

Analysis of Premium Motor Spirit (PMS) Distributed in Warri Metropolis, Nigeria

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Abstract

This research was on investigating the quality of premium motor spirit (PMS) that is distributed in Warri Metropolis, Warri, Nigeria. Premium motor spirit samples from four different tank farms in Warri Metropolis were analyzed. The physical properties were studied as well as density test, distillation test, octane number test, Reid vapor test, sulphur content test, copper strip corrosion test, methanol and ethanol content test. The results obtained are as follows: density test 0.7751 ± 0.0359 , research octane number test 103.2 ± 24.59 , methanol and ethanol were absent, distillation test at the final boiling point 193 ± 15.8614 °C, Reid Vapor Pressure test 4.5 ± 1.7 , the sulphur content test 0.0113 ± 0.0021 . Though the study suggests that the PMS quality was within ASTM Standards, it is imperative that regular quality tests be conducted randomly to check for adulteration.

Key words: Premium Motor Spirit, Adulteration, Research Octane Number, Copper Strip, Reid Vapor

Introduction

Petroleum which is also known as “Black Gold” or “Crude Oil” is a naturally occurring, yellow-to-black liquid which is found in geologic formations beneath the Earth's surface (O'Connor & Gronewold, 2013). Also, petroleum is a mixture of hydrocarbons that exists as a liquid in natural underground reservoirs and remains liquid when brought to the surface (Al-Areeq, 2018). Petroleum products are produced from the processing of crude oil or petroleum at refineries and the extraction of liquid hydrocarbons at natural gas processing plants. Petroleum is the broad category that includes both crude oil and petroleum products (Lahiri et al., 2021).

Petroleum is formed when large quantities of dead organisms, usually zooplankton and algae are buried underneath sedimentary rock and subjected to intense heat and pressure. It is formed when the remains of marine algae and animals gradually settle on sea beds over the years and tend to be covered with mud, silt and other sediments (Abdulredha et al., 2020). As the sediments are piled up, their mass exerts a great pressure on the lower layers, changing them to hard sedimentary rocks. As a result of bacterial activity, coupled with heat and pressure, it then changes the plant and animal remains into crude oil or petroleum (De Araujo et al., 2012). Premium Motor Spirit (PMS) popularly called petrol in Nigeria with boiling range of 40-200°C (consists of 5 to 12 carbon atoms) is a complex mixture of hydrocarbons produced by mixing fractions obtained from the distillation of crude oil with brand-specific additives to improve its performance (Wale-awe & Sulaiman, 2020). Petrol is a major product from the fractional distillation of petroleum (Odeyoma et al., 2022).

Adulteration of petroleum products has been a common trend in developing countries in which Nigeria is also a culprit. This act is perpetrated with the intention of maximizing profit notwithstanding its hazardous effects on the environment and final consumers (Ofualagba, 2020). Adulteration is the deliberate mixing of petroleum products with partially refined products or condensates (reservoir gases that condense to liquid hydrocarbon when produced) with products that are in high demand like PMS, AGO or DPK with a singular aim of making

more profit (Joel & Okoro, 2019). PMS that are contaminated or whose quality has been weakened by adding inferior quality ones or products of lower grade are referred to as adulterated PMS. Adulteration of PMS initially involves adding kerosene or diesel to the PMS. But due to high cost of kerosene and diesel; it is mostly done with naphthalene and boosted with methanol or ethanol (Mahajan et al., 2020). This problem can be tackled if proper and regular analysis which involves the quality control tests is carried on the PMS to ascertain its composition (Olotu et al., 2021).

There are different tests that are carried out on PMS to ascertain its quality. These include: density test, distillation test, octane number test, Reid vapor test, sulphur content test, copper strip corrosion test, methanol and ethanol content test. PMS sample is said to be non-adulterated, when the results of the analysis is within the ASTM (American Society for Testing and Materials) specifications (Manneh et al., 2020).

Density hydrometer tester is used to measure the specific gravity of PMS. It involves the laboratory determination using a glass hydrometer in conjunction with series of calculations of the density, relative density or API gravity of PMS (Rajalakshmy et al., 2022). It is normally handled as liquid having a vapor pressure of 14.696 psi or less. Values are determined at existing temperature and corrected to 15 °C or 60 °F by means of calculations and international standard tables. This analysis works with Archimede's principle of buoyance; which states that the upward buoyant force that is exerted on a body immersed in a fluid, whether partially or fully is equal to the weight of the fluid that the body displaces (Dahl et al., 2020). This test is significantly important for accurate determination of the density, relative density or specific gravity for the conversion of measured volumes to volumes or masses at standard temperatures and corrected to 15 °C or 60 °F.

Distillation test is done to ascertain the boiling range of PMS, for the purpose of sample characterization, product and quality control. This test works with principle of boiling, evaporation and condensation (El-Ghonemy, 2018). When the sample in liquid phase is heated, there is an increase in the kinetic energy; which escapes to vapor phase when the kinetic energy increases. Eventually a point is reached when the molecules in the sample have acquired enough kinetic energy to vaporize and then begin to boil. As the liquid boils and vaporizes, it enters into the chamber which is controlled by compressor and this condenses the vapor back to the liquid phase which comes out distilled. This test is significantly important to determine the boiling range of PMS which can as well determine if the product is adulterated (Garzoli et al., 2019).

Octane number test is used to measure the performance of PMS in an internal-combustion engine. When PMS is burned in an internal combustion engine to CO₂ and H₂O, there is a tendency for many gasoline mixtures to burn unevenly (Jiang et al., 2019). Such non constant and unsmooth combustion creates a "knocking" noise in the engine. Knocking signifies that the engine is not running as efficiently as it could. It has been found that certain hydrocarbons burn more smoothly than others in a gasoline mixture. In 1927 a scale that attempted to define the "antiknock" properties of gasoline was created (Chen et al., 2020). Octane rating is a standard measure of PMS ability to withstand compression in an internal combustion engine without detonating. However, the higher the octane number, the more the compression can withstand before detonating. A poor quality fuel tends to 'knock' or explode unevenly or prematurely especially in a high compression engine (Rodriguez et al., 2020). Isooctane also known as 2, 2,4 Trimethyl pentane is a good fuel, because it burns smoothly and does not cause knocking. It is, therefore, assigned the arbitrary octane number of 100 (on a zero-to-100 scale). Heptane is a bad fuel, because it is particularly inclined to causing knocking. It is, therefore, assigned the octane number of zero. The octane number or octane rating of PMS is, therefore, the percentage of 'iso-octane' blended with heptane which reflects the knocking characteristics

of the fuel. It is a measure of its performance in an internal-combustion engine (Rashid et al., 2019).

Reid Vapor Pressure (RVP) is a common measure of the volatility of PMS. It is defined as the absolute vapor pressure exerted by the vapor of the liquid and any dissolved gases/moisture at 37.8°C (100°F). The test was determined by the test method ASTM-D-323, which was first developed in 1930 and has been revised several times (the latest version is ASTM D323-15a). NMDPRA regulates the vapor pressure of PMS sold at retail stations to reduce evaporative emissions from gasoline that contribute to ground-level ozone and diminish the effects of ozone-related health problems (Nurullayev, 2014).

Sulphur content test is done using sulphur analyzer. The test was done in accordance with ASTM D4294 (Standard Test Method for Sulphur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy). This method is applicable to both volatile and non-volatile petroleum products with sulphur concentrations ranging from 0.05% to 5%. Sulphur is considered an undesirable contaminant because, when burned, it generates sulphur oxides. Consequently, PMS have a limit on how much sulphur they can contain, making sulphur removal an important part of the overall refinery process (Agocs et al., 2021).

After combustion in the engine, the sulphur in PMS forms particulates that are a primary contributor to air pollution and the cause of harmful corrosion in the engine (Ejaz et al., 2022).

Corrosiveness tester for copper strip helps to determine the relative degree of corrosiveness of PMS. This test significantly helps to check the level and susceptibility of PMS to corrode parts of engines (Khiar et al., 2019).

The use of fuel additives is very important because many of these additives can be added to PMS in order to improve its efficiency and its performance. Some of the most important additives to improve fuel performance are oxygen containing organic compounds (oxygenates); such as ethanol and methanol. Among the various alcohols, ethanol and methanol are known as the most suitable fuels for spark ignited (SI) engines (Nda-Umar et al., 2018). The use of oxygenated fuel additives provides more oxygen in the combustion chamber and has a great potential to reduce emissions from SI engines. Methanol and ethanol test was determined using ASTM D5845 (Infrared Spectroscopy). This test method determines ethers and alcohols in PMS and it is applicable to both quality control in the production of PMS and for the determination of deliberate or extraneous oxygenate additions or contamination (Schlagbauer et al., 2020).

Materials and Methods

Materials

PMS samples used for this study were collected from four different tank farms at Ifie area of Warri metropolis and analyzed to determine its composition and to check for adulteration. The samples were collected with 2 liter and 4 liter transparent sampling jerry cans with the aid of sampler.

The materials used for the analysis were 100 ml measuring cylinder, 500 ml measuring cylinder, 700-750mmHg hydrometer, handheld thermometer, octane analyzer, round bottom distilling flask, mercury in glass thermometer, distillation unit, Reid vapor analyzer, sulphur analyzer, methanol/ethanol analyzer and copper strip corrosion tester.

Methods

All the equipment used for the analysis were pre-calibrated before usage for quality assurance purposes; and the tests carried out were based on American Standard and Testing Methods (ASTM). Density hydrometer was used to check the density of PMS (ASTM D1298). Distillation tester was used to carry out distillation to ascertain the boiling range of PMS.

Octane analyzer was used to determine the research octane number (RON) of PMS (ASTM D2699). Reid vapor pressure tester was used to check the pressure of PMS (ASTM D323). Sulphur analyzer was used to check the sulphur content of PMS (ASTM D4294). Corrosiveness tester was used to determine the corrosiveness of PMS to parts of engine. Octane and Fuel analyzer was used to determine the methanol and ethanol content of PMS.

Results and Discussion

Physico-Chemical Characteristics of the PMS Samples

All the analysis carried out on the PMS samples were based on ASTM standard. The physicochemical characteristics of the four PMS samples were based on the appearance, color, specific gravity, free water, suspended matter, copper strip corrosion, Research Octane Number (RON), Motor Octane Number (MON), Anti Knock Index (AKI), total sulphur and Reid Vapor Pressure. The appearance was checked visually and the other parameters were checked based on specific ASTM standard as shown in Table 1. It can be seen in Table 1 that sample 1, sample 2 and sample 3 were within the specifications of NMDPRA and S.O.N; while sample 4 was not within the specifications except copper strip corrosion, total sulphur and Reid Vapor Pressure which were within the specifications.

The density obtained for sample 1, sample 2 and sample 3 which were within the ASTM density range (0.720-0.780), indicates that the samples were neither too light nor too heavy. Sample 4, was above the ASTM density range; this indicates that the sample was heavier than the standard PMS. The value of the RON, MON and AKI which are the measure of the PMS ability to knock or ping in an engine for sample 1, sample 2 and sample 3 were above the minimum value specified by NMDPRA and S.O.N. This shows that the samples were of high grade. Sample 4 was far beyond the specifications; which indicates that the sample was over boosted with naphthalene, methanol or ethanol. All the samples were within the specifications for total sulphur content. There was no methanol and ethanol in sample 1, sample 2 and sample 3; but sample 4 had high content of methanol and ethanol.

Table 1: The Physico-Chemical Characteristics of the PMS Samples

Parameter	Unit	Method	Specification NMDPRA/ SON	Result Sample 1	Result Sample 2	Result Sample 3	Result Sample 4
Appearance	-	Visual	Clear & Bright	Clear & Bright	Clear & Bright	Clear & Bright	Cloudy
Color	-	ASTM D1500	Golden yellow	Golden yellow	Golden yellow	Golden yellow	Dyed
Specific gravity @ 15/15°C	g/ml	ASTM D1298	0.720 – 0.780	0.7514	0.7617	0.7588	0.8285
Free water	-	ASTM D4176	NIL	NIL	NIL	NIL	Present
Suspended matter	-	ASTM D4176	NIL	NIL	NIL	NIL	Present
Copper strip corrosion @ 50oC	Class	ASTM D130	1b max	1a	1a	1a	1a
Research Octane Number (RON)	-	ASTM D2699	91 min	91.8	88.6	92.4	>140
Motor Octane Number	-	ASTM D2699	81min	81.8	78.6	82.4	>130
Anti-knock index (AKI)	-	Calculated	86min	86.8	83.6	87.4	>135

Total Sulphur	% Wt	ASTM D4294	0.10 max	0.0006	0.0432	0.0005	0.0006
Reid Vapor Pressure (RVP)	Psi	ASTM D323	9.0 max	4.6	6.6	4.2	2.4
Methanol	% v/v	ASTM 4815	Nil	Nil	Nil	Nil	124.3
Ethanol	% v/v	ASTM 4815	Nil	Nil	Nil	Nil	>124.3

Results of Distillation Profile of the PMS Samples

The results of the distillation profile of the PMS samples analyzed is shown in Table 2. The distillation profile is planned to show the reported result in the distillation temperatures; usually observed when the level of the distillate reaches each 10% mark on the graduated receiver, the temperatures for 50% and 90% marks, the final boiling point (which is the highest thermometer reading observed during distillation) the recovery, the residue and finally the distillation loss. The results obtained from the PMS sample1, sample 2 and sample 3 were within the specification standard; while sample 4 was not within the specification as seen in Table 2.

Table 2: Distillation Profile of the PMS Samples

Test	Unit	Method	Specification NMDPRA/ SON	Result Sample 1	Result Sample 2	Result Sample 3	Result Sample 4
10 % Recovery	°C	ASTM D86	70 max	62	65	65	55
50 % Recovery	°C	ASTM D86	125 max	103	115	110	65
90 % Recovery	°C	ASTM D86	180 max	165	175	180	142
Final Boiling Point (FBP)	°C	ASTM D86	210 max	200	190	209	172
Residue	% v/v	ASTM D86	2 max	1.5	0.5	1.5	0.5

Table 3: Statistical Analysis of the Results

Test	Test Result 1	Test Result 2	Test Result 3	Test Result 4	Mean $\frac{\sum x}{n}$	Mean Deviation $\frac{(\sum x-\bar{x})}{n}$	Variance $\frac{(\sum x-\bar{x})^2}{n}$	Standard Deviation $\sqrt{\frac{(\sum x-\bar{x})}{n}}$
Specific gravity @15/15°C	0.7514	0.7617	0.7588	0.8285	0.7751	0.0267	0.0013	0.0359
RON	91.8	88.6	92.4	140	103.2	18.4	604.6667	24.59
MON	81.8	78.6	82.4	130	93.2	18.4	604.6667	24.59
AKI	86.8	83.6	87.4	135	98.2	18.4	604.6667	24.59
Total Sulphur	0.0006	0.0432	0.0005	0.0006	0.0113	0.016	0.0005	0.00214
RVP	4.6	6.6	4.2	2.4	4.5	1.15	2.9701	1.7234
Distillation@ Final Boiling Point	200	190	209	172	192.75	11.75	251.58	15.86

Conclusion

This study has shown that sample 4 of PMS studied was adulterated probably with methanol, ethanol and other constituents while the other three samples were of good quality. This can be clearly seen in Table 1 and Table 2; where the adulterated sample was not within the specifications of Nigerian Mid-Stream and Downstream Petroleum Regulatory Authority (NMDPRA) and Standard Organisation of Nigeria (SON), while the other three samples were within the specifications of NMDPRA and SON.

There is need for regular quality assurance tests to be conducted randomly on the PMS produced or imported into the country to check for adulteration for maximum productivity and pollution free environment.

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