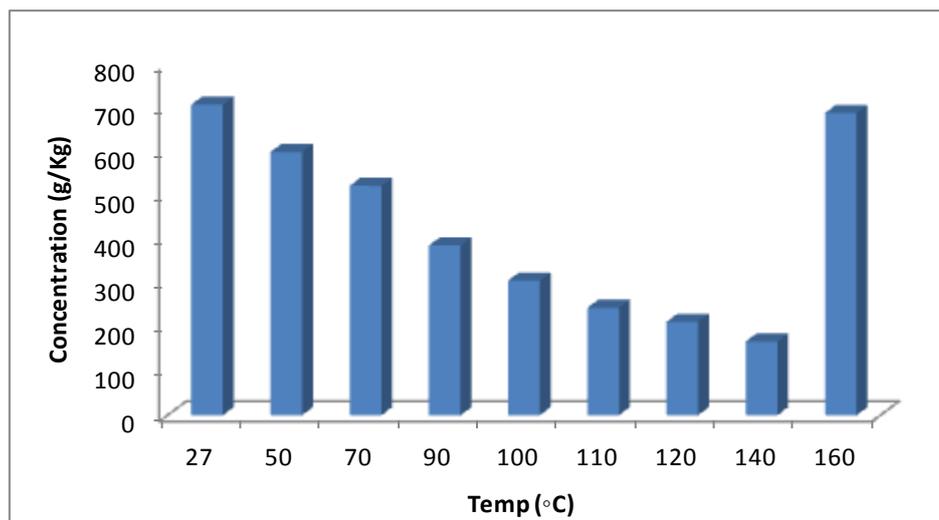


Figure 2: Effect of Temperature on TPAHs in ANB

Table 4: Effect of Heat on Groups Distribution of PAHs in ANB

Group of PAHs (No of rings)	Concentration of PAH (µg/g)								
	27°C	50°C	60°C	70°C	90°C	100°C	120°C	140°C	160°C
2	393.77 (1)	376.40 (1)	323.79 (1)	162.87 (1)	126.59 (1)	117.03 (1)	84.11 (1)	52.43 (1)	303.82 (1)
3	274.98 (5)	174.54 (5)	160.77 (5)	191.00 (5)	144.39 (5)	103.29 (5)	91.51 (5)	73.01 (5)	311.79 (5)
4	38.75 (2)	44.63 (4)	36.97 (4)	33.00 (3)	36.32 (4)	24.76 (4)	30.29 (4)	38.21 (4)	73.36 (4)
5	Nil	4.40 (2)	1.96 (1)	Nil	Nil	Nil	57.01 (2)	4.25 (2)	Nil

* Value in parentheses denotes number of PAHs in the samples

CONCLUSION

Heating of Agbabu natural bitumen at low temperatures (27- 140°C) for five hours caused a decrease in the quantity of aliphatic and polycyclic aromatic hydrocarbons of the bitumen. A redistribution of the abundance of each hydrocarbon compound in the fractions was also noticed in the samples heated at low temperatures. However, sample heated at 160°C for five hours experienced an increase in its aliphatic and aromatic fractions. It is suggested that the decomposition of asphaltene component of the bitumen might have begun at temperature (160°C) leading to generation of more aliphatic and polycyclic hydrocarbons.

This finding has shown that heat at low temperature is capable of affecting the balance between the various fractions in the Agbabu bitumen. Since a balance between the constituents groups in the bitumen is a prerequisite for bitumen performance and durability, it thus became imperative to pay very careful attention to temperature regulation while preparing pavement from Agbabu natural bitumen.



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