Egyptian Journal of Petroleum (2012) **21**, 135–138

Egyptian Petroleum Research Institute

**Egyptian Journal of Petroleum**

www.elsevier.com/locate/egyjp
www.sciencedirect.com

FULL LENGTH ARTICLE

# Behavioural characteristics of adulterated Premium Motor Spirit (PMS)

**M.C. Onojake *, Leo C. Osuji, N. Atako**

*Petroleum Chemistry Research Group, Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B. 5323, Choba, Port Harcourt, Nigeria*

Received 9 January 2012; accepted 18 March 2012
Available online 4 January 2013

**KEYWORDS**

Adulteration;
Premium Motor Spirit;
Atmospheric distillation;
Research Octane Number

**Abstract** Distillation profiles and chemical characteristics of ten suspected adulterated Premium Motor Spirit samples randomly collected from different dispensing points were analysed to determine the chemical characteristics of these samples when compared to a reference sample that is not adulterated. Results of the analyses show, Research Octane Number values ranged from 60.10 to 93.30, specific gravity ranged from 0.75 to 0.79, Reid Vapour Pressure ranged from 0.28 kgf/cm$^2$ to 0.60 kgf/cm$^2$ while Atmospheric distillation ranged from 189 to 251 °C. The results of this research reveal that most of the products are highly adulterated and may pose problems when sent to the market for intended end users.



## 1. Introduction

Petroleum products are complex mixtures of hundreds of hydrocarbon compounds, ranging from light, volatile, short-chained organic compounds to heavy, long-chained, branched compounds. The exact chemical composition of petroleum products varies depending upon the source of the crude oil and the refining practices used to produce the products.

* Corresponding author. Tel.: +234 8035404696.
E-mail addresses: ononed@yahoo.com, mudiaga.onojake@uniport.ng (M.C. Onojake).

Peer review under responsibility of Egyptian Petroleum Research Institute.

ELSEVIER Production and hosting by Elsevier

Premium Motor Spirit (PMS) is one of the products of fractional distillation of petroleum. This product is in high demand in the developing countries as a result of their inability to refine enough quantities of the product to meet the consumers' need. Adulteration of petroleum products is an act perpetrated daily by unscrupulous people in the developing countries like Nigeria with the intention of maximizing profit in their business with total disregard of the hazardous effect their actions could have on end users. It is the deliberate mixing of petroleum products with a product of 'lower grade', partially refined products or condensates (reservoir gases that condense to liquid hydrocarbon when produced) with products that are in high demand like PMS, DPK with a singular aim of making more profit. Condensates which are the major components used for the adulteration of PMS (gasoline) and DPK (Dual purpose kerosene) are in abundant supply in countries like Nigeria. They are composed mainly of a light range of hydrocarbons (butanes, pentanes and hexanes); though some

1110-0621 © 2012 Egyptian Petroleum Research Institute. Production and hosting by Elsevier B.V. Open access under CC BY-NC-ND license.
http://dx.doi.org/10.1016/j.ejpe.2012.11.004

countries like Russia, Canada, Israel and Gulf Coast have condensates with a high percentage of aromatic or naphthenic hydrocarbons [1]. Niger Delta a significant province in Nigeria is known for the production of hydrocarbons with about 1.3 trillion cubit standard feet of condensate and gas reserve [2]. PMS (gasoline) or 'petrol' has a little different composition and chemical characteristics from the condensate which is used for the adulteration of the product. Most condensates are composed of *n*-paraffins within the light gasoline range which are responsible for their high API gravity. The light hydrocarbon contents explain why condensates have low octane numbers and inferior quality as automobile fuel [3]. PMS (gasoline) is a complex mixture which contains over 1500 hydrocarbon compounds, these include paraffins, naphthenes and olefins. It has a general hydrocarbon distribution consisting of 4–8% alkanes, 2–5% alkenes, 25–40% isoalkanes, 3–7% cycloalkanes, 1–4% cycloalkenes, and 20–50% aromatics with aliphatic hydrocarbons ranging from $C_5$–$C_{12}$ carbon atoms per molecule [4,5].

PMS (gasoline) can be classified into three grades according to their octane rating. Regular PMS (have octane rating greater than 85 but less than 88), mid grade PMS have (octane rating greater than 88 but less than 90) and Premium PMS (have octane rating greater than 90) [6]. Octane rating is a measure of the auto ignition resistance of PMS and other fuels used in spark ignition internal combustion engines. It can be said to be a measure of anti-detonation of PMS. Octane number gives the percentage by volume (% v/v) of iso-octane and heptane that would have the same antiknocking capacity as the fuel under consideration [7]. The most common type of octane rating world-wide is the, Research Octane Number (RON), although there is another type of octane rating called "Motor Octane Number (MON)".

### *1.1. Reid Vapour Pressures (RVP)*

The Reid Vapour Pressure (RVP) is an important physical property of volatile liquids. It is the pressure a vapour exerts on its surrounding. It is an indirect measure of evaporation. The volatile property of PMS is of paramount importance to spark ignition engines.

### *1.2. Specific gravity (SG)*

It is the ratio of the density of a given substance to the density of water. Substances with SG > 1 are denser than water while those with SG < 1 are lighter than water. SG is density of a substance/density of water. Atmospheric distillation is carried out to purify an impure liquid to the pure state. These liquids should show a marked difference in the Initial Boiling Point (IBP) and Final Boiling Point (FBP).

## 2. Experimental (materials and methods)

Ten samples of suspected adulterated Premium Motor Spirit (PMS) were randomly collected from different dispensing points and analysed to determine the behaviour of these samples collected from different dispensing points in Nigeria. Another sample which was used as reference standard was collected from the Nigeria National Petroleum Corporation (NNPC) laboratory. All samples were analysed according to the ASTM test method.

### *2.1. Determination of specific gravity*

A 100 ml measuring cylinder was properly rinsed with a small amount of the sample, washed and blown dry then filled with the sample to be analysed. A hydrometer with calibration from 0.50 to 0.85 was submerged into samples and SG reading was taken at the point of observation of the floating hydrometer. A thermometer submerged into the measuring cylinder was used to stir samples and its reading noted to obtain the temperature of the samples. The temperature values are converted into °F to obtain the correct SG.

### *2.2. Atmospheric distillation*

The test samples (100 ml) were measured into a round bottom flask. Anti-bombing granules were added to the flask to prevent explosion. The distillation machine was turned on to a temperature of 300 °C heating power. Readings were taken for the Initial Boiling Point (IBP) temperature as soon as samples start dropping into the measuring cylinder. The temperature of the machine is increased and readings of the Final Boiling Point (FBP) temperature and the Total Recovery (TR) temperature noted.

### *2.3. Determination of Reid Vapour Pressures (RVP)*

The (RVP) was determined as described in the ASTM test method for vapour pressure of petroleum products as reported by Osuji et al. [2]. The Reid Vapour Pressure machine used was filled with 50 ml of the sample under study and then submerged into the RVP water bath. The RVP bath was adjusted to a temperature of 38 °C for the samples to attain the same temperature with the water bath. After about thirty minutes, the light ends of the samples under investigation begin to escape and the machine detects the pressure of the escaping vapours and the reading on the gauge is recorded as the Reid Vapour Pressure in $kg/cm^2$.

### *2.4. Determination of Research Octane Number (RON)*

About 300 ml of each sample was introduced into the carburettor and the machine switched on. The selector valve of the machine is allowed to run for some minutes until the equilibrium condition is attained. The cylinder height for the knockmeter reading is adjusted between 45 and 47. The cylinder height

**Table 1** Results of SG and API gravity for PMS samples.

| Samples | SG at 60 °C | API gravity (°) |
|---|---|---|
| 1 | 0.75 | 56.59 |
| 2 | 0.75 | 56.59 |
| 3 | 0.77 | 51.96 |
| 4 | 0.76 | 54.44 |
| 5 | 0.75 | 57.02 |
| 6 | 0.75 | 57.98 |
| 7 | 0.79 | 47.95 |
| 8 | 0.76 | 54.29 |
| 9 | 0.75 | 55.60 |
| 10 | 0.76 | 54.17 |
| Refr. sample | 0.75 | 56.94 |

*Note:* API = 141.5/SG (60 °C) – 131.5. Refr. (Reference)

**Table 2** Results for Reid Vapour Pressure (RVP) @ 38 °C.

| Samples | RVP (kg/cm$^2$) |
|---|---|
| 1 | 0.57 |
| 2 | 0.46 |
| 3 | 0.28 |
| 4 | 0.66 |
| 5 | 0.42 |
| 6 | 0.64 |
| 7 | 0.40 |
| 8 | 0.50 |
| 9 | 0.58 |
| 10 | 0.56 |
| Refr. Samp. | 0.58 |

**Table 3** Results of the Research Octane Number (RON) for research samples.

| Samples | RON (%) |
|---|---|
| 1 | 94.6 |
| 2 | 62.0 |
| 3 | 61.0 |
| 4 | 90.5 |
| 5 | 90.0 |
| 6 | 92.3 |
| 7 | 60.5 |
| 8 | 57.0 |
| 9 | 90.5 |
| 10 | 60.2 |
| Refr. Samp. | 91.1 |

*Ethanol content minimal.

for the knock meter reading is finally adjusted to 50 after locating the fuel level for maximum knock. The Research Octane Number is carried out to obtain the maximum knock fuel ratio and standard knock intensity.

## 3. Results and discussion

Results from Table 1 show, the specific gravity/The American Petroleum Institute gravity, ranged from 0.75 to 0.79 (57.98–47.95) API gravity. The value of the reference sample is 0.75 (56.94) API gravity, they are within the same range. The samples are neither too light nor too heavy [4].

The RVP is a measure of the volatility of the PMS (gasoline) when in use in the automotive engines. According to the American standard measurement specification [8], the maximum Reid Vapour Pressure value should not be above 0.6 kgf/cm$^3$, if this value is exceeded, it depicts that the samples have light ends and high volatility. Results from Table 2 show that the reference samples fall below this maximum specification and can vapourize readily in pumps, fuel lines and carburettors and will cause a decrease in fuel flow to engines [9]. Conversely, samples 3, 5 and 7 have RVP less than 0.45 kgf/cm$^3$. This connotes that the samples are heavy which means that either the samples were partially refined or have been adulterated. The implication is that they may contain heavy fractions of petroleum products.

The results of the Research Octane Number (RON) are shown in Table 3. The reference sample shows the percentage by volume of isooctane as 91.1% and 8.9%. The RON values of research samples 1, 4, 5, 6 and 9 are within the range of PMS (gasoline) RON rating of 90 (%v/v) by ASTM. Table 3 also shows that samples 2, 3, 7, 8 and 10 fall below the minimum RON value of 85 (%v/v) for regular PMS (gasoline) grade. This is connected with adulteration which is a common practice in the developing countries like Nigeria. The implication of the low RON values is that products of low grade are pushed into the market with low antiknock rating [2]. Knocking is the metallic noise usually observed in spark ignited engines as a result of low octane rating of PMS (gasoline) [10]. High octane rating of PMS (gasoline) is necessary for better performance of the internal combustion engines [8]. Low octane rating of PMS (gasoline) also could hinder engine power performance [7].

### *3.1. Atmospheric distillation profile*

The results of the Atmospheric distillation profile are shown in Tables 4 and 5. According to the American Standard of testing and materials (ASTM), for PMS (gasoline), 10 ml recovery should not exceed 70 °C. This is the range at which the auto ignition spark plug will be first ignited. Also the specified limit for 50 ml recovery and Final Boiling Point should not exceed a maximum of 125 °C and 205 °C respectively. A close look at Table 4 shows samples 1, 5, 6 and 9 are unadulterated when compared to the distillation profile of reference sample in Table 5. This is because they have 10 ml recovery temperature of less than

**Table 4** Results of the distillation profile of the PMS research samples.

| Samp 1 | | Samp 2 | Samp 3 | Samp 4 | Samp 5 | Samp 6 | Samp 7 | Samp 8 | Samp 9 | Samp 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Vol | Temp | Temp | Temp | Temp | Temp | Temp | Temp | Temp | Temp | Temp |
| IBP | 39 | 47 | 49 | 40 | 42 | 43 | 64 | 47 | 41 | 57 |
| 10 | 58 | 73 | 77 | 62 | 65 | 62 | 88 | 82 | 61 | 75 |
| 20 | 67 | 78 | 92 | 72 | 75 | 70 | 101 | 94 | 76 | 82 |
| 30 | 78 | 91 | 103 | 84 | 86 | 79 | 113 | 104 | 86 | 94 |
| 40 | 89 | 101 | 111 | 95 | 96 | 88 | 121 | 114 | 97 | 101 |
| 50 | 101 | 113 | 127 | 110 | 107 | 100 | 134 | 124 | 109 | 118 |
| 60 | 113 | 125 | 138 | 121 | 117 | 112 | 147 | 137 | 120 | 131 |
| 70 | 127 | 159 | 154 | 131 | 133 | 127 | 167 | 154 | 133 | 149 |
| 80 | 144 | 199 | 161 | 145 | 152 | 144 | 193 | 179 | 145 | 174 |
| 90 | 169 | 251 | 198 | 165 | 175 | 169 | 233 | 215 | 168 | 225 |
| FBP | 189 | 251 | 225 | 202 | 198 | 190 | 245 | 251 | 185 | 232 |
| TR | 99% | 95% | 97% | 99% | 96% | 98% | 97% | 96% | 99% | 96% |

**Table 5** Results of distillation profile of the reference PMS samples.

| Vol distilled (ml) | Recovery temp. (°C) |
|---|---|
| IBP | 39 |
| 10% | 56 |
| 20 | 64 |
| 30 | 74 |
| 40 | 85 |
| 50 | 98 |
| 60 | 115 |
| 70 | 128 |
| 80 | 142 |
| 90 | 162 |
| FBP | 193 |
| TR | 99% |

*Note:* IBP, Initial Boiling Point; FBP, Final Boiling Point; TR, Total Recovery.

70 °C and Final Boiling Point (FBP) less than 205 °C. By comparison with the result of the distillation profile from the reference sample which have a 10 ml recovery temperature of 56 °C and Final Boiling Point (FBP) less than 70 °C samples 2, 7, 8 and 10 have 10 ml recovery temperature greater than 70 °C and FBP well above the maximum limit of 205 °C. These samples are said to be adulterated or may have been blended with other products that are not properly refined and are therefore low quality grade products. This may affect the chemical characteristics of the petroleum products when put to intended use.

## 4. Conclusion

This research has shown that most of the PMS samples from the area under study are adulterated with low grade or partially refined petroleum products. This act is capable of altering the chemical and behavioural characteristics of the Premium Motor Spirit (PMS) under investigation as some of the investigated samples varied widely in chemical characteristics from the reference sample obtained from the laboratory of Nigerian National Petroleum Corporation (NNPC).

## Acknowledgements

The authors are sincerely grateful to the staff of quality control and research laboratory of the Port Harcourt Refinery (A subsidiary of the Nigerian National Petroleum Corporation) for their immense contribution towards this research.

## References

[1] J.F. Kenny, Science of Gasoline, second ed., Joint Institute of Russian Press, 1994.
[2] L.C. Osuji, R.E. Ogali, U.U. Usen, Helvetica Chimica Acta 92 (2009) 328–334.
[3] I.P. Okoye, Fundamentals of Petroleum and Hydrocarbon Chemistry, University of Port Harcourt Press, 2009.
[4] ATSDR, Agency for Toxic Substances and Disease Registry Atlanta, GA, U.S., 1995.
[5] L.C. Litchy, Introduction to Internal Combustion Engines, John Wiley, 1986.
[6] O. Olayinka, An Introduction to Modern Petroleum Science, University of Ibadan Press, 2006.
[7] B.K. Shammah, Introduction to Automotive Spirit, Indian Academy Press, 2006.
[8] G.V. Chilingar, L.A. Buryakovsky, N.A. Eremenko, Geology and Geochemistry of Oil and Gas, first ed., Elsevier, 2005.
[9] ASTM, Annual Book of ASTM Standard, 1979.
[10] L.R. Snowdon, T.G. Powell, AAPG Bulletin 66 (1982) 775–788.