Effect Of Ultraviolet Radiation On The Aliphatic And Polycyclic Aromatic Hydrocarbon Profiles Of Agbabu Natural Bitumen

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Abstract: The quality of wide a variety of synthetic or naturally occurring materials which are used for outdoor applications are known to be adversely affected by environmental factors. These materials absorb solar ultraviolet radiation leading to changes in their structures and compositions. The consequences of these changes lead to degradation of the materials. Bitumen is one of the materials which is mostly used in outdoor applications, making it to be routinely exposed to sunlight during use. Sequel to this, the effects of ultraviolet radiation on the aliphatic and polycyclic aromatic hydrocarbon profiles of Agbabu natural bitumen found in South Western Nigeria were investigated. The bitumen sample was exposed to ultraviolet radiation (365nm) for seven hours and samples were withdrawn and analyzed at intervals of one, three and seven hours respectively. The irradiated sample was separated into the maltenes and asphaltene fractions and the maltenes fractions further subjected to column chromatography to separate it into aliphatic hydrocarbon, polycyclic aromatic hydrocarbon and polar compounds. The aliphatic and polycyclic aromatic hydrocarbon fractions were analyzed using Gas chromatography (GC). Results of GC analysis showed that the total aliphatic and aromatic hydrocarbon contents in the ultraviolet irradiated samples were found to be less than the total aliphatic and aromatic hydrocarbon contents of the unirradiated sample. The results indicates that there was a decrease in the amount of both the total aliphatic hydrocarbon content and polycyclic aromatic hydrocarbon content of the Agbabu Natural Bitumen as a result of exposure to ultraviolet radiation.

Key words: Bitumen, Agbabu, ultraviolet radiation

INTRODUCTION

Bitumen is a semi-solid material consisting mainly of hydrocarbon compound. It is called natural bitumen when it occurs naturally and artificially when it is produced from certain crude oil by distillation (Polacco et al., 2006). It consists mainly of asphaltene and maltenes fractions. The asphaltene fraction is colloidally dispersed into an oily matrix constituted by saturates, aromatics and resins which make up the maltenes fractions (Leusseur, 2009). The chemical composition of bitumen depends primarily on its crude source and processing. Bitumen physicochemical behaviour depends on the relative concentration of its different fractions and its mechanical properties and chemical reactivity are thus strongly affected by variation in its composition (Becker et al., 2003, Igbal et al., 2006) which in turn can largely affect its application. Bitumen has a wide range of engineering applications which include road construction, roofing of residential and industrial buildings, construction of dams and airways tarmac (Arie, 1978). However, the use of bitumen in road construction has been questioned because of the fact that it is normally brittle and hard in cold environments and soft in hot environment (Redelius, 2004), which leads to different road distresses. These road distresses which include rutting at high temperatures, fatigue cracking and thermal cracking may be overcome by modification of bitumen with polymers (Morrison et al., 1994, Wypych, 1990). Also bitumen is very difficult to characterize and reproduce poorly in viscosity and ductility measurements because it often hardens over a period of time when heated and poured (Masson et al., 2005)

Environmental factors such as water, heat and sunlight are known to have deteriorating effects on many natural and synthetic materials. The useful life time of such materials is a function of environmental factors. As a result of the large application of bitumen, it is important to understand the effects of environmental changes/factors on bitumen composition. Bitumen has been reported to be more applicable when modified with other substances to improve its performance. It has been modified with an elastomer (Kraus, 1982, Polacco et al., 2004), a plastomer (Airey, 2003, Giavarini et al., 1996, Jew et al., 1986, Marthi Nadal-Jason et al., 2006), a thermostat (Lee et al., 1997, Petrossi et al., 1972), sulphur (Fritschy et al., 1981, Olabemiwo et al., 2010) and mineral acid (Giavarini et al., 2000). Previous Studies have evaluated the effect of sunlight on the infrared spectrum and compositional pattern of natural bitumen (Newmann, 1998, Olabemiwo et al., 2008) which could affect its application and the level of its modification. Also, it is often very difficult to predict the effect of a particular modifier on bitumen and also to determine in advance the level of modifier required to achieve a given characteristic (Masson, 2008) when structural changes occur in bitumen as a result of environmental
changes. Thus, the need to study the extent of structural changes that takes place in bitumen when exposed to environmental factors in form of radiations. As part of efforts to studying the effects of different radiation on the composition and structure of Agbabu natural bitumen, the effect of ultraviolet radiation on the bitumen has been examined in this study.

**Experimental:**

Sample Collection & Purification

Sample of Agbabu natural bitumen was obtained from one of the observatory bitumen wells in Agbabu, Ondo State, Nigeria. The raw natural bitumen was purified as described by Olabemiwo et al (2008)

Irradiation Of Bitumen Samples:

10g of purified bitumen sample was accurately weighed into a dried and pre-weighed petri dish (pyrex). The sample was spread to form a thin layer of about 0.1cm thickness. The petri dish containing the bitumen samples was then exposed to ultraviolet radiation (wavelength). The exposure was carried out for a period of seven hours. At intervals of one, three and seven hours, part of the sample was withdrawn from the petri dish into a labeled sample bottle for further analysis. Out of the withdrawn sample, 0.4g of the sample was accurately weighed into a beaker and 20cm³ of iso-octane (2,2,4-trimethylpentane) added to precipitate out the Asphaltene component. The resultant solution was filtered using filter paper. The residue (asphaltene) was washed thrice with 20ml iso-octane. The filtrate (maltene) was collected into a sample bottle.

Separation of the maltene fraction into saturated hydrocarbons, polycyclic aromatic hydrocarbons and polar compounds was achieved by column chromatograph as described by Olabemiwo et al (2008)

Gas Chromatographic Analysis:

A 5890 series Hewlet Packard gas chromatograph equipped with flame ionization detector was used for the gas chromatographic analysis. A fused-silica capillary column(30m x 0.25um i. d.) stationary phase coated with 0.25m film of HP-5 stationary phase was employed for the analysis. For saturated hydrocarbons, 2uL of sample was injected. The column temperature started at 60°C, held isothermally for 2 minutes and then increased to 200°C at the heating rate of 10°C/ min for 20 minutes. It was held at this temperature for 2 minutes and then increased to 320°C at the heating rate of 12°C/min for 5 minutes and held at this temperature for 2 minutes. Nitrogen was used as carrier gas at a pressure of 30 psi. Hydrogen and air were introduced at pressures of 22 and 28psi respectively. Injector and detector temperatures were 300 and 320°C respectively.

The column temperature for the aromatic hydrocarbon started at 68°C and was held at this temperature for 2 minutes, it was later increased to 260°C at heating rate of 12°C/min for 16 minutes. It was held isothermally at 260°C for 4 minutes and then increased to 320°C at heating rate of 15°C/min for 4 minutes and held at this temperature for 8 minutes. The carrier gas used is nitrogen at a pressure of 35 psi. Hydrogen and air were introduced at pressures of 25 and 30 psi respectively. The injector and detector temperatures were 300 and 320°C respectively and the volume of sample injected was 2 uL. 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 Agbabu natural bitumen at various period of its exposure to ultraviolet radiations is presented in Table 1 and Figure 1. It is evident from the figure 1 that there were compositional changes in the structure of the bitumen as a result of the ultraviolet radiation. The total aliphatic hydrocarbons in the untreated sample were found to be 620 g/kg. This was found to decrease as the period of exposure of the bitumen to ultraviolet radiation increased. The Carbon Preference Index (CPI) for the non-irradiated sample and samples irradiated with ultraviolet radiations for one, three and seven hours respectively were found to be greater than 2 (CPI >2) indicating a predominance of odd-numbered carbon atoms for both the non-irradiated and irradiated bitumen sample. It was observed that the Carbon Preference index for the irradiated samples were greater than that of the non-irradiated bitumen samples suggesting possible increase in odd-numbered carbon atoms as a result of exposure to ultraviolet radiation.

The sum of concentrations of aliphatic compounds in the bitumen decreased as the time of exposure to UV radiation increased. The concentration of individual aliphatic compound (C1-C29) detected in the bitumen sample decreased in the first three hours of exposure to UV radiation. However, there was a slight increase in concentrations of these compounds (except C12 and C24) in the sample of the bitumen exposed to UV radiation for seven hours. For instance, the concentration of C26 compounds (Hydrocarbons compounds with 26-carbons atoms) in the unirradiated sample of the bitumen was 39.15g/kg whereas, in samples exposed to UV radiation for 1, 3 and 7 hours, the concentrations of these C26 compounds were 25.93, 17.22 and 26.22g/kg respectively.

Aliphatic compounds with C12 and C24 maintained a gradual decrease in concentrations throughout the period of irradiation. The concentrations of C12 compounds were 3.78, 2.97, 2.34 and 2.14g/kg in the control
sample, and one, three and seven hours irradiated samples respectively. The only plausible explanation for the decrease in concentrations of these hydrocarbon was cracking, while increase in concentration was done to recombination of lower molecular mass hydrocarbons from cracking process. This is in agreement with findings earlier reported by some authors that absorption of solar ultraviolet radiation by some materials lead to their photolytic degradation. (Olabemiwo et al., Stern and Stern 1971)

Table 1: Aliphatic hydrocarbon profile of Agbabu natural bitumen at different time(hr) of exposure to ultraviolet radiation(365nm)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (g/kg)</th>
<th>Period(hours) of exposure of bitumen to ultraviolet radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOCA</td>
<td>421</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>337</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>291</td>
<td>7</td>
</tr>
<tr>
<td>TECA</td>
<td>199</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>163</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>112</td>
<td>7</td>
</tr>
<tr>
<td>CPI</td>
<td>2.12</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2.53</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2.72</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>2.59</td>
<td>7</td>
</tr>
<tr>
<td>TPAHS</td>
<td>620</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>576</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>461</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>403</td>
<td>7</td>
</tr>
</tbody>
</table>

TPAHs: Total aliphatic hydrocarbons, CPI: carbon preference index=TOCA/TECA,
TOCA: Total odd-numbered carbon atoms, TECA: Total even-numbered carbon atoms

Fig. 1: Concentration of total aliphatic hydrocarbon with time of exposure to ultraviolet radiation

The effect of ultraviolet radiation on the polycyclic aromatic hydrocarbon profile of Agbabu bitumen as a function of time of exposure to the radiation is as given in Figure 2 and Table 2. A progressive decrease in the total concentration of the polycyclic aromatic hydrocarbon was evident as the period of exposure to ultraviolet radiation increases. This suggests that there was de-aromatization which resulted in the aromatic moiety being broken and/or volatilized thereby leading to a decrease in the total concentration of the polycyclic aromatic hydrocarbons. Most of the individual polycyclic aromatic hydrocarbons were found to decrease in concentrations as the time of exposure to ultraviolet radiation was increased. The distribution of the concentration of most of the individual polycyclic aromatic hydrocarbons of the irradiated samples had an inverse relationship to the period of exposure to the ultraviolet radiation. Naphthalene, which had the highest concentration in the control sample (0.712g/kg) when compared to all the other polycyclic aromatic hydrocarbons, had its concentration reduced to 0.118g/kg after seven hours of exposure to ultraviolet radiation.

It was also noticed that for both the non-irradiated and irradiated samples, 2 and 3-rings polycyclic aromatic hydrocarbons were in greater dominance when compared to the other polycyclic aromatic hydrocarbons. Acenaphthylene was found to be below the detection limit (10^{-5} g/kg) in the control sample but on exposure to ultraviolet radiation for one hour, a minute concentration (0.00156 g/kg) was observed. However, this compound (acenaphthylene) disappeared as the time of exposure of the bitumen to ultraviolet radiation is increased. Benzo[a]anthracene and Chrysene were also observed to be below the detection limit for the non-irradiated sample but on exposure to ultraviolet radiation were detected at minute concentrations. This could be as result of rearrangement of some saturated hydrocarbons such as naphthenes to polycyclic aromatic hydrocarbons. Reforming processes have been used to produce high octane aromatics from Naphthenes[Stern and Stern, 1971]. Benzo[b]fluoranthene and Benzo[k]fluoranthene were below detection limit after three hours of irradiation but were subsequently detected as the period of exposure is increased. Benzo[a] pyrene and
Dibenzo [a,h] anthracene were below detection limit for both non-irradiated and irradiated samples. Indeno[1,2,3-cd] pyrene and Benzo [g,h,i] perylene were below the detection limit on exposure to ultraviolet radiation.

Table 2: Polycyclic aromatic hydrocarbon profile of Agbabu natural bitumen at different time (h) exposure to ultraviolet radiation.

<table>
<thead>
<tr>
<th>Number of rings</th>
<th>Concentration (g/Kg)</th>
<th>Period(hours) of exposure of bitumen to ultraviolet radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.712</td>
<td>0.255</td>
</tr>
<tr>
<td>3</td>
<td>0.454</td>
<td>0.102</td>
</tr>
<tr>
<td>4</td>
<td>0.041</td>
<td>0.036</td>
</tr>
<tr>
<td>5</td>
<td>0.133</td>
<td>0.004</td>
</tr>
<tr>
<td>6</td>
<td>0.109</td>
<td>0.025</td>
</tr>
<tr>
<td>TALPHs</td>
<td>1.449</td>
<td>0.397</td>
</tr>
</tbody>
</table>

Fig. 2: TPAHs: Total polycyclic aromatic hydrocarbons.

The rate of degradation achieved in this study appeared to be greater than that achieved in the study of Olabemiwo et al (2008) in which the Agbabu bitumen was exposed to sunlight for six months. In this study, within seven hours of exposure of the bitumen to ultraviolet radiation the total concentration of aliphatic hydrocarbons in the bitumen sample had reduced from 620 g/kg to 403 g/kg compared to the reduction from 485 to 392 g/kg in six months on exposure to sunlight as reported by Olabemiwo et al (2008). Also, using ultraviolet radiation alone and within 7 hours of exposure, the degradation of PAHs in Agbabu bitumen was much more rapid and effective than what was earlier reported for sunlight irradiation by Olabemiwo et al (2008). However, six months, solar irradiation of the Agbabu bitumen led to total degradation of all 3 and 4 and 5 rings PAHs in the bitumen. But these 3, 4, and 5 rings PAHs were still present in the sample of the bitumen irradiated with UV radiation for 7 hours. The rapid degradation of PAHs observed in this study is in agreement with the findings of Marti Nadal–Jason et al, (2006) who also observed significant photo degradation rates of PAHs sorbed to an organic solvent.

Conclusion:
The composition of Agbabu bitumen exposed to UV radiation was found to vary with time of exposure. Aliphatic and polycyclic aromatic hydrocarbons components of the bitumen had their concentrations reduced as a result of exposure of the bitumen to UV radiation. This implies that the absorption of UV radiation by the Agbabu bitumen led to the photolytic degradation of the aliphatic and polycyclic aromatic hydrocarbon components of the bitumen. The degradative effects of the UV radiation on Agbabu bitumen were much more than that of sunlight on the bitumen. In view of this, UV radiation may be a useful means of remediating a land polluted with bitumen spill. Extensive investigation into the applicability of UV radiation in environmental remediation of bitumen polluted environment is therefore suggested.
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