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GC-MS ANALYSIS OF ARTISANAL REFINED AND REGULAR AUTOMOTIVE GASOLINE: COMPARATIVE STUDY OF QUALITY

[1]G.J. Udo*, [2]J.J. Awaka-Ama, [3]A.E. Nyong, [4]A.N. Ekanem, [5]R.C. Igwe
[1,2,3,4,] Department of Chemistry, Akwa Ibom State University, PMB,116, Uyo, Akwa Ibom State, Nigeria, [5] NNPC E&P Ltd Head office Airport Road Benin, Edo State, Nigeria.

Abstract A comparative analysis of hydrocarbon composition of Regular Automotive Gasoline (RAG) and Artisanal Refined Gasoline (ARG) was conducted using GC-MS. Results of the analysis revealed gasoline(C_4-C_{12}) composition of 83% and (69%) in ARG and RAG, kerosene (C_{13}-C_{18}) composition in ARG (16 %) and RAG (28%); diesel (C_{19}-C_{23}) amount in ARG was (0%) and 3% in RAG. No residual oil (>C_{24}) was detected in both samples. Pristane/phytane ratio was1.53 and 2.16 for RAG and ARG. Concentrations of n-alkane were RAG (112, 277.15 mg/l) and ARG (67,532.74 mg/l). The percentage of kerosene and diesel boiling range were higher in RAG compared to ARG. The hydrocarbon compositions of both samples were comparatively similar though in varying concentrations. Based on these findings indigenous technologies and innovations in harnessing of crude oil should be regulated and quality of gasoline distributed monitored.

Key Words: Gasoline, Concentration, Refinery, Hydrocarbons, Pristane , Phytane**.**

1. INTRODUCTION

Gasoline is a complex mixture of hydrocarbons and other chemical compounds used as fuel for spark-ignition internal combustion engines (Tamm et al, 2018). 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 (Onojake et al, 2012). Gasoline comes primarily from petroleum cuts with carbon composition of C_4-C_{12} and boiling point range of 150 – 205 ºC (El-naggar, and Al majthoub, 2013).

Local refining of crude oil has grown swiftly over the past years, providing communities with employment opportunities and filling the energy supply gap of refined fuels in the Niger Delta (Onojake et al, 2012). Though gasoline produced by artisan refiners is not tested to certify its compliance to any local or international standards; it still finds its way into the market. However, non-compliance of artisanal refiners with locally and international best practices can lead to engine malfunctioning, environmental pollution and danger to humans. Poorly produced gasoline burns at a pressure lower than the referenced sample due to adulteration (Peretomode, 2018). It has been reported that the Nigerian refined gasoline has low octane number due to the poor condition of the refineries, adulteration and negligence by the regulators (Faruq et al, 2012).

Makeshift techniques are used by artisanal refiners in processing the raw crude oil via thermal cracking into useful products. These procedures may be unsophisticated and unsafe to the operators but can be effective in some cases. The petroleum fractions obtained by local refiners are skeptically referred to as ‘bunkering oil or adulterated products’ and have been generally assumed to have substandard quality. The quality of the artisanal gasoline can be enhanced through upgrading refinery operation conditions and the introduction of gasoline additives (Udo et al, 2020). The determination of hydrocarbon types like: saturated hydrocarbons, olefins, and aromatics in petroleum fractions are important in characterizing the quality of petroleum products.

NEED OF THE STUDY.

There is a need for periodic quality control in any petroleum products distributed in study area to check adulteration and substandard petroleum products. Furthermore, indigenous innovation and ingenuity in harnessing our natural resources should be regulated and the products assessed to ascertain their compliance with international standards. this research was designed to these objectives through comparing *n*-alkanes profiles in automotive gasoline produced by artisanal refiners with regular automotive gasoline.

3. MATERIALS AND METHODS

3.1 Sample Collection

Gasoline samples were randomly collected from different sampling stations using labeled 2.5 L amber sample bottles with a glass stopper. At each of sampling station, the sample bottle was rinsed with the gasoline sample to be collected; the gasoline samples were added via the nozzle of the gasoline dispenser and labeled as Regular Automotive Gasoline (RAG). Also, at Eastern Obolo Creek, gasoline samples were collected from artisanal refiners through local gasoline vendors

The gasoline sample was introduced into the sample bottle through a glass funnel, sealed and labeled as Artisanal Refined Gasoline (ARG).

3.2 GC-MS analysis

GC-MS analysis was carried out with reference to the USEPA 8015C standard procedure. Gasoline samples (1µl) were injected into a GC-MS (Agilent 6890) without extraction or further dilution. The equipment was calibrated using 35 components Hydrocarbons windows, ACUU standard (USA) and gasoline samples were eluted with helium through the GC column at 50º C. Sample analysis was carried out using Gas Chromatography/ Mass spectrometer (GC-MS). The analytes were detected as they emerged from the column by a mass spectrometer detector (MS) based on the summation of characteristic mass fragments, to determine the concentration of the hydrocarbon types. The GC-MS instrumental parameters and conditions are shown on table 1. Results of the analysis were integrated using Automated Chem. station Software and presented in a chromatogram as shown on fig. 1. The average number of carbon atoms of the sample is estimated from spectral data and calculations were made from calibration data which are dependent on the average number of carbon atoms of the sample (Nadkarni, 2007).

3.3 Operational condition used for GC analysis is stated below as presented in Table 1.

Table 1: Operational condition for GC-MS

GC general condition		
Column oven temperature	50 °C	
Injection mode	Direct	
Injection temperature	50ºC	
Injection volume	µl	
Average velocity	36.445 cm/sec	
Column pressure	7.6522 psi	
Column flow	1.2211 ml/min	
Carrier gas	Helium 99.9995% purity	
Frequency	50 Hz	
Electron multiplier volts	1024.9	
Column oven temperature		
Progress		
Rate (°C/min)	Temperature(°C)	Hold time (min)
–	50	0
8	300	9
Column		
Length	30.0 m	
Diameter	250 µm	
Film thickness	0.25 µm	
Total runtime	32 min	
MS conditions		
Source temperature	**230 °C**	
Start mass range m/z	**50**	
End mass range m/z	**550**	

3. RESULTS AND DISCUSSION

3.1 Individual Hydrocarbon Concentration

Fifteen (15) individual hydrocarbons at varying concentrations were detected in both RAG and ARG as shown in Tables 2-3 and Fig. 1. The composition of hydrocarbon as indicated by GC-MS analysis was mostly paraffinic (Tables 2-3, Fig. 1). This may be attributed to the refining oppressions employed. Thermal cracking and hydrocracking give predominantly paraffinic gasoline (Guiqian et al, 2015). The alkane concentration in RAG and ARG was 112,777.15 mg/l and 67,532.738 mg/l respectively as presented in Tables 2 and 3. The two gasoline samples contained the same compositions of hydrocarbons, although with varying concentrations and were mainly paraffinic straight run gasoline. The results indicated that ARG contained less amount of alkanes compared to RAG. High concentration of n-decane as indicated in ARG may infer lower octane number in ARG (Han et al, 2018). This may lead internal combustion engine malfunctioning. Reducing alkane contents of gasoline will reduce severe pollution that results from vehicle exhaust emissions (Guiqian et al, 2015). Also, (Piehl et al, 2018) reported that one of the major components in gasoline is *n*-alkane, which constitutes approximately 9.5%. In this study, it was observed that C_4-C_7 n-alkanes were not detected in both samples; butane increased vapor pressure and enhances the octane number of motor gasoline; hexane is an additive in gasoline (David et al, 2018).

Table 2: Hydrocarbon composition of Artisanal Refined Gasoline (ARG)

Retention time (mins)	Area (pa*s)	Amount (mg/l	Amount (ppm)	Amount (%)	Name of Hydrocarbon
4.824	239.3443	14.2041	3399.6736	10	Octane
5.894	988.1605	16.2479	16055.5	17	Nonane
6.862	1090.3565	18.6737	20361	5	Decane
7.744	213.2529	17.4512	3721.5257	44	Undecane
8.64	156.3655	15.5691	2434.4629	7	Dodecane
9.528	226.1984	14.4704	3273.1696	8	Tridecane
10.519	449.5116	12.6705	5695.5197	3	Tetradecane
11.541	598.5659	9.7107	5812.5009	1	Pentadecane
12.47	401.5476	6.9171	2777.5248	2	Hexadecane
13.263	61.8288	5.2739	326.0777	1	Heptadecane
13.344	256.4522	5.0345	1291.1174	1	Pristane
14.153	174.933	3.6752	642.9098	0	Octadecane
14.233	147.481	4.0455	596.6346	0	Phytane
14.904	142.8759	2.8316	404.5686	0	Nonadecane
15.904	95.6517	2.3479	224.5765	0	Eicosane
16.254	62.9652	1.9931	125.4978	0	Heneicosane
16.838	23.356	1.4124	32.9885	0	Docosane
17.45	37.8611	1.5292	57.8962	0	Tricosane
18.003	59.7381	1.7434	104.1487		Tetracosane
18.533	41.8164	1.5173	63.4462		Pentacosane
19.039	47.9728	1.5267	73.2415		Hexacosane
19.526	19.2405	0.8903	17.1306		Heptacosane
19.993	26.9224	0.9707	26.1345		Octacosane
20.448	19.0688	0.3855	7.3508		Nonacosane
20.912	22.1021	0.3684	8.1414		Triacontane
21.412	10.4381	0	0		Henetriacontane
21.949	10.7951	0	0		Dotriacontane
22.55	10.2999	0	0		Tritriacontane
23.22	9.8146	0	0		Tetratriacontane
23.999	4.4466	0	0		Pentatriacontane
24.892	1.2346	0	0	0	Hexatriacontane
25.898	0.6951	0	0		Heptatriacontane
27.138	0.8318	0	0		Octatriacontane
28.566	0	0	0		Nonatriacontane
30.257	0	0	0		Tetracontane
Totals			**67532.738**		

Table 3: Hydrocarbon composition of Regular Automotive Gasoline (RAG)

Retention time (mins)	Area (pa*s)	Amount (mg/l	Amount (ppm)	Amount (%)	Name of Hydrocarbon
4.88	800.434	14.6712	11406.3	5	Octane
5.892	1144.9388	12.5588	18611.1	24	Nonane
6.813	331.1291	9.6075	6105.2569	30	Decane
7.811	2790.2415	6.8996	49878.3	6	Undecane
8.647	505.4791	5.2553	7981.2119	4	Dodecane
9.585	611.473	14.6712	8971.0329	5	Tridecane
10.507	239.4995	12.5588	3007.8236	8	Tetradecane
11.523	167.4778	9.6075	1609.0422	9	Pentadecane
12.46	248.5101	6.8996	1714.6195	4	Hexadecane
13.335	184.2547	5.2553	968.7058	0	Heptadecane
13.386	156.2438	5.0351	786.7058	2	Pristane
14.145	119.6703	3.6765	439.9687	1	Octadecane

14.227	126.6613	4.0478	512.7033	1	Phytane
14.897	78.8894	2.8296	223.2232	1	Nonadecane
15.596	56.5841	2.3304	131.8618	0	Eicosane
16.249	47.7433	1.9499	93.0935	0	Heneicosane
16.862	54.7664	1.7691	96.8876	0	Docosane
17.443	34.6563	1.4844	51.4422	0	Tricosane
17.976	26.0304	1.4146	36.8229	0	Tetracosane
18.528	43.3576	1.5347	66.5415	0	Pentacosane
19.018	34.7912	1.3473	46.8727	0	Hexacosane
19.523	15.7868	0.6309	9.9595	0	Heptacosane
19.979	26.4303	0.951	25.1344	0	Octacosane
20.444	13.2445	0	0	0	Nonacosane
20.902	16.9214	0	0	0	Triacontane
21.407	13.9621	0	0		Henetriacontane
21.942	10.8045	0	0		Dotriacontane
22.539	5.748	0	0		Tritriacontane
23.219	3.1542	0	0		Tetratriacontane
23.956	2.8799	0	0		Pentatriacontane
24.888	18.197	0.1396	2.5401	0	Hexatriacontane
25.884	5.3188	0	0		Heptatriacontane
27.145	4.0493	0	0		Octatriacontane
28.64	0.3242	0	0		Nonatriacontane
30.221	1.3325	0	0		Tetracontane
Totals			**112,777.15**		

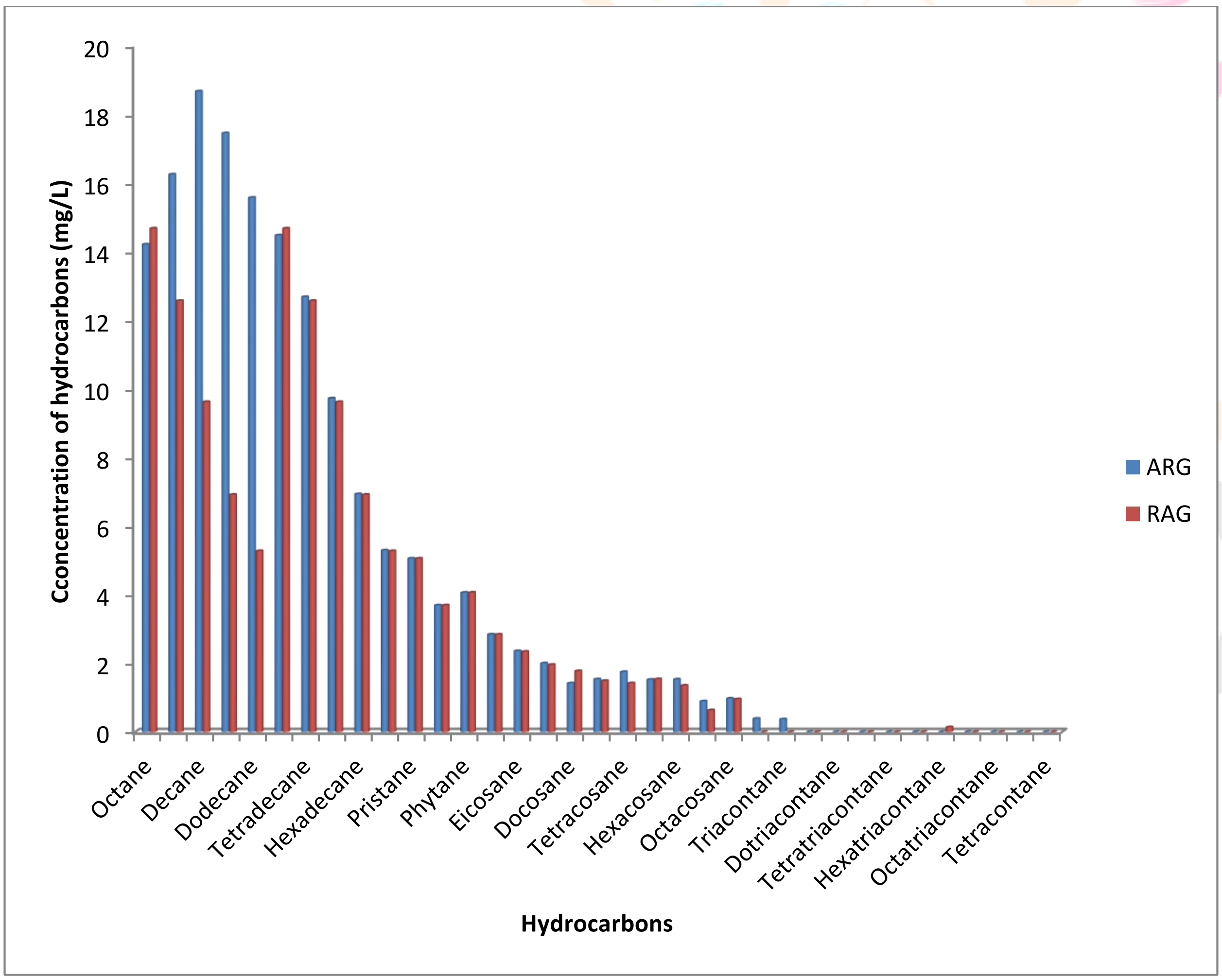

Figure 1: Levels of hydrocarbon in ARG and RAG

The percentage of n-octane in RAG was 10 %. This was higher than percentage in ARG (5 %) as shown on Tables 2-3. The high percentage of n-octane in RAG may imply higher octane number signifying better performance of RAG in internal combustion engine. In a related study, (Faruq et al, 2012) recorded 5.98 %, 7.0 %, 6.31% and 7.99% of octane in gasoline samples from Nigeria, Brazil, Kuwait and Russia.

This study also revealed 17 % and 24% nonane in RAG and ARG (Tables 2 and 3). Also, the percentage of decane was 5% and 30% for RAG and ARG respectively (Tables 2 and 3). Decane is a volatile organic pollutant (Chemcyclopedia, 2002), with octane rating of -30. Also, decane is present in gasoline and kerosene (Runzhao et al, 2012). Undecane composition in ARG and RAG were 44 % and 6 % respectively. High concentration of n-decane as indicated in ARG may infer lower octane number in ARG Han et al, 2018. This may lead internal combustion engine malfunctioning. Naggar et al, 2018 in a related study, reported 3.365 % wt. and 7.306 % wt. of decane from different gasoline. Low boiling n-alkanes C_5 – C_7 were not detected in both samples (Tables 1-2 and Fig. 1). This could be attributed to poor operational conditions.

3.2 Composition of gasoline (C_4 - C_{12}), Kerosene (C_{13} - C_{18}), Diesel (C_{19}-C_{23}) and Residual oil (> C_{24})

The study revealed hydrocarbon fractions in gasoline, kerosene and diesel boiling ranges at varying concentrations with no residual oil (Table 4, Fig. 2). The investigation also showed that, the percentage of gasoline (C_4–C_{12}) range was 83% in ARG, and was higher than 69% recorded in RAG (Table 4, Fig. 2). This implies that ARG contained more gasoline range fraction than RAG. The gasoline compositions in the samples were mostly paraffinic (Vempatapu and Kanaujia, 2017). In a similar research by (Tang et al, 2015), 44.7% and 50.2 % of alkane were recorded in gasoline samples. The gasoline from large-scale oil-refining companies exhibited low alkane content while small scale refineries had higher quality standard (Guiqian et al, 2015). Furthermore, (Cachon et al, 2013) found that oil refined in Italy and Brazil gave a 36.68-44.75 and 10.10-13.70% respectively, of akanes in gasoline. This study also revealed that the percentage of kerosene (C_{13}-C_{18}) range was 16% in ARG and 28% in RAG (Table 4 and Fig 2). The kerosene hydrocarbon range was higher in RAG compared to ARG implying adulteration. The percentage of diesel (C_{19} - C_{24}) range was 3 % in RAG and 0 % in ARG, as indicated in Table 4 and Fig. 2.

Table 4: Percentage composition of gasoline (C_4-C_{12}), Kerosene (C_{13}-C_{18}), Diesel (C_{19}-C_{23}) and Residual oil (> C_{24})

Hydrocarbon Range	ARG	RAG
Gasoline (C_4 - C_{12})	83 %	69 %
Kerosene (C_{13} - C_{18})	16 %	28 %
Diesel (C_{19}-C_{23})	0 %	3 %
Residual oil (> C_{24})	0 %	0 %

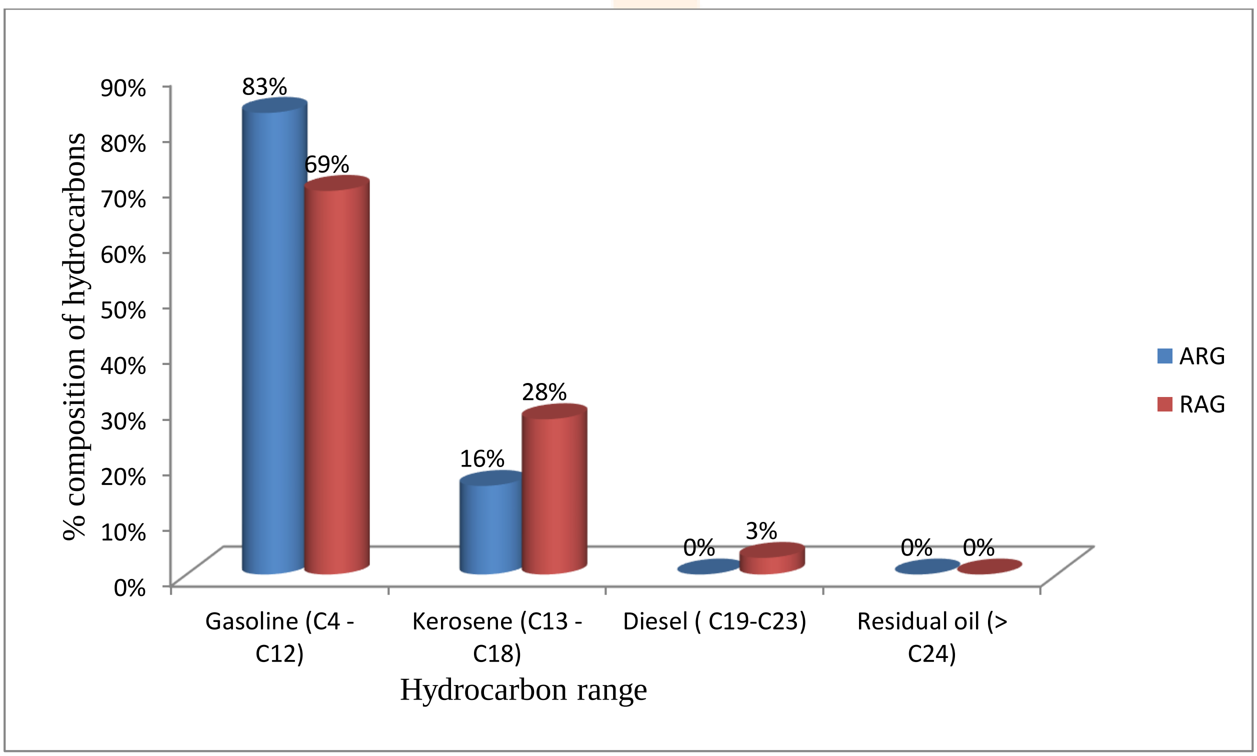

Figure 2:% Composition of Gasoline (C_6-C_{12}), Kerosene (C_{13}-C_{18}), Diesel (C_{19}-C_{23}) and Residual oil (>C_{24}) Fractions

3.4 Pristane/Phytane Ratio

Table 5: Pristane/Phytane Ratio

Sample	Pristane Composition (ppm)	Phytane composition (ppm)	Pristane /Phytane ratio
RAG	786.7058	512.7033	1.53
ARG	1291.1174	596.6346	2.16

The pristine/phytane ratio of 1.53 and 2.16 were recorded for RAG and ARG, as presented in Table 5. This indicated that the crude oil was from plant and terrestrial origin. Udoetok and Osuji, 2008 stated that oils from rocks deposited under open-ocean conditions showed $Pr/nC_{17} < 0.5$, while those from inland peat swamp had ratios greater than 1.Therefore, the pristane/phytane (Pr/Ph) ratio is one of the most commonly used geochemical indicators of depositional environment (Onojake et al, 2015 and Peters et al, 2005).

4. CONCLUSION

The findings indicated that both gasoline samples contained hydrocarbons in gasoline boiling range with percentage in locally refined gasoline (ARG) higher than regular automotive gasoline (RAG). The hydrocarbons in gasoline range were mainly paraffinic in the samples. The percentage of kerosene and diesel boiling range were higher in RAG compared to ARG, implying adulteration or poor refinery processes. The hydrocarbon compositions of the ARG and RAG were comparatively similar though in varying concentrations. Based on these findings, there is need for adequate and periodic quality control investigation on gasoline samples circulated in the study area to ensure compliance with international standards.

5. RECOMMENDATIONS

The relevant regulatory agencies should carry out routine quality assurance investigation in gasoline samples circulated in the study area. Indigenous innovation and ingenuity in harnessing natural resources should not be outlawed, but regulated. This will ensure sustainable economic growth and protection of the environment. Government should develop a legal frame work to integrate artisanal refiners into the downstream petroleum sub sector in view of the proposed modular refineries development.

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