Nigerian Research Journal of Chemical Sciences (ISSN: 2682-6054)
Volume 12, Issue 1, 2024

IMPACTS OF FRACTIONAL DISTILLATION (REFINING) ON THE CHARACTERISTICS OF PREMIUM MOTOR SPIRIT, AUTOMOTIVE GAS OIL AND HOUSEHOLD KEROSENE OBTAINED FROM BONNY LIGHT CRUDE

*CHIKWE, T.N., EBOSELE, F.

Petroleum and Environmental Chemistry Research Group

University of Port Harcourt, Port Harcourt

Rivers State, Nigeria

*Corresponding Author: templechikwe@yahoo.co.uk

Accepted: May 10, 2024. Published Online: May 16, 2024

ABSTRACT

Fractional distillation was carried out on crude oil obtained from Niger Delta area of Nigeria. The physicochemical characteristics of the petroleum products (premium motor spirit (PMS_{ND}), automotive gas oil (AGO_{ND}) and household kerosene (HHK_{ND}) from the distillation process were determined and compared with those from imported petroleum products (PMS_{IP}, AGO_{IP}, HHK_{IP}) and illegally refined products (PMS_{LR}, AGO_{LR}, HHK_{LR}). Results obtained showed density (g/cm^3): 0.7604, 0.8744,0.8201; specific gravity: 0.7612, 0.8752, 0.8209; American Petroleum Institute (API) gravity: 54.3900, 30.1800, 40.8700; kinematic viscosity (mm^2/sec): 0.7212, 1.6700, 1.4800); reid vapour pressure (RVP) (psi): 14.0100, 0.1530, 0.1480; cloud point (°C): -10.000, 20.000, -10.0000; pour point (°C) : -40.0000, -10.000, -20.0000; flash point (°C): 15.0000, 55.0000, 43.0000; gum content (mg/100 ml): 10.0000, 9.0000, 10.0000 for $PMS_{ND,}$ $AGO_{ND,}$ HHK_{ND} respectively. The research octane number (RON) and cetane number (CN) for PMS_{ND} and AGO_{ND} were 88.2000 and 52.0000 respectively while the burning characteristic of HHK_{ND} represented by the flame height, flame width, burning rate, smoke point and colour of chimney deposits were 35.2000 mm, 38.0000 mm, 26.1000 g/h, 40.5000 mm and None/ light respectively. Results show that all the physicochemical properties of PMS_{ND}, AGO_{ND}, HHK_{ND}, PMS_{IP}, AGO_{IP} and HHK_{IP} were within Department of Petroleum Resources (DPR) acceptable limit with a deviation of ≤ 0.5% except the cloud points of AGO_{IP} and AGO_{ND} which were 30.0000 °C respectively with deviations of 0.7% with respect to DPR specification. The reid vapour pressure, cloud point, pour point, flash point and RON of PMS_{LR} were off DPR acceptable limit. All the burning characteristics of illegally refined HHK (HHK_{LR}) apart from the smoke point (33.500) with a deviation of 0.38% were off DPR acceptable limit explaining the high rate of kerosene explosion.

Key Words: Petroleum products, crude oil, fractional distillation, physicochemical characteristics, refining, volatility.

INTRODUCTION

Petroleum is a complex mixture of hydrocarbons, encompassing various classes such as alkanes, cycloalkanes, aromatics, and heterocyclic compounds. The composition of petroleum is influenced by its source and can exhibit significant variation even within the Niger Delta region, in Nigeria, owing to differences in reservoir geology and fluid properties [1]. The formation of petroleum involves the geological transformation of organic matter over millions of years; Understanding this evolution is crucial in comprehending the diverse composition and properties of petroleum and its distillate fractions [2, 3].

Petroleum refining refers to a group of chemical engineering processes employed in transforming crude oil into useful products. In petroleum refining, processes such as cracking, coking and Vis breaking are used in breaking large petroleum molecules into smaller ones while polymerization and alkylation are used to combine small petroleum molecules into larger ones [4]. Prior to the refining of petroleum, crude oil was only available in natural seepage of subsurface oil in various areas throughout the world however, such limited availability restricted the uses of petroleum [5].

The primary process employed in petroleum refining is fractional distillation. Fractional distillation is the process of separating petroleum into various constituents or fractions with the use of a fractionating column. The different fractions in petroleum are separated at their respective boiling points along the column beginning with the lower boiling point fractions [6]. Petroleum fractions which are also referred to as petroleum products diversifies the importance and uses of petroleum which were restricted in use before the refining process, which of course increase the value and cost of petroleum. Petroleum products obtained from petroleum through fractional distillation include liquified petroleum gases, paraffin, premium motor spirit, automotive gas oil, kerosene, jet fuel and lubricating oils [7]. A typical fractionating column is shown in Figure 1. Fractional distillation is considered the most important process in petroleum refining because it produces the major fractions from petroleum while the other processes such as cracking, coking, alkylation, reforming and treating makes the products available in other valuable forms as well as improve the quality and quantity of the products [8]. It is worthy to note that the value placed on petroleum is majorly centered on the value of its products hence the importance of petroleum refining (fractional distillation) [9]. The source of petroleum as well as the refining process play major roles in determining the physicochemical characteristics of petroleum products. The quality of petroleum products has a lot of impact on engines, humans, environment and the ecosystem [10].

Fractional distillation has been an age long practice in petroleum refining operations however much studies have not been carried out on its impact on the characteristics of the product. A lot of techniques are employed by illegal refiners for lack of understanding of the criticality of the refining process on the products usability to engines as well as effects on the environment. Unveiling the impacts of fractional distillation by extension refining on the characteristics and quality of PMS, AGO and HHK will boost the confidence of petroleum refining operations within the country rather than reliance on imported products.

The aim of this study is to carry out a comparative evaluation of the physicochemical characteristics of petroleum products, basically, premium motor spirit (PMS), automotive gas oil (AGO), and household kerosene (HHK) obtained from fractional distillation with imported and illegally refined products. Further studies will be aimed at evaluating the impact of the characteristics of the crude on the quality of the refined products.

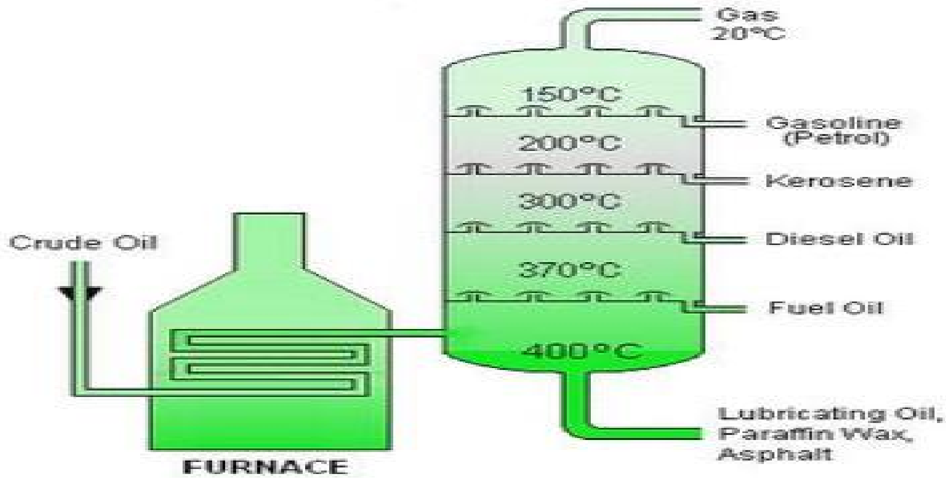

Figure 1: Fractionating Column

MATERIALS AND METHODS

Sample Collection and Preparation

i. Samples of premium motor spirit (PMS), automatic gas oil (AGO) and household kerosene (HHK) were obtained from Nigerian National Petroleum Company Limited (NNPCL) to represent imported petroleum products. These samples were labelled PMS_{IP}, AGO_{IP} and HHK_{IP} respectively.

ii. Samples of PMS, AGO and HHK were obtained from an illegally operated roadside refinery in Rivers State, Nigeria to represent illegally refined petroleum products labelled as PMS_{LR}, AGO_{LR} and HHK_{LR} respectively.

iii. Samples of PMS, AGO and HHK were obtained as fractional distillates from fractional distillation of bonny light crude oil sample obtained in Niger Delta Nigeria under adequately controlled laboratory condition. These samples were labelled PMS_{ND}, AGO_{ND} and HHK_{ND} respectively.

All samples were obtained using clean dry plastic bottles and the physicochemical characteristics of the samples determined using standard methods.

Fractional Distillation of Crude Oil

A 250 ml portion of a light crude oil contained in a round bottom flask was measured into a 500 ml distillation flask. The distillation flask was covered with a cork and thermometer was placed on top of it and 5 mm below the condenser tube to measure the temperature, and then heated with high pressure steam. The heat at this stage was regulated so that there is a specific interval between the first application of the heat which is the initial boiling point (IBP). The temperature at which the first drop of the distillate entered the receiving cylinder recorded as initial boiling point (IBP) and the last drop as final boiling point (FBP) at every voltage. The crude mixture starts boiling with the formation of vapour. The vapour, which is made up of various substances, rises through the fractional distillation column. Premium motor spirit, the crude fraction with the least boiling point was obtained at a temperature between 75 - 150 ℃. Household kerosene was obtained at a temperature between 150 – 220 ℃ and Automotive gas oil was obtained at a temperature between 220 – 310 ℃. Other fractions were obtained at higher temperatures [11].

Atmospheric Distillation of PMS, AGO, HHK

A 100 ml portion of the test sample in a graduated cylinder was introduced into a 250 ml round bottom flask containing boiling chips to prevent explosion. The flask was heated in a regulated rate to obtain a uniform average rate of condensation in mL/min. The thermometer reading indicating the vapour temperature was recorded as the initial boiling point (IBP) as soon as the first drop of condensed liquid drops at the lower end of the condenser. Temperatures at various % volume distilled were recorded up to the final boiling point (FBP) and then heating was discontinued. The round bottom flask was allowed to cool and the volume of the remaining liquid was measured and recorded as the recovery [12].

Specific Gravity of PMS, AGO, HHK

A 400 ml graduated cylinder was filled with the sample to be analysed. A hydrometer with calibrations of 0.70 or 0.75 was submerged into it and readings were taken as the hydrometer floats on the sample. A thermometer was then inserted into the graduated cylinder for 10 s and the temperature recorded. Specific gravity values corresponding to the temperature in ℃ were read as values for the corrected specific gravity [13]-

Reid Vapour Pressure of PMS, AGO, HHK

The Reid vapor pressure (RVP) machine was filled with 100 ml of the sample to be analysed before being submerged into the RVP water bath. The RVP water bath was adjusted to boiling of the sample at 38 ℃ before measurement. A minimum of three measurements were carried out to obtain a stable and representative value [14].

Density and Kinematic Viscosity of PMS, AGO, HHK

The cells of the equipment were thoroughly cleaned. Exactly 2 ml of the test sample was introduced into the equipment through the connector installed for filling samples into the measuring cells with the use of a suitable syringe after proper agitation of the test sample. Density, kinematic viscosity and dynamic viscosity readings were displayed and the readings recorded. [15].

Cloud Point of PMS, AGO, HHK

The test sample was poured into the test jar to the level mark and then closed tightly by the cork bearing the test thermometer. The test jar was inserted in the jacket of the cooling bath maintained at a temperature of 0 +/- 1.5 ℃. At each test thermometer reading that is a multiple of 1 ℃ the test jar was removed from the jacket quickly without disturbing the sample, cloud was inspected, and test jar replaced into jacket. The cloud point was reported to the nearest 1 ℃. The cloud point is the temperature at which cloud is observed basically from the bottom of the test jar [16].

Pour Point of PMS, AGO, HHK

The test sample was poured into the test jar to the level mark. The test jar was closed with a cork carrying the high pour thermometer. The appearance of the test sample was examined when the temperature of the test sample was 9 ℃ above the expected pour point. The pour point is the temperature at which the sample ceases to flow. This was recorded for all the test samples [17].

Flash Point of PMS, AGO, HHK

Abel flash point testers were used in measuring the flash point of samples. A 100 ml of the sample was introduced into the flash point tester. Naked flames were introduced on the sample through an intermediary medium in the form of a liquid intermittently every 2 ℃ rise in temperature. The heating is minimal and therefore good for light samples. The temperature at which the flame is extinguished is the flash point [18].

Gum Content of PMS, AGO, HHK

A 100 ml of the test sample was evaporated with heptane under controlled conditions of temperature and flow of air or steam. The resulting residue was weighed before and after extracting with heptane and the results reported as milligrams per 100 ml. During the test procedure, a measured quantity of the sample (100 ml) was evaporated under controlled temperature conditions by a constant flow of either hot air or steam. The beaker containing the sample was weighed before and after the evaporation to determine the weight of the gum content [19].

Research Octane Number (RON) OF PMS

A 400 ml portion of the PMS was introduced into a carburetor, and the RON machine was switched on. A midscale of the sample was established by its compression ratio. After the machine was switched on and the sample introduced into the carburetor, the fuel level of the carburetor was set at the maximum knock position. The machine was allowed to run for 1 h to attain equilibrium conditions before the cylinder height was adjusted for a knock meter reading between 45 and 47 before measuring the RON [20].

Cetane Number (CN) of AGO

A 100 ml portion of AGO was injected into a constant volume combustion chamber in which the ambient temperature was approximately 575 ℃. The fuel combusts and the high rate of pressure change within the chamber defines the start of combustion. The ignition delay of the fuel which is a function of the cetane number of the fuel was then calculated as the time difference between the start of fuel injection and the start of combustion [21].

Burning Quality of HHK

The wick of a lantern was dried in an oven at 105 ℃ for I hour. The hot wick was soaked in the test sample and inserted in the wick guide. The reservoir of the lamp was rinsed several times with the sample and the sample was filtered through a coarse textured filter paper to remove suspended matter. A 900 ml of the filtered sample was poured into the reservoir, the wick of the lamp was trimmed, and the lamp assembled. The lamp was allowed to burn for 0.5 hour and then the flame was readjusted to the standard dimensions. At the end of this period the lamp was weighed while burning to the nearest 1 g on a platform balance. The lamp was weighed again after 1 h. The wick was further trimmed until the rate of sample consumption is within 22 +/- 4g/h. The sample was then allowed to burn continuously without further adjustment for 16 hours which was the duration of the test. At the end of the test the entire assembly was reweighed to the nearest 1g and then changes in flame height, width and burning rate were recorded [22].

Smoke Point of HHK

A piece of extracted and dried wick of 125 mm long was soaked in the test sample and placed in the wick tube of the candle. A 20 ml of the test sample was introduced into a clean, dry candle. The wick tube was placed in the candle and screwed. The candle was lighted, and the wick adjusted so that the flame was approximately 10 mm high and the lamp was allowed to burn for 5mins. The candle was raised until a smoky tail appears, then the candle was lowered slowly. The height of the smoke of the flame was determined to the nearest 0.5 mm [23].

RESULTS AND DISCUSSION

Table 1 shows the distillation profile of imported petroleum products (PMS_{IP}, AGO_{IP}, HHK_{IP}**)**

Table 1: Distillation Profile of Imported PMS_{IP}, AGO_{IP}, HHK_{IP}

	Recovery Temperature (°C)		
Volume Distilled	PMS_{IP}	AGO_{IP}	HHK_{IP}
IBP	29	202	121
10	38	228	134
20	51	242	145
30	59	255	156
40	67	264	164
50	83	272	177
60	102	279	185
70	112	288	192
80	129	296	205
90	140	308	211
FBP	152	312	220
TR	98 ml	98 ml	98 ml

Table 2 shows the distillation profile of illegally refined petroleum products (PMS_{LR}, AGO_{LR}, HHK_{LR})

Table 2: Distillation Profile of Illegally Refined PMS_{LR}, AGO_{LR}, HHK_{LR}

	Recovery Temperature (°C)		
Volume Distilled	PMS_{LR}	AGO_{LR}	HHK_{LR}
IBP	65	210	149
10	84	267	163
20	93	273	178
30	105	280	191
40	116	291	220
50	124	303	239
60	141	315	248
70	160	326	260
80	178	337	274
90	205	348	280
FBP	252	360	288
TR	95 ml	95 ml	97 ml

Table 3 shows the distillation profile of distillate fractions of PMS, AGO and HHK obtained from fractional distillation (PMS_{ND}, AGO_{ND}, HHK_{ND})

Table 3: Distillation Profile of Distillate Fractions Of PMS_{ND}, AGO_{ND}, HHK_{ND} from Fractional Distillation

	Recovery Temperature (°C)		
Volume Distilled	PMS_{ND}	AGO_{ND}	HHK_{ND}
IBP	33	205	125
10	45	232	138
20	54	246	147
30	61	258	159
40	72	269	167
50	86	278	181
60	105	282	188
70	117	295	199
80	131	302	208
90	143	309	215
FBP	154	315	224
TR	98 ml	97 ml	97 ml

Table 4 shows the characteristics of imported petroleum products (PMS_{IP}, AGO_{IP}, HHK_{IP})

Table 4: Characteristics of Imported Petroleum Products (PMS_{IP}, AGO_{IP}, HHK_{IP}

Parameters	PMS_{IP} Average Reading	AGO_{IP} Average Reading	HHK_{IP} Average Reading
Sp. Gr. @ 60 °C	0.7542	0.8708	0.8207
Density @ 60 °C (g/cm^3)	0.7534	0.87	0.8199
API gravity	56.1200	30.9900	40.9100
Kin. Vis. @ 20 °C (mm^2/sec)	0.8000	1.8000	1.5000
Reid Vapour Pres. (Psi)	8.2000	0.0750	0.1500
Cloud Point (°C)	-20.0000	30.0000	-10.0000
Pour Point (°C)	-30.0000	6.0000	-20.0000
Flash point (°C)	22.0000	85.0000	45.0000
Gum Content (mg/100 ml)	10.0000	9.0000	10.0000
Research Octane Number	90.9000	NA	NA
Cetane Number	NA	55.0000	NA

Table 5 shows the characteristics of illegally refined petroleum products (PMS_{LR}, AGO_{LR}, HHK_{LR})

Table 5: Characteristics of Illegally Refined Petroleum Products PMS_{LR}, AGO_{LR}, HHK_{LR}

Parameters	PMS_{LR} Average Reading	AGO_{LR} Average Reading	HHK_{LR} Average Reading
Sp. Gr. @ 60 °C	0.7612	0.8751	0.8213
Density @ 60 °C (g/cm^3)	0.7604	0.8743	0.8205
API gravity	54.3900	30.2000	40.79
Kin. Vis. @ 20 °C (mm^2/sec)	0.7210	1.6800	1.4600
Reid Vapour Pres. (Psi)	14.0100	0.1530	0.1900
Cloud Point (°C)	-10.0000	20.0000	-10.0000
Pour Point (°C)	-40.0000	-10.0000	-30.0000
Flash point (°C)	15.0000	55.0000	25.0000
Gum Content (mg/100 ml)	10.0000	9.0000	10.0000
Research Octane Number	71.9000	NA	NA
Cetane Number	NA	32.0000	NA

Table 6 shows the characteristics of distillate fractions of PMS, AGO and HHK obtained from fractional distillation (PMS_{ND}, AGO_{ND}, HHK_{ND})

Table 6: Characteristics of Distillate Fractions of PMS_{ND}, AGO_{ND}, HHK_{ND} Obtained from Fractional Distillation

Parameters	PMS_{ND} Average Reading	AGO_{ND} Average Reading	HHK_{ND} Average Reading
Sp. Gr. @ 60 °C	0.7585	0.8725	0.8208
Density @ 60 °C (g/cm^3)	0.7577	0.8718	0.8200
API gravity	55.05	30.6800	40.8900
Kin. Vis. @ 20 °C (mm^2/sec)	0.7865	1.7900	1.5000
Reid Vapour Pres. (Psi)	7.8780	0.0710	0.1500
Cloud Point (°C)	-20.0000	30.0000	-10.0000
Pour Point (°C)	-30.0000	-3.0000	-20.0000
Flash point (°C)	21.0000	80.0000	42.0000
Gum Content (mg/100 ml)	10.0000	9.0000	10.0000
Research Octane Number	87.9000	NA	NA
Cetane Number	NA	52.0000	NA

Table 7 shows exclusive characteristics of HHK

.Table 7: Exclusive Characteristics of HHK

Parameters	HHK_{IP}	HHK_{LR}	HHK_{ND}
Flame Height (mm)	34.80	44.80	35.20
Flame Width (mm)	36.00	47.50	38.00
Burning Rate (g/h)	25.10	37.80	26.10
Smoke Point (mm)	42.80	33.50	40.50
Colour of Chimney Deposit	None/light	Yellow/medium	**None/light**

Table 8 shows the extent of deviation in the physiochemical characteristics of imported products with respect to DPR specification.

Table 8: Deviations of Physio-Chemical Characteristics of Imported Products) from DPR Limits

Parameters	PMS_{IP}		AGO_{IP}		HHK_{IP}	
	DPR SPEC	% Deviation	DPR SPEC	% Deviation	DPR SPEC	% Deviation
Sp. Gr. @ 60 °C	0.7500	0.0017	0.8600	0.0041	0.825	0.0017
Density @ 60 °C (g/cm^3)	0.7400	0.0055	0.8300	0.0154	0.816	0.0015
API gravity	57.1000	0.0461	32.9000	0.1201	41.17	0.0143
Kin. Vis. @ 20 °C (mm^2/sec)	1.0000	0.0750	1.9000	0.0000	2.0000	0.1336

Reid Vapour Pres. (Psi)	8.0000	0.0248	0.1000	0.0299	0.2000	0.0247
Cloud Point (°C)	-20.0000	0.0000	20.0000	0.7071	-10.0000	0.0000
Pour Point (°C)	-30.0000	0.0000	3.0000	0.5000	-20.0000	0.0000
Flash point (°C)	25.0000	0.2190	90.0000	0.1889	50.0000	0.2565
Gum Content (mg/100 ml)	10.0000	0.0000	10.0000	0.1147	10.0000	0.0000
Research Octane Number	95.0000	0.1504	NA	NA	NA	NA
Cetane Number	NA	NA	55.0000	0	NA	NA

Table 9 shows the extent of deviation in the physiochemical characteristics of illegally refined products with respect to DPR specification.

Table 9: Deviations of Physio-Chemical Characteristics of Illegally Refined Products from DPR Limits

Parameters	PMS_{LR}		AGO_{LR}		HHK_{LR}	
	DPR SPEC	% Deviation	DPR SPEC	% Deviation	DPR SPEC	% Deviation
Sp. Gr. @ 60°C	0.7500	0.0046	0.8600	0.0057	0.8250	0.0014
Density @ 60 °C (g/cm^3)	0.7400	0.0080	0.8300	0.0169	0.8160	0.0018
API gravity	57.1000	0.1283	32.9000	0.0170	41.1700	0.0209
Kin. Vis. @ 20 °C (mm^2/sec)	1.0000	0.1063	1.9000	0.0581	2.0000	0.1452
Reid Vapour Pres. (Psi)	8.0000	0.6405	0.1000	0.0527	0.2000	0.0080
Cloud Point (°C)	-20.0000	0.9129	20.0000	0.0000	-10.0000	0.0000
Pour Point (°C)	-30.0000	0.5976	3.0000	2.4568	-20.0000	0.7071
Flash point (°C)	25.0000	0.7906	90.0000	1.4533	50.0000	1.4434
Gum Content (mg/100 ml)	10.0000	0	10.0000	0.1147	10.0000	0
Research Octane Number	95.0000	0.8940	NA	NA	NA	NA
Cetane Number	NA	NA	55	1.2329	NA	NA

Table 10 shows the extent of deviation in the physiochemical characteristics of distillate fractions of PMS, AGO and HHK with respect to DPR specification.

Table 10: Deviations of Physio-Chemical Characteristics of Distillate Products from DPR Limits

Parameters	PMS_{ND}		AGO_{ND}		HHK_{ND}	
	DPR SPEC	% Deviation	DPR SPEC	% Deviation	DPR SPEC	% Deviation
Sp. Gr. @ 60°C	0.7500	0.0035	0.8600	0.0047	0.8250	0.0001
Density @ 60 °C (g/cm^3)	0.7400	0.0073	0.8300	0.016	0.8160	0.0001

API gravity	57.1000	0.0977	32.9000	0.1392	41.1700	0.0200
Kin. Vis. @ 20 °C (mm^2/sec)	1.0000	0.0798	1.9000	0.0313	2.0000	0.1400
Reid Vapour Pres. (Psi)	8.0000	0.0152	0.1000	0.03506	0.2000	0.0400
Cloud Point (°C)	-20.0000	0.0000	20.0000	0.7071	-10.0000	0.0000
Pour Point (°C)	-30.0000	0.0000	3.0000	0.0002	-20.0000	0.0000
Flash point (°C)	25.0000	0.2949	90.0000	0.0087	50.0000	0.3600
Gum Content (mg/100 ml)	10.0000	0.0000	10.0000	0.1147	10.0000	0.0000
Research Octane Number	95.0000	0.2512	NA	NA	NA	NA
Cetane Number	NA	NA	55.0000	0.0962	NA	NA

Table 11 shows the extent of deviation in the exclusive characteristics of HHK with respect to DPR specification.

Table 11: Deviations of Exclusive Characteristics of Imported (IP), Locally Refined and Distillate Product (ND) Of HHK From DPR Limits

Parameters	HHK_{IP}		HHK_{LR}		HHK_{ND}	
	DPR SPEC	% Deviation	DPR SPEC	% Deviation	DPR SPEC	% Deviation
Flame height (mm)	33.0000	0.1093	33.0000	0.6689	33.0000	0.1332
Flame width (mm)	35.0000	0.0593	35.0000	0.6881	35.0000	0.1756
Burning rate (g/h)	25.0000	0.0071	25.0000	0.8076	25.0000	0.0769
Smoke point (mm)	40.0000	0.1539	40.0000	0.3791	40.0000	0.0279

Petroleum refining is very critical in upgrading the value of petroleum as well as diversifying its use. Petroleum as a commodity has very limited use outside refining processes. Fractional distillation is the major procedure that takes place in the refining of petroleum, and it is responsible in separating petroleum into several other useful and valuable products [8].

Tables 1, 2 and 3 show the distillation profiles of imported petroleum products (PMS_{IP}, AGO_{IP} and HHK_{IP}), illegally refined products (PMS_{LR}, AGO_{LR} and HHK_{LR}) as well as fractions obtained from fractional distillation (PMS_{ND}, AGO_{ND} and HHK_{ND}). The distillation profile of petroleum products is a very critical quality that unveils the volatility characteristics of the product as well as takes advantage of the boiling point properties of the products [7]. Tables 1, 2 and 3 show the volume of the products distilled at various temperatures beginning from the initial boiling point (IBP) which refers to the temperature at which the first drop of product was produced to the final boiling point (FBP) which refers to the temperature at which the last drop of the product was recovered. The FBP of petroleum products during distillation profile analyses is expected to be very close to the temperature at which the product was distilled during fractional distillation if the distillation process was properly done. With values of 150 ℃ for PMS, 310 ℃ for AGO and 220 ℃ for HHK obtained during fractional distillation of the crude, results obtained from Tables 1, 2 and 3 show that the FBP of imported products (PMS_{IP}, AGO_{IP} and HHK_{IP}) and products from fractional distillation (PMS_{ND}, AGO_{ND} and HHK_{ND}) were very close to the upper limit of the distillation temperature of the products with an acceptable temperature variation between 2 to 5 ℃. On the other hand, the FBP of illegally refined products (PMS_{LR}, AGO_{LR} and HHK_{LR}) with values of 252 ℃ for PMS, 360 ℃ for AGO and 288 ℃ for HHK were much higher than the distillation temperature of the products. The volatility characteristics of petroleum products have a great deal of impact to engine performance. For instance, petroleum products (PMS and AGO) with high recovery temperature during distillation analyses will cause hard start in engines while products with recovery temperatures below acceptable limits will easily evaporate during operation thereby negatively impacting on the engines. The chemical make-up and composition of petroleum are impacted as they volatilize from liquid to vapor [6, 24].

Other characteristics that impact on the quality of PMS, AGO and HHK are highlighted. Tables 4, 5 and 6 show other characteristics of imported petroleum products (PMS_{IP}, AGO_{IP} and HHK_{IP}), illegally refined products (PMS_{LR}, AGO_{LR} and HHK_{LR}) and products obtained from fractional distillation (PMS_{ND}, AGO_{ND} and HHK_{ND}) respectively. These characteristics include specific gravity, density, American petroleum institute (API) gravity, kinematic viscosity, reid vapor pressure, cloud point, pour point, flash point and gum content. Research octane number and cetane number are exclusive characteristics of PMS and AGO respectively while Table 7 shows the characteristics of HHK represented by the flame height, flame width, burning rate, smoke point and color of chimney deposits.

The specific gravity of petroleum product can be defined as the mass of a unit volume of the product to the mass of the same volume of water at the standard temperature of 60 ^{0}F or 15.56 ^{0}C. The density of petroleum products refers to the ratio of the mass of the product per unit volume, it defines the amount of energy stored within the product. The specific gravity and the density of the products gives an idea of the chemical composition of the product that is if the product contains light or heavy fractions, if it contains sulphur etc [25]. The density of petroleum products is one of the most important variables because it validates other parameters such as API gravity, kinematic viscosity, reid vapor pressure, cloud point, pour point and flash point. The API gravity is obtained from the density and specific gravity, it determines the market value of the product, and it is inversely proportional to the density [2].

Kinematic viscosity of petroleum products can be defined as the products internal resistance to flow under gravitational forces. It is determined by measuring the time in seconds required for a fixed volume of the product to flow through a known distance by gravity through a capillary within a calibrated viscometer [26]. Density and viscosity are two independent parameters that are not directly related. However, they are related indirectly through temperature as such the higher the temperature, the lower the density and the more viscous the product. Most engines are designed to operate at specific densities and viscosities. As such an alteration or deviation totally jeopardizes the engine performance [27].

Another parameter that determines the volatility characteristics of petroleum products is the reid vapor pressure. RVP of petroleum product can be defined as the vapor pressure of the product at 100 ^{0}F or 37.8 ^{0}C. RVP determines the ability of the product to vaporize and form volatile emissions at specified temperatures. Petroleum products with RVPs below acceptable standards as specified by Department of Petroleum Resources (DPR) will easily vaporize thereby negatively affecting its engine performance, fuel optimization and increase the release of hydrocarbon emissions to the environment while products with high RVP can cause autoignition problems and even outright detonation of automotive engines in the case of PMS [24].

One important parameter that is affected by the vapor pressure is the flashpoint. Flashpoint of a petroleum product can be defined as the minimum temperature at which the vapor concentration near the surface of the product becomes high enough to form an ignitable mixture. The higher the boiling point of a product, the higher its vapor pressure and the lower its flash point [8].

The flow assurance parameters of petroleum product are represented by their cloud and pour points. The cloud point of a petroleum product is the temperature at which wax begins to separate from the product. The formation of wax in a product is usually indicated by a cloudy appearance on the other hand the pour point of a petroleum product is the lowest temperature at which the product can flow under gravity as such petroleum products cannot be stored below its pour point [28]. The cloud point is directly proportional to the pour point as such the tendency of products to stop flowing is higher with the appearance of wax. Petroleum products with high cloud and pour points are better in temperate regions while those with low cloud and pour points are better in tropical regions. Petroleum products with cloud and pour points above acceptable limits can plug filters thereby negatively affecting engine performance [29].

The gum content of petroleum products refers to the nonvolatile residue that is left after evaporating the sample under controlled conditions. Petroleum products (PMS and AGO) with high gum content above DPR specification can lead to the plugging of fuel injectors thereby resulting in bad engine performance [9].

Research octane number (RON) is an exclusive property of PMS, it is defined as the percentage volume of iso-octane in a mixture of iso-octane and n-heptane that knocks with the same intensity as the fuel under test. Knocking is a loud rapping noise in a spark ignition engine associated to PMS with low octane rating. Research octane number indicates the combustibility of engine fuel at low speeds and temperatures. The higher the RON rating the more compressions the spark ignition engines can withstand. The minimum allowable RON as specified by DPR is ≥95 [24].

The cetane number is an exclusive property of AGO, It is defined as the percentage by volume of hexadecane in a combustible mixture that contains cetane and 1-methylnaphthalein with the same performance as the fuel under test. The cetane number is an indicator of the combustion speed of diesel fuel and compression needed for ignition. The higher the cetane number the better the performance of AGO. However, diesel engines function optimally with AGO with cetane number around 55 as specified by DPR [8].

Tables 8, 9 and 10 show the deviations of the physicochemical properties of the imported products (PMS_{IP}, AGO_{IP}, HHK_{IP}), illegally refined products (PMS_{LR}, AGO_{LR}, HHK_{LR}) and fractions obtained from fractional distillation (PMS_{ND}, AGO_{ND}, HHK_{ND}) with respect to Department of Petroleum Resources (DPR) specification. Results obtained show that all the physicochemical properties of PMS_{ND}, AGO_{ND}, HHK_{ND}, PMS_{IP}, AGO_{IP} and HHK_{IP} were within DPR acceptable limit with a deviation of $\leq 0.5\%$ except the cloud points of AGO_{IP} and AGO_{ND} with deviations of 0.7% respectively. The reid vapour pressure, cloud point, pour point, flash point, RON of locally refined PMS were off DPR acceptable limit. All the burning characteristics of illegally refined HHK (HHK_{LR}) apart from the smoke point with a deviation of 0.379% were off DPR acceptable limit justifying the high rate of kerosene explosion.

CONCLUSION

The physicochemical characteristics of petroleum products (PMS, AGO, HHK) are very critical in petroleum product specification and quality control. The effectiveness of PMS and AGO in powering spark ignition and compression ignition engines is dependent on the RON of PMS and CN of AGO respectively. The optimal performance of engines as well as the by-products released to the environment during operations are highly dependent on the physicochemical characteristics of the petroleum products. The characteristics of petroleum products such as PMS, AGO and HHK can be traceable to the refining process as such accurate and proper adherence to the process of fractional distillation is critical in ensuring that the quality of petroleum products meet acceptable international standards. A comparative evaluation of the physicochemical characteristics of imported petroleum products (PMS_{IP}, AGO_{IP} and HHK_{IP}) and products obtained from a properly carried out fractional distillation process (PMS_{ND}, AGO_{ND}, HHK_{ND}) on a Niger Delta crude, gave results that are within acceptable international standards as corroborated by the Department of Petroleum Resources. However, there are discrepancies with the illegally refined products whose parameters especially as regards PMS and HHK were off DPR acceptable limit. Lack of adherence to procedures in terms of reaction conditions (pressure, volume and temperature), inadequate equipment and poor environment which characterized illegal refining are responsible for the poor quality of the petroleum products (PMS_{LR}, AGO_{LR}, HHK_{LR}). The results obtained from the characteristics of PMS_{ND}, AGO_{ND}, HHK_{ND} is a proof that Nigeria can save a lot of cost and create foreign reserves through refining its petroleum within the shores of the nation.

REFERENCES

[1] Hsu, C. S., Robinson, P. R., Hsu, C. S. & Robinson, P. R. (2019). Characteristics and Historical Events. *Petroleum Science and Technology*, 3-18.

[2] Ejechi, B. O. & Ozochi, C. A. (2015). Assessment of the physicochemical and microbiological status of western Niger Delta soil for crude oil pollution bioremediation potential. *Environmental Monitoring and Assessment*, *187*, 1-11.

[3] Akinlua, A., Ajayi, T. R. & Adeleke, B. B. (2007). Organic and inorganic geochemistry of northwestern Niger Delta oils. *Geochemical journal*, *41*(4), 271-281.

[4] Ofodile, S. E., Boisa, N., Obunwo, C. C. & Frank, O. M. (2018). Characterisation of oil properties from Niger Delta crude. *J Environ Anal Toxicol*, *8*(2), 1-7.

[5] Ogbesejana, A. B., Bello, O. M. & Okunola, O. J. (2021). Occurrence and geochemical significance of fluorene and alkylfluorenes in crude oils and source rock extracts from Niger Delta basin, Nigeria. *Heliyon*, *7*(3).

[6] Liu, Q., Yang, S., Liu, Z., Liu, Q., Shi, L., Han, W. & Li, M. (2021). Comparison of TG-MS and GC-simulated distillation for determination of the boiling point distribution of various oils. *Fuel*, *301*, 121088.

[7] Muller, H., Saleem, Q., Alawi, E. A., Alsewdan, D. A., Naqvi, I. A., Saleh, A. H. & Rowaished, T. A. (2021). Narrow distillation cuts for an improved characterisation of crude oil: an insight on heteroatoms in heavy fraction molecules. *International Journal of Oil, Gas and Coal Technology*, *26*(1), 40-59.

[8] Odebunmi, E. O., Ogunsakin, E. A. & Ilukhor, P. E. P. (2002) Characterization of crude oils and petroleum products:(I) Elution liquid chromatographic separation and gas chromatographic analysis of crude oils and petroleum products. *Bulletin of the Chemical Society of Ethiopia*, *16*(2), 115-132.

[9] Patil, A., Arnesen, K., Holte, A., Farooq, U., Brunsvik, A., Størseth, T. & Johansen, S. T. (2021). Crude oil characterization with a new dynamic emulsion stability technique. *Fuel*, *290*, 120070.

[10] Onyema, M. O., Okoroh, N. C., Okorie, I. H. & Osuji, L. C. (2020). Geochemical Characterization of Two Niger Delta Crude Oils and Their Mixtures II: Correlation of Bulk Properties and Aliphatic Hydrocarbons. *Science*, *8*(5), 107-112.

[11] American Society for Testing Materials (ASTM D2892) (2010). Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column), vol 2, 6-5.

[12] American Society for Testing Materials (ASTM D86) (2022). Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, vol 1, 21.

[13] American Society for Testing Materials (ASTM D1298) (2002). Standard Test Method for Density,Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method, vol 1, 7-5.

[14] American Society for Testing Materials (ASTM D323) (2020) Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method), vol 2, 4-6.

[15] American Society for Testing Materials (ASTM D4052) (2002) Standard Test Method for Density,Relative Density and API Gravity of Liquids by Digital Density Meter, vol 3, 4-6.

[16] American Society for Testing and Materials (ASTM D5771) (2002). Standard test method for cloud point of petroleum products vol 3, 3-4.

[17] American Society for Testing and Materials (ASTM D97 – 06) (2012). Standard test method for pour point of petroleum products, vol 2, 2-3.

[18] American Society for Testing Materials (ASTM D93) (2020). Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester, vol 2, 4-7.

[19] American Society for Testing Materials (ASTM D381) (2022). Standard Test Method for Gum Content in Fuels by Jet Evaporation, vol 2, 2-3.

[20] American Society for Testing Materials (ASTM D2699) (2021) Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel, vol 2, 2-3.

[21] American Society for Testing Materials (ASTM D613) (2021). Standard Test Method for Cetane number of Diesel fuel oil, vol 1, 20.

[22] American Society for Testing Materials (ASTM D187) (2018). Standard Test Method for Burning Quality of Kerosene, vol 3, 2-3.

[23] American Society for Testing Materials (ASTM D1322) (2022). Standard Test Method Smoke Point of Kerosene and Aviation Turbine Fuels, vol 4, 3-5.

[24] Chikwe, T. N. & Onojake, M. C. (2018). Characterization of some crude oil samples from Niger delta area of Nigeria using infrared absorption spectrometric technique. *Chemistry International*, *4*(3), 163-169.

[24] Dehkissia, S., Larachi, F., Rodrigue, D. & Chornet, E. (2004). Characterization of Doba–Chad heavy crude oil in relation with the feasibility of pipeline transportation. *Fuel*, *83*(16), 2157-2168.

[25] Chmielowiec, A., Woś, W. & Gumieniak, J. (2021). Viscosity approximation of PDMS using Weibull function. *Materials*, *14*(20), 6060.

[26] Khatir, B. & Golovin, K. (2021). Ultrasmall volume single-droplet viscometry: Monitoring cornering instabilities on omniphobic polydimethylsiloxane brushes. *Langmuir*, *37*(44), 12812-12818.

[27] Husein, N., Ismail, I., Boyou, N. V., Mani, S. V. S., Wong, Z. K. & Sulaiman, W. R. W. (2021). Experimental investigation of different simulated formation water salinity in three-phase waxy crude oil-water-gas flow in horizontal pipes. *Journal of Petroleum Science and Engineering*, *207*, 109160.

[28] Lim, Y. K., Lee, J. M., Jeong, C. S., Kim, J. R. & Yim, E. S. (2011). Improvement of Low Temperature Fuel Characteristics by Pour Point Depressant. *Tribology and Lubricants*, *27*(2), 109-114.