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Full Length Research Article

Comparative Studies of Gasoline Samples Used in Nigeria

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ABSTRACT: Comparative analysis was carried out on five samples of gasoline in the Nigerian market based on octane number, sulphur content, Reid vapour pressure, specific gravity, boiling point characteristics and chemical content. The result revealed that, Nigerian and Kuwait gasolines have low octane numbers in comparison to others. The Nigerian sample has the least sulphur content while the Holland has the highest. The specific gravities were all within the acceptable range of 0.75-0.85. Likewise the boiling point characteristics of all the samples were within suitable values in favour of Nigerian weather conditions. Chemical composition analysis shows high proportion of aromatics, above acceptable limits and low oxygenated compounds. The findings revealed that the quality of some gasolines being sold in Nigeria is below the international standard.
Keywords: Gasoline, hydrocarbons, octane number, sulphur content, specific gravity and API gravity

INTRODUCTION

Gasoline is obtained from crude oil through blending of atmospheric distillation naphtha and products from other complex refinery processes (Handwerk, 2001). Refinery processes have developed in response to changing market demand and stricter environmental laws. With the advent of the internal combustion engine production of gasoline have dominated the refining processes (Hinks, 2004). This is because the quantities of gasoline obtainable from distillation alone were insufficient to satisfy consumer demand. Therefore, to meet the gasoline demand some petroleum fractions must be converted to gasoline by processes like Cracking, Hydroprocessing, Alkylation and catalytic reforming (Handwerk, 2001).

The typical composition of gasoline hydrocarbons (% volume) is: 4-8% alkanes; 2-5% alkenes; 25-40% iso-alkanes; 3-7% cycloakanes; 1-4% cycloalkenes; and 20-50% total aromatics (0.5-2.5% benzene) (Hoekman, 1992). Additives and blending mixture are also added to improve its performance and stability. These compounds include anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents and dyes. At the end of the production process, finished gasoline typically contains more than 150 separate compounds although as many as 1,000 compounds have been identify in some blends (Hoekman, 1992). Hence, in spite of the fact that gasoline is solely used in internal combustion engine, its chemical composition varies depending on the crude oil used, the refinery processes available, the overall balance of product demand and the product specifications.

Over the years, the advocacy on human health and general environmental concern has forced the refineries to balance the composition of gasoline to meet the high engine performance requirements without jeopardizing human and environmental safety. Yet some sub-standard gasolines still find their way into the market. For example, in Nigeria, where most of the gasoline being consumed is imported through independent marketers, there is the temptation of profit maximization through either adulteration or importation of substandard products. In view of the above, this paper presents compositional study on different gasoline samples in Nigerian market with the view of assessing the level of compliance to international specifications on gasoline products.

MATERIALS AND METHODS

Collection of Gasoline Samples

Two litters each of Nigerian produced gasoline and those imported from Kuwait, Brazil, Holland, and Russia were collected from designated deports in Lagos in July 2009 and kept in tightly closed clean and dry metallic containers at laboratory temperature until needed for analysis. The imported samples were identified by the Vessels Managers of the Deports in Nigeria.

Determination of Reid Vapour Pressure (ASTMD-323, Liptak 2003)

The liquid chamber of the RVP kits apparatus was filled with a gasoline sample that has been pre-chilled to 4^0C and the liquid chamber was connected to the vapour chamber fitted with a pressure gauge. The entire assembly was immersed in the pre-heated water bath at 37.8^oC. After 5 mins., the assembly was removed, shaken and the pressure gauge was read.

The assembly was then re-immersed and removed after another two minutes, shook and the pressure guage read again. The procedure was repeated until two successive readings are within 0.35 kPa. The gauge reading was corrected to obtain the Reid vapour pressure.

Determination of Octane Number (RON) of Gasoline (ASTM D-38)

RON was determined using single cylinder test engine knock meter at Kaduna Refining and Petrochemicals (KRPC) according to ASTM D-38 standard procedure.

Octane Number Sulphur Determination by Energy Dispersive X-Ray Fluorescence Spectrometry (ASTM D-4294)

The sample cell of the machine was filled with the gasoline sample above a minimum depth. The cell containing the sample was placed in the sample compartment along the path of beam emitted by X-ray source. The resultant characteristics X-ray fluorescence from the sample was measured and the accumulated count was compared with that of calibration sample to obtain the sulphur concentration in mass percentage.

Determination of Specific Gravity and API Gravity (ASTMD - 1298)

Hydrometer cylinder containing the sample was cooled to constant temperature of 28 ^{0}C. The hydrometer was inserted and allowed to come to rest floating freely away from the walls and bottom of the cylinder and the specific gravity value was read directly from the calibration of the hydrometer.

Determination of Initial and End Boiling Point of Gasoline (ASTMD-86)

100 ml of the gasoline sample was transferred into a distillation flask. The flask was stoppered and a thermometer was inserted vertically into the distillation flask. The flask was then heated and the distillate was condensed in a brass tube condenser, surrounded by water bath kept at 0 ^{0}C by ice water mixture. The temperature at which the first drop of distillate was obtained was recorded as the initial boiling point of the gasoline. The distillation was continued and the temperatures at which 5, 20, 30, 40, 50, 60, 70, 80, 90, 95 cm^3 and the last drop of the distillate were received and recorded.

Compositional Analysis Using Gas Chromatography/Mass Spectrometry (GC/MS)

The machine (SHIMADZU QP2010) was warmed for recommended period of time and then programmed such that the temperatures of the injection port, ion source and interface were at 240, 200 and 250 ^{o}C, respectively. Helium was used as the mobile phase at flow rate of 1.64 ml/minute. The ovum, housing DB-MS-1 capillary column of 30m nominal length and 250 μm internal diameter was set at initial temperature of 45 ^{o}C and programmed at heating rate of 15^{o}C/min to 210^{o}C which was maintained for 10 minutes.

At the end of each run the total ion chromatogram (TIC) and mass spectrum of each of the separated compounds was produced and printed out. The mass spectrum of each peak was compared with 2004 NIST e-library to bring out compounds with identical or similar spectrum for easy identification.

IR Analysis

The Shimadzu 4800S FTIR machine was turn on and allowed to worm for 30mins. The machine was programmed to scan between 400 and 4000 cm^{-1} at resolution of 4 cm^{-1}. The background spectrum was then scanned and saved. The sample was smeared on one pre-prepared KBr window and covered by another so that a thin film of the sample liquid was formed between the two KBr windows. The KBr windows containing the sample were transfer into the sample compartment and attached to the sample holder. The sample was then scanned and the spectrum was produced and display on the computer screen. The spectrum was smoothen to remove noise signals with the help of "IR solution" software installed into the system. The smoothened spectrum was then printed. The same procedure was followed for the other samples.

RESULTS AND DISCUSSIONS

The results of the experiments are presented in Tables 1-5. Table 1 above shows the result of the Reid Vapour Pressure (RVP) and Research Octane Number (RON) analyses. From the result it can be seen that Kuwait gasoline has the highest value of 0.56 while Hollandian gasoline has the least value of 0.44. The relatively high RVP of Kuwaiti and Russian gasolines indicates that they contains higher amounts of volatile hydrocarbons which may not be very good for hot weather experienced in Nigeria because of the tendency of such fuels to cause vapour locks when use in internal combustion engine (Finlayson-pitt and Pitt-jnr 1993). Such gasolines also have high tendency of being lost to vapourisation (Schuetzle *et al* 1994) in addition to fire hazard. On the other hand, the Hollandian sample with low RVP (low volatile components) may have its own problems especially during the cold season where such fuels cause difficulty in cold ignition. However, since the difference in temperature between summer and winter is not very wide in the tropical climates found in countries like Nigeria, the little difference in the RVP between the samples may not cause any significant problem.

The results of the Octane Number analysis (Table 1) show that Nigerian gasoline has the lowest octane number of 86.5. This is lower than the minimum desired value of 91 for internal combustion engine (Mustafa, 2004). This means that Nigerian gasoline has the tendency to cause engine knock especially in modern improved engines. All other samples have octane number within the standard range.

The low octane number of the locally refined gasoline is an indication of poor product regulation. Low octane number gasoline is an issue of high concern particularly to the new improved high compression engines vehicle being imported into the country.

The result of the sulphur content analyses (Table 1) shows that Hollandian gasoline has the highest sulphur concentration of 0.081%wt, followed by Brazilian gasoline (0.04%wt) and Nigerian gasoline has the lowest (0.025%wt). The maximum concentration allowed in any gasoline sample is 0.05%wt (Assi 2008), but some European countries have mandated that sulphur in gasoline should be kept as low as 10ppm (0.001%). However Nigerian refineries still allows sulphur content to be as high as 0.2%wt (KRPC). Therefore, the sulphur contents of all the fuels fall within the Nigerian standard. It is nevertheless worrisome to notice that while other countries are lowering the tolerable sulphur contents of their gasolines to protect people and environment, Nigeria still allows high sulphur content with the implication that the gasolines that are not acceptable in other countries due to their high sulphur contents are being imported into the country at the detriment of the citizens and the environment. Sulphur content in gasoline is kept low because it is toxic, causes corrosion of metals and its combustion products are environmentally hazardous (Wormsbecher *et al*, 1993).

Table 1 gives results of specific gravity (S.G.) analysis. All the values obtained also fall within the standard range of 0.749 to 0.850. Nevertheless, the Russia gasoline has the highest specific gravity value of 0.7620 and the Kuwaiti gasoline has the lowest value of 0.7493. Therefore, from the SG result the gasolines are not expected to cause any problem in usage.

Result of the boiling point characteristics of the samples (Table 2) shows all the samples have initial boiling points (IBP) of around 40°C which is 5°C above the minimum value of 35°C quoted as the standard. This could be deliberately designed in consideration of the Nigerian climate where normal atmospheric temperature is commonly above 30°C. Therefore Nigerian gasoline should have high IBP to avoid significant looses of the volatile components to evaporation which could cause vapour locks in engines.

The IR analysis indicated the presence of alkanes and aromatics compounds through appearance of peaks that corresponding to these. However, the IR results (Table 3) indicate the presence of oxygenated compounds in the Russian sample where absorption for alcohols were observed in all the expected regions. This serve to confirm that the sample contain some alcohols the quantity of which may be ascertain in the GC/MS result.

The GC/MS analysis (Table 4) shows that Nigerian and Hollandian gasoline do not contain any cyclo-alkanes, while Brazilian, Kuwaiti and Russian gasoline contain 21.74, 8.08 and 4.12% cyclo-alkanes, respectively. However, all the gasoline samples contain aromatic compounds in very high concentration. Kuwaiti gasoline has the highest concentration with 85.61% while Russian gasoline has the lowest aromatics concentration with 65.51%. Nigerian, Brazilian and Hollandian gasoline contain 71.77, 71.26 and 80.52 % of aromatics, respectively.

Similarly, all the gasoline samples contain *n*-alkanes. Nigerian gasoline has significant amounts of branched-alkanes (14.56%) although lower than the Russian gasoline (19.46%). The Hollandian and Kuwaiti gasoline have no branched-alkanes. On the other hand Brazilian and Kuwaiti gasoline do not contain branch alkanes. Looking at the result, it is clear that the main Octane Number enhancers in all the samples are the aromatics (Calingaert, 1998). This is another point of concern because aromatics are known to be toxic (Fishbien *et al*., 1987). This is why their concentration in gasoline is usually limited to 50% and the octane number, is raised to specification using oxygenated compounds like ethers and alcohols. Siu (2005) has shown that oxygen containing compounds are added to gasoline to improve performance and reduce exhaust emission. In some countries, oxygenates, particularly alcohols constitute about 20% of the gasoline blend to ensure safety, environmental friendliness and quality. Amazingly none of the samples analyzed was found to have any oxygenated components not even the Nigerian sample. The absence of alcohol in the GC/MS result in contrast to the IR may be that the alcohol content is very small.

Table 1: Results of Reid Vapour Pressure (RVP), Octane Number (RON), Sulphur Content and Specific Gravity Determinations.

SOURCE	RVP (PSI) at 37.8^{O}C	RON	Sulphur Content (%wt)	Specific Gravity at 25^{o} C
Brazil	0.50	94.6	0.041	0.7542
Holland	0.44	91.7	0.081	0.7503
Kuwait	0.56	89.5	0.029	0.7493
Russia	0.55	93.2	0.032	0.7620
Nigeria	0.48	86.5	0.025	0.7571
ASTM Standard	Variable	90-94	0.01-0.05	0.749-0.850

Table 2: Results of Boiling Point Range at Atmospheric Pressure Distillation.

	Temperature of Recovery (^{o}C)					
% Recovery	**Brazil**	**Kuwait**	**Holland**	**Russia**	**Nigeria**	**ASTM Standard**
Initial Boiling Point	40	39	43	40	40	35-39
5%	55	50	59	54	56	
10%	60	55	62	60	61	60
20%	71	66	75	71	70	
30%	84	77	84	85	82	
40%	97	89	93	95	99	
50%	110	102	104	106	110	110
60%	123	117	111	125	123	
70%	135	127	120	151	138	
80%	149	145	134	167	150	
90%	168	164	153	176	168	170
95%	184	179	174	183	184	
End Boiling Point	194	192	186	198	201	195-204
Total Recovery (cm^{3})	96	98	97	97	96	

Table 3: Results of IR Analysis

Absorption band (cm^{-1})	Group	Brazil	Holland	Russia	Nigeria	Kuwait
750-700	Monosubstituted benzene	720	720	720	-	-
800-750	Disubstitute benzene	-	760	760	760	760
1060-1040	Primary alcohol			1040		
1470-1350	Alkanes	1400, 1440	1440, 1360	1440, 1360	1440 1360	1440 1360
1680-1040	C=C alkenes					1600
2820-2720	Aldehyde	2790		2720	2720	
2960-2850	C-H alkane	2960	2880 2960		2960	
3000 - 2500	OH Phenols alcohol			2500		
3600-3200	Hydrogen bounded alcohols			3600		3560

Table 4: Results of Compositional Analysis using GC/MS

Hydrocarbon type	Concentration (%)				
	Nigeria	**Brazil**	**Holland**	**Kuwait**	**Russia**
Aromatics					
Ethylbenzene	11.97	17.41		12.0	5.27
Proplybenzene		5.67			
1-ethyl-3-methybenzene		9.79	19.74	17.41	19.15
3–propyl-1-methylbenzene			6.78	7.99	12.56
Isopropylbenzene	5.12				
2,4-dimethylstyrene	2.29		2.82	3.16	
O-xylene	17.85	15.89	29.42	17.52	9.75
p-Xylene,2-ethyl				4.54	
Toluene	19.45	22.50	21.76	22.99	18.78
1-ethyl-3-methylbenzene	15.09				
Total Aromatics	**71.77**	**71.26**	**80.52**	**85.61**	**65.51**
Cyclo Alkanes					
4,7–methano–1-H-octahydroindene,		5.89			
4,7–methano-1H-indene,3a,4,5,6,7,7a-hexahydro		12.50			
1,3,5-cycloheptatriene				8.08	
1,2 –dimethylcyclohexane					4.12
9-methylene-tricycle (4.2.1. (95) decane		3.35			
Total cycloalkanes	**0.00**	**21.74**	**0.00**	**8.08**	**4.12**
n-Alkanes					
Octane	5.98	7.0		6.31	7.99
Undecane	7.69				2.91
2,4-dimethyheptane			9.51		
4-methyloctane	6.42				9.03
2-methylhaptane	8.14		9.95		10.43
Total n - Alkanes	**28.23**	**7.0**	**19.46**	**6.31**	**30.36**

CONCLUSION AND RECOMMENDATION

From the results obtained it can be generally concluded that all the samples are sub-standard with each having one problem or the other. The Nigerian refined gasoline has low octane number, the Holland sample has high sulphur content, and the Kuwaiti sample has high Reid Vapour Pressure. All these are in addition to the generally high aromatic content of the gasolines and absent of oxygenates.

The low Octane Number may result in poor engine performance. The reason for low RON in the Nigerian gasoline is not immediately clear, but it may not be unconnected with the poor condition of our refineries and or negligence from the regulatory bodies. This is because, the essence of regulation is safeguarding the nation from all possible hazards and loses but that is not really reflected in allowing the country to import and supply substandard product to its citizens when there are alternatives. High sulphur is environmentally hazardous and high vapour pressure result in high volatility thereby releasing large quantity of hydrocarbons into the atmosphere. High aromatic content is, on the other hand, hazardous to health.

It is therefore necessary to call on the Nigerian authorities to ensure strict compliance to standards by both local producers and importers of gasoline for the welfare of the entire nation. Furthermore, the environmental concern is rather global, therefore issues that affect the lager environment like sulphur emission is the concern of every one and every nation.

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