

Assessment of Combustion and Pollution Potentials of Premium Motor Spirit [PMS] and Automotive Gas Oil [AGO].

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Abstract

In the past decade, there has been a growing concern over the increase in the use of electric generating sets in Nigeria due to incessant power outages. These sets are either powered by Premium Motor Spirit (PMS) or automotive gas oil (AGO) and their combustion usually generate compounds/products which have serious environmental consequences. To this end, these products were combusted in a specially fabricated combustion chamber in order to determine their pollution potentials. The combustion effluents as well as particulate matter were trapped in dichloromethane and the resulting solution filtered to recover the particulate matter which represents the actual quantity of particulate matter liberated into the atmosphere, when a given quantity of refined product is combusted. PMS yielded 1.9g/l while AGO yielded 2.7g/l of particulate matter. The recovered particulates and combustion residues were separately subjected to soxhlet extraction using dichloromethane as solvent. The extracts and effluents were concentrated and analyzed via flame ionization detector chromatography. The chromatograms show evidence of Polyaromatic hydrocarbons of retention times ranging from 8.800 to 26.999mins. These results obtained go a long way in giving some insights into the extent of pollution generated from the combustion of the selected petroleum products.

Key words: PAHs , Particulates ,PMS,AGO and Effluents ,Extracts.

1.0 Introduction

The term polyaromatic hydrocarbons or polycyclic aromatic hydrocarbons (PAHs) refers to a large class of organic compounds containing two or more fused aromatic rings made up of carbon and hydrogen atoms (May and Wise 1984). Some authors refer to polycyclic aromatic compounds as polycyclic organic matter and then the term “polynuclear” is frequently used for polycyclic as in polynuclear aromatic compounds.

They are formed during incomplete burning of coal, oil, gas, wood, garbage or other organic substances such as tobacco and charbroiled meat (Liste and Alexander 1999; Jones et al. 1989), slow maturation of sedimentary organic matter to yield fossil fuels, e.g. coal and petroleum and rapid aromatization of organic substances in modern sediments. PAHs generally occur as complex mixtures, as part of combustion product such as soot not as single compounds. They occur naturally in crude oil, coal, coal tar, pitch, creosote, asphalt, roofing tar, among others. However, they can be manufactured as individual compounds for research purposes; but not as the mixtures found in combustion products.

Polyaromatic hydrocarbons are found throughout the environment in the air, water, and soil (Baek et al. 1991; Lorber et al. 1994; Yang et al. 1998). They are present in air as vapour or stuck to the surfaces of small solid particles (Schneider et al. 1996) PAHs were the first compounds whose potential carcinogenic effects were discovered. Toxic, genotoxic and mutagenic properties of PAHs have been extensively studied to date (Harvey 1985; Fu et al. 1980; Busby et al. 1984; Busby et al. 1988; Kalf et al. 1997; McConkey et al. 1997; Monson et al. 1999).

2.0 Methodology

2.1 Sampling: - The premium motor spirit (PMS) and Automated gasoline oil (AGO) used for this work were bought from Prince Oil Filing Station at Nsukka, Enugu State, Nigeria.

2.2 The Combustion Equipment:-

The combustion chamber was constructed using gauge 14 (12.74mm) metal sheets and 25mm angle iron bars by welding, a chamber of dimensions 30cm³ x 30cm³ x 30cm³ was constructed. This gave an external volume of 27,000cm³ and internal volume of 330.60cm³. Directly opposite the door, a heat resistant glass was fitted and secured in place with heat resistant fitters. The edge of the door was lined with insulating materials to ensure airtightness and to avoid losing smoke to the atmosphere/environment.

The chamber door has 2 screw nuts that ensured effective tightening. At the top of the chamber, a 4mm internal diameter pipe was fitted and used as delivery tube for the collection of combustion effluents. This delivery tube was in turn connected to five 250cm³ pyrex glass receivers arranged in series, each filled with 200cm³ of dichloromethane, to ensure maximum absorption. A clip was inserted at the end of the last delivery tube to let off air that is free of smoke particles.

At the left hand side of the chamber, 2 inlets approximately 3mm internal diameter allow oxygen and compressed nitrogen gas from a cylinder to be introduced into the chamber.

Inside the chamber, a short four-legged stand with the top made of wire gauze was constructed for placing the crucible containing the already measured fuel samples (PMS and AGO). The gas inlets of oxygen and nitrogen gas terminate under the stand.

2.3 Combustion Equipment:-

100cm³ of Premium motor spirit (PMS) was put in a weighed crucible and placed in the combustion chamber, ignited and burnt.

Nitrogen gas was then used to flush out all the effluent hydrocarbons and residual gases from the combustion chamber into the serially connected dichloromethane trap chambers.

The process was repeated until the measured PMS in the crucible was completely burnt. Residues were left behind in the crucible as well as the combustion chamber. The crucible was cooled and weighed again. The difference in the mass was recorded as mass of residue. This procedure was repeated for AGO.

2.4 Dissolution Of Effluent Hydrocarbons From The Combustion Of Samples In Dichloromethane: -

The effluents suspected to be hydrocarbon and particulates generated from combustion of PMS were delivered through a delivery tube into serially connected receivers each containing dichloromethane. To ensure maximum absorption of each effluent, 200cm³ of dichloromethane, was added to five 250cm³ containers connected in series. The procedure was repeated for AGO

2.6 Recovery Of Particulates: -

The particulates generated during combustion of PMS were recovered by filtering the dichloromethane solution used as trap. An already weighed filter paper was used for filtration. After filtering, the filter paper and particulate were washed thoroughly with dichloromethane, dried (in an oven of temp 120°C) cooled and weighed again. The differences in mass were than recorded. The same procedure was repeated for AGO.

2.7 Soxhlet Extraction Of Residue:-

The particulates recovered from 2.6 above were placed in a thimble, 1 liter of dichloromethane used as extracting solvent was poured into a flask and heated. The vapours rose through the side arm and were condensed in the condenser. The condensed solvent dropped into the thimble/chamber containing the particulate, extracting it by contact. When the level of the liquid rose up to the top of the siphon tube the liquid content was automatically filtered through the thimble and siphoned into the flask. The process was continued for 3 hours. The extract was then concentrated using a rotary/vacuum evaporator. The same procedure was used for both the particulate and residues of AGO.

2.8 Determination Of Polyaromatic hydrocarbons By Gas Chromatography:-

The equipment used was gas chromatography flame ionization detector (Agilent, HP 6890). It has an oven temperature of 280°C. and an inlet temperature of 250°C. Helium was used as the carrier gas at a flow rate of 198psi pressure.

2.8.1 Detector parameters:-

The temperature was 300°C while the gas was hydrogen with a flow rate of 30psi and air with a flow rate of 250psi. The make-up gas is nitrogen at 20psi.

Column :-

The column was filled with highly packed cross linked methyl siloxane model 910192 – 41, with film thickness of 0.25 micrometer. The length is 30 meters, while the face ratio is 320. The column id is 0.32 meter. The standard used was an external standard

2.8.2 Method :-

The standard used was an external standard where 1 micrometer was injected into the injection pot of the inlet and the system was allowed to run for 45 minutes.

2.9 Calculation Of Actual Concentration And Percentage Composition Of PAHs:-

The actual total of emitted PAHs was calculated by adding the total amount of PAH in sample solution multiplied by 0.02L which is the volume to which sample solutions were concentrated using rotary evaporator.

$$\text{Actual total PAH emitted} = A_T \times 0.02L$$

Where A_T = Total amount of PAH in sample solutions,

0.02L = volume to which samples were concentrated

Actual quantity of individual/component PAH librated is calculated by using the formular:-

$$\frac{A_C}{A_T} \times T_A$$

I.e.
$$\frac{\text{Amount of component}}{\text{Total amount of PAH in sample solution}} \times \text{Actual total emitted}$$

Where: A_c = Amount of component
 A_T = Total amount of PAH in sample solution
 T_A = Actual total emitted

Percentage PAH in sample is calculated by using the formular

$$\% \frac{A_c}{A_T} \times \frac{100}{1}$$

Where: A_c = Amount of component
 A_T = Total amount of PAH in sample solution

The process was repeated for AGO.

3.0 Result And Discussion

During combustion, PMS burnt out faster than AGO. This trend could be attributed to the fact that PMS is of lower molecular weight, more volatile and is highly inflammable. In both cases, residues remained in the combustion chamber, indicating that there was incomplete combustion due to insufficient supply of air/oxygen in the combustion chamber.

The combustion of PMS and AGO yielded much soot and particulates, some of which adhered to the walls of the combustion chamber. Some were flushed by nitrogen gas and trapped by the dichloromethane trap chambers and recovered by filtration.

This represented the actual amount of particulates librated into the environment. PMS yielded 1.9g/l while AGO yielded 2.7g/l. These values are very significant when compared to the emission limits for particulates from stationary sources as given by Federal Environmental Protection Agency [FEPA] 1981

The concentrated filtrates as well as concentrates of extracts from residues and particulates were analysed for Polyaromatic hydrocarbons using gas chromatography. The flame ionization detector (FID) was chosen because of its excellent linearity, sensitivity and reliability of response as well its reproducibility. It is also very fast as the run time was 45 minutes.

The concentrates of combustion effluents of PMS showed peaks at retention times, 8.918, 13.027, 20.900, 21.370, 24.698 and 24.792 minutes These correspond to naphthalene, acenaphthylene, fluoranthene, pyrene, chrysene and benzo[a]anthracene, in actual concentrations of 36.5, 146.0, 41.60, 16.5, 61.8, 3.3mg/l accounting for 11.95, 47.76, 13.61, 5.38, 20.21, 1.09 percent.

AGO combustion effluents concentrates showed peaks at retention times 8.872, 13.071, 13.643, 14.981, 17.618, 17.733, 20.800, 21.398, 24.793, 24.921, 26.995 minutes. These correspond to naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, flouranthene, pyrene, benzo[a]anthracene, chrysene, and benzo[b]fluoranthene in actual concentrations of 117.3, 1029.0, 355.3, 872.7, 6885.8, 2541.6, 3648.2, 10744.1, 3214.1, 949.5 and 65051.1mg/l being 0.12%, 1.08%, 0.37%, 0.91%, 7.22%, 2.66%, 3.82%, 11.26%, 3.37%, 1.00% and 68.18% of the total PAH.

The particulate extract concentrates of PMS showed peaks at retention times 8.900, 13.082, 13.653, 14.657, 17.494, 17.762, 20.826, 21.384, 24.743 and 25.07 minutes. These correspond to naphthalene, acenaphthylene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysen in actual concentrations of 9.1, 68.8, 289.6, 390.7, 4351.9, 2189.1, 5210.5, 4206.7, 647.1 and 2397.8mg/l accounting for 0.05%, 0.35%, 1.47%, 1.97% 22.02%, 11.08%, 26.37%, 21.29%, 3.27% and 12.13% of the total PAH.

The particulate extract concentrates of AGO showed peaks at retention times, 8.895, 13.094, 13.602, 15.034, 17.596, 17.696, 20.904, 21.363, 24.667, 25.015 and 26.951 minutes corresponding to naphthalene, acenaphthylene, acenaphtene, fluorene, phenathrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene and benzo[a]fluoranthene. In actual concentrations of 1.1mg, 31.9mg, 19.6mg, 27.1mg, 10.9mg, 29.7mg, 13.9mg, 24.7mg, 59.9mg, 31.8mg, 18.2mg/l being 0.41%, 11.87%, 7.29%, 10.07%, 4.07, 11.03% 5.15%, 9.25%, 22.28%, 11.82%, 6.76% of the total PAH.

The residue extract concentrates of PMS showed peaks at retention times, 8.897, 13.028, 13.593, 15.052, 17.611, 17.668, 20.903, 21.369, 24.837 and 24.891 minutes corresponding to naphthalene, acenaphthylene acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysene in actual concentrations 15.3mg, 191.8, 65.6, 38.2, 48.7, 131.6, 127.6, 94.5, 323.3, 735.7 being 0.86%, 10.82%, 3.70%, 2.15%, 2.75%, 7.43%, 7.20%, 5.33%, 18.24%, 41.51% of the total PAH.

The residue extract concentrates of AGO showed peaks at retention times 8.875, 13.154, 13.328, 17.274, 17.707,

20.810, 21.343, 24.819, 24.966 and 26.953 minutes corresponding to naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene and benzo[b]fluoranthene in actual concentrations of 1.7, 2.1, 1.1, 1.1, 11.3, 3.2, 9.6, 45.3, 73.2, 37.9mg/l being 0.92%, 1.14%, 0.61%, 0.59%, 6.06%, 1.72%, 5.14%, 24.29%, 39.23%, 20.30% the total PAH.

From the above results, it is observed that polyaromatic hydrocarbons (PAH) were emitted during the combustion of premium motor spirit (PMS) and automated gasoline oil (AGO). They are in part fixed on the particulates which were present in the effluent gases, residues left behind in the crucible used for combustion and the effluent gases. The effluents of AGO yielded 95408.7mg/l of PAH while PMS emitted 305.7mg/l PAH. For the particulate extracts PMS gave 19761.3mg/l of PAHs while AGO gave 269.0mg/l PAHs. For the residue extracts, PMS residue yielded 772.4mg/l while AGO residue gave 186.5mg/l.

Conclusion

The analysis described here has established that the PAHs emitted during combustion of PMS and AGO are in part fixed on the particulates which are present in the effluent gases, residues left behind in the crucible and the effluent gas.

This study lends support to calls from environmentalists to source for alternative renewable energy and to end the dependency of Nigeria on the use of generator as source of energy due to incessant power outage. Also in the Niger Delta region of Nigeria where gas flaring has been going on for a long time, this calls for a review and a break in the energy dependence of Nigeria on fossil fuel. It also calls for the development of solar energy as an alternative energy source since it is cheap and environmentally friendly. Finally the study suggests that measures to reduce societal reliance on electric generating machines should be implemented and its use as a show of affluence should be discouraged.

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TABLE 1 Data for PMS Effluents
 Total PAH emitted = 305.7mg/l

Name of compound	Retention time [min]	Concentration in effluent sample solution mg/l	Actual conc. In PMS effluent [mg/l]	% PAH in Effluent
Naphthalene	8.918	182.61	36.5	11.95
Acenaphthylene	13.027	730.12	146.0	47.76
Fluoranthene	20.900	208.04	41.6	13.61
Pyrene	21.370	82.31	16.5	5.38
Chrysene	24.698	309.01	61.8	20.21
Benzo[a]anthracene	24.792	16.52	3.3	1.09
Total		1528.6807mg/l	305.7mg/l	100

TABLE 2: Data for AGO Effluents
 Total PAH emitted: 95408.7mg/l

Name of compound	Retention time [min]	Concentration in effluent sample solution mg/l	Actual conc. In PMS effluent [mg/l]	%PAH in effluent
Naphthalene	8.872	586.47670	117.3	0.12
Acenaphthylene	13.071	5145.00846	1029.0	1.08
Acenaphthene	13.643	1776.41115	355.3	0.37
Fluorene	14.981	4363.33363	872.7	0.91
Phenanthrene	17.618	3.44289×10^4	6885.8	7.22
Anthracene	17.733	1.27080×10^4	2541.6	2.66
fluoranthene	20.800	1.82413×10^4	3648.2	3.82
Pyrene	21.398	5.37203×10^4	10744.1	11.26
Benzo[a]anthracene	24.793	1.60703×10^4	3214.1	3.37
Chrysene	24.921	4747.57962	949.5	1.00
Benzo[b]Fluoranthene	26.995	3.25256×10^5	65051.1	68.18
Total		477043.6096	95408.7	99.99

TABLE 3: Data for PMS particulates extract
 Total PAH = 19761.3mg/l

Name of compound	Retention time [min]	Concentration in sample solution mg/l	Actual conc. In PMS Particulate Extract[mg/l]	%PAH in particulate Extract
Naphthalene	8.900	45.69789	9.1	0.05
Acenaphthylene	13.082	344.17126	68.8	0.35
Acenaphthene	13.653	1448.05114	289.6	1.47
Fluorene	14.657	1953.53718	390.7	1.97
Phenanthrene	17.494	2.17594×10^4	4351.9	22.02
Anthracene	17.762	1.09453×10^4	2189.1	11.08
Fluoranthene	20.826	2.60524×10^4	5210.5	26.37
Pyrene	21.384	2.10334×10^4	4206.7	21.29
Benzo[a]anthracene	24.743	3235.28930	647.1	3.27
Chrysene	25.017	1.19894×10^4	2397.8	12.13
Total		98806.64677	197661.3	100

TABLE 4: Data for AGO Particulate Extract
 Total PAH = 269.0mg/l

Name of compound	Retention time [min]	Concentration in sample solution mg/l	Actual conc. In Particulate Extract[mg/l]	%PAH in particulate Extract
Naphthalene	8.895	5.51840	1.11	0.41
Acenaphthylene	13.094	159.61824	31.9	11.87
Acenaphthene	13.602	98.05118	19.6	7.29
Fluorene	15.034	135.41849	27.1	10.07
Phenanthrene	17.596	54.74163	10.9	4.07
Anthracene	17.696	148.40675	29.7	11.03
Fluoranthene	20.904	69.33498	13.9	5.15
Pyrene	21.363	124.35575	24.9	9.25
Benzo[a]anthracene	24.667	299.67660	59.9	22.28
Chrysene	25.015	159.01683	31.8	11.82
Benzo[a]Fluoranthene	26.951	90.93923	18.2	6.76
Total		1345.07808	269.0	100

TABLE 5: Data for PMS residue extract
 Total PAH = 1772.4mg/l

Name of compound	Retention time[min]	Concentration in sample solution mg/l	Actual conc.PMS residue extract[mg/l]	%PAH in PMS residue extract
Naphthalene	8.897	76.48031	15.3	0.86
Acenaphthylene	13.028	958.93420	191.8	10.83
Acenaphthene	13.593	328.12312	65.6	3.70
Fluorene	15.052	190.91751	38.2	2.15
Phenanthrene	17.611	243.73613	48.7	2.75
Anthracene	17.668	658.16328	131.6	7.43
Fluoranthene	20.903	638.19291	127.6	7.20
Pyrene	21.369	472.57760	94.5	5.33
Benzo[a]anthracene	24.837	1616.30376	323.3	18.24
Chrysene	24.891	3678.65483	735.7	41.51
Total		8862.08361	1772.4	99.99

TABLE 6: Data for AGO residue extract

Name of compound	Retention time[min]	Concentration in sample solution [mg/l]	Actual conc.AGO residue extract mg/l	% PAH in PMS residue extract
Naphthalene	8.974	8.53763	1.7	0.92
Acenaphthalene	13.154	10.63613	2.1	1.14
Acenaphthene	13.328	5.71286	1.1	0.61
Phenanthrene	17.274	5.46132	1.1	0.59
Anthracene	17.707	56.53569	11.3	6.06
Fluoranthene	20.810	16.04130	3.2	1.72
Pyrene	21.343	47.99094	9.6	5.14
Benzo[a]anthracene	24.819	226.51812	45.3	24.29
Chrysene	24.966	365.89303	73.2	39.23
Benzo[b]fluoranthene	26.953	189.32615	37.9	20.30
Total		932.65317	186.5	100

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