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Comparative Analysis of HHK Samples from Artisanal and Legal Refineries Based on International Standards

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Abstract: *Physicochemical properties of artisanal refined gasoline (ARG), arstisanal refined HHK, regular refined HHK and regular automotive gasoline (RAG) sampled from the Eastern Kolo Creek and a tank farm depot in Delta State, Nigeria were investigated. This was to compare the physicochemical properties of the samples with each other and their compliance with American Society for Testing and Materials (ASTM) standards. The finding revealed that the artisanal refined products quality did not comply with ASTM standards. The research octane number, motor octane number, Reid vapor pressure, and specific gravity of RAG were (ASTM) compliant while only the final boiling point of ARG were within ASTM range. Based on the findings, the artisanal refined products might have been poorly refined or adulterated and could constitute problems in automotive engines if used. However, this crude technology can be upgraded and the gasoline quality improved through alkylation, isomerization, and cyclization. Artisanal refiners should be trained to become proficient with the intent of becoming incorporated into the upstream petroleum sector.*

Keywords: Petroleum, HHK, ASTM, Artisanal, Refined AGO, Flash Point, Octane Number

INTRODUCTION

Petroleum, meaning literally "rock oil, "is the term used to describe a myriad of hydrocarbon-rich fluids that have accumulated in subterranean reservoirs, Speight (2002). It is usually found with gases in its free form or in its dissolved form. Petroleum (also called crude oil) varies dramatically in colour, odour, and flow properties that reflect the diversity of its origin, Speight (2002). Little wonder Achuba (2006) described petroleum as a brown to black viscous liquid found beneath the sedimentary rock on the earth crust. Petroleum, originally distilled and sold as fractions with desirable physical properties, has been recorded as the world's main source of energy and petrochemical feedstock. In recent times, crude oil is distributed in diverse forms which includes: gasoline, diesel and jet fuel, kerosene, lubricant oils, asphalts etc. or it is converted to petrochemical feed stocks. Feed stocks form the basis for, among others, the plastics, elastomer, and artificial fiber industries. Some feed stocks include: ethylene, propylene, butene, butadiene, and isoprene. In brief, a refinery must be recognized as a complex network of integrated unit processes for the purpose of producing a variety of products from petroleum (Speight, 1999; Speight and Ozum, 2002). These petroleum fractions or products are obtained from refining carried out in refineries.

Conversion processes include coking, hydrocracking and catalytic cracking to break large molecules into smaller fractions; hydro treating to reduce heteroatoms and aromatics, creating environmentally acceptable products; and isomerization and reforming to rearrange molecules into those with high value, e.g., gasoline with a high-octane number (Speight, 2002). This refining method gives rise to the following products: gasoline (PMS), kerosene (DPK), diesel (AGO), bitumen, asphalt, liquefied natural gas (LPG), and others depending on the prevailing conditions. Gasoline is obtained from crude oil through blending of atmospheric distillation naphtha and products from other complex refinery processes Handwerk (2001) while HHK is obtained from fractional distillation of crude samples.

Experimental Procedures

MATERIALS AND METHODS

Petroleum

Petroleum is a complex gaseous, liquid, or solid mixture of hydrocarbons found on the earth's surface. The term "petroleum," which comes from the Latin words "petra" (rock or stone) and "oleum," was first used in a treatise by Georg Bauer in 1556. (Riva, 2006). More than 5000 years ago, the Sumerians, Assyrians, and Babylonians used crude oil and asphalt (James H. Gary, Glenn E. Handwerk, Mark J. Kaiser 2007). The Egyptians utilized oil as a weapon of war; the Arabs and

Persians distilled crude oil to make combustible products early in the Christian period; and, most likely as a result of the Arab invasion of Spain, distillation became available in Western Europe by the year 1000. Petroleum and its derivatives were not widely used in ancient times. Oil became a commercial commodity only after the discovery of kerosine (James H. Gary, Glenn E. Handwerk, Mark J. Kaiser, 2007). Abraham Gesner discovered a method for producing a liquid fuel from coal in 1846, which he dubbed "kerosine" (or coal oil) and sold in Halifax, Nova Scotia (Knowles 1983; Yergin 1993). Since man has been using oil since Biblical times, petroleum has held a significant role in human history. Petroleum, often known as crude oil, is a fossil fuel that is formed when dead creatures trapped beneath sedimentary rocks are exposed to extreme heat and pressure. Petroleum is a naturally occurring mixture of hydrocarbons that may also contain sulfur, nitrogen, oxygen, metals, and other elements in a liquid form (ASTM D-4175). According to (Adebayo, 1999), petroleum is thought to be generated from aquatic plants and animals that lived millions of years ago and whose remains were mingled with mud and sand in layered deposits before transforming geologically into sedimentary rock. After migrating from the source bed to more porous and permeable rocks (sandstone and siltstone), the petroleum is trapped in a reservoir (Adegeye et. al. 1993).

Crude Oil

Crude oil is a liquid that can be found deep within the Earth's crust in various formations. This liquid is formed by the decomposition of organic material that has been around for millions of years. Crude oil is a mixture of complex hydrocarbon molecules and other organic substances, as revealed by its chemistry. Petroleum is another name for this material, albeit that term also refers to goods made from refined material. Crude oil is distilled after it has been extracted. Depending on the liquid's particular composition, this process breaks it down into several components of varying weights. The major products of crude are used to create energy carriers such as gasoline, jet fuel, diesel, and heating oil. Tar, asphalt, paraffin wax, and lubricating lubricants are all made with heavier materials. Sulfur, petroleum coke, and petrochemicals are among the substances that can be extracted from the liquid. There are about 6000 things derived from petroleum byproducts in addition to the products directly obtained from crude oil. Fertilizer, perfume, pesticides, soap, and vitamin capsules are just a few examples.

Kerosene

The lighter end of a collection of petroleum streams known as the middle distillates is referred to

as kerosene. Kerosene is produced by distilling crude oil at atmospheric pressure (straight-run kerosene) or catalytic, thermal, or steam cracking of heavier petroleum streams (cracked kerosene). To eliminate or lower the level of sulfur, nitrogen, or olefinic components in the kerosenes, a range of methods (including hydrogenation) are used. The exact composition of any given kerosene will be determined by the crude oil used to make it and the refining methods utilized to make it. Regardless, kerosenes are primarily composed of C9 to C16 hydrocarbons and boil at temperatures ranging from 145 to 300 degrees Celsius. The main constituents of kerosenes include branched and straight chain paraffins, as well as naphthenes, which make up around 70% of the substance. Aromatic hydrocarbons, primarily alkylbenzenes and alkylnaphthalenes, make up less than 25% of kerosene streams. Olefins typically make up less than 5% of kerosenes.
Kerosene's normal color is white, and it's often referred to as "the white product"; colorimeters are used to measure its color. If the fractions aren't tuned appropriately, they can be dangerous to people, engines, and the environment. Kerosene is categorized into two kinds: domestic kerosene, also known as household kerosene (HHK), and jet kerosene, also known as aviation turbine kerosene (ATK). Kerosene is the main fuel used in Nigeria by the majority of third-class citizens for cooking and lighting as a substitute for electricity and gas (ASTM 2005). Other uses include fire breathing, fire juggling, fire dancing, antidote for snakebites,local insecticides on stagnant water,local disinfectant to treat cuts and burns, & solvent for removal mucilage & candle wax on glass, & lubricant for cutting glass & machining aluminum. Kerosene density varies between 0.74 and 0.85g/cm3 & it is miscible with petroleum solvents but immiscible with water (ASTM 2005).

Gasoline

Gasoline is a refined product of petroleum consisting of a mixture of hydrocarbons, additives, and blending agents. The composition of gasolines varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. The typical composition of gasoline hydrocarbons (percent volume) is as follows: 4-8 percent alkanes; 2-5 percent alkenes; 25-40% isoalkanes; 3-7% cycloalkanes; l-4% cycloalkenes; and 20-50% total aromatics (0.5-2.5% benzene) (IARC 1989). To increase the performance and stability of gasoline, additives and blending agents are added to the hydrocarbon mixture (IARC 1989; Lane 1980). Anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, and anti-rust agents are among these substances, agents, anti-icing agents, lubricants for the upper cylinders, detergents, and dyes (IARC 1989; Lane 1980). Finished gasoline typically contains more than 150 different components at the end of the manufacturing process. Although some blends have had as many as 1,000 compounds identified (Domask 1984;Mehlman, 1990).
According to Vempatapu and Kanaujia (2017), physicochemical properties like distillation profile,

research octane number (RON), motor octane number (MON), and Reid vapor pressure are frequently used to detect the adulteration and quality of gasoline. It is on this basis that this research was designed to compare the physicochemical properties of regular automotive gasoline and house hold kerosene and locally refined gasoline and house hold kerosene and their compliance with ASTM standards.

Operating Systems

Upstream Operating Systems

Exploring crude oil resources and crude oil production are examples of upstream operations. Corporations that operate with oil drilling rights (such as ExxonMobil) and corporations that provide support services to the drilling sector of the industry are examples of companies that belong in the upstream segment of the industry (e.g. Halliburton).

Operations in the Midstream

The transportation of crude oil to refiners, the refining of crude oil into commercially viable products, and the distribution of products to wholesalers and retailers are all examples of midstream activity. Companies that transport oil by pipeline, truck, or barge (e.g., Magellan Pipeline) are examples of companies that belong in the midstream section of the industry.
as well as refineries of crude oil (e.g., Tesoro).

Operations in the Downstream

The retail of petroleum products is part of downstream activity. The most prominent downstream companies are gasoline stations, but companies that distribute heating oil or propane would also fall into this group. Some petroleum firms engage in activities that fall into the upstream, midstream, and downstream categories. ExxonMobil is an example of a company like this. Others have activities that are primarily focused on a single market niche. Petroleum refineries are massive industrial facilities that convert crude oil into marketable petroleum products (and sometimes other feedstocks like biomass). Petroleum refining and quality analysis, which covers this scope of study, is a mid-stream operation.

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Figure 1: Pictorial Representation of Upstream, Midstream and Downstream (Angela *et al*, 2018)

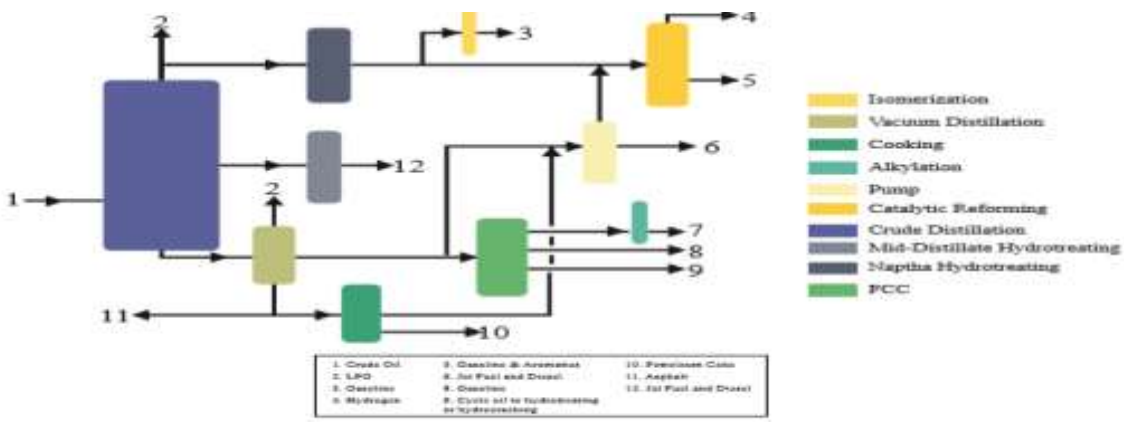

Figure 2: Typical Complex Oil Refinery (Plant Process Equipment Incorporated) (Angela et. al. 2018)

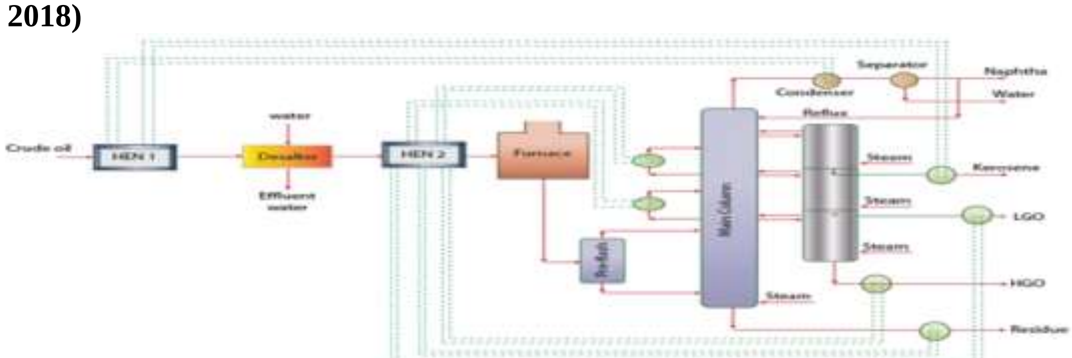

Figure 3: Process Flow Sheet (Angela *et al,* 2018)

Petroleum Products

Although the average consumer tends to think of petroleum products as consisting of a few items such as motor gasoline, jet fuel, home heating oils, and kerosine, a survey by the American Petroleum Institute (API) conducted at petroleum refineries and petrochemical plants revealed over 2000 products made to individual specifications (API 1958).

Materials

The following equipment's and glass wares will be used for products analysis:

Reid vapor pressure tester, Flash point tester, Octane rating tester, Distillation column, Round bottom flask, Measuring cylinder, Refrigerator, Gas cylinder, Sampling cans, Hydrometer, Thermometer

Two samples each of artisanal refined gasoline (ARG) and artisanal refined house hold kerosene (HHK) will be randomly collected from the Ogbia Creek in Niger Delta, Nigeria and two samples each of regular automotive gasoline (RAG) and regular house hold kerosene samples will also be randomly obtained from Matrix Energy Limited, Warri depot tank farm. All samples will be Labeled in sample bottles (2.5 L). At each sampling station, the sample bottle will be rinsed with the sample to be collected. The sample will be introduced into the sample bottle via the dispenser nozzle, labeled, and transported to the laboratory for treatment and analysis. ASTM standards will be used as reference standards and all samples analyzed according to ASTM test methods.

SOME OF THE GLASSWARES AND EQUIPMENTS USED:

Figure 4: AGO and HHK

Figure 6: Abel Closed Cup Flash Point Machine

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Figure 8: Petrotest DU 4 Distillation Unit

Figure 7: Measuring Cylinder

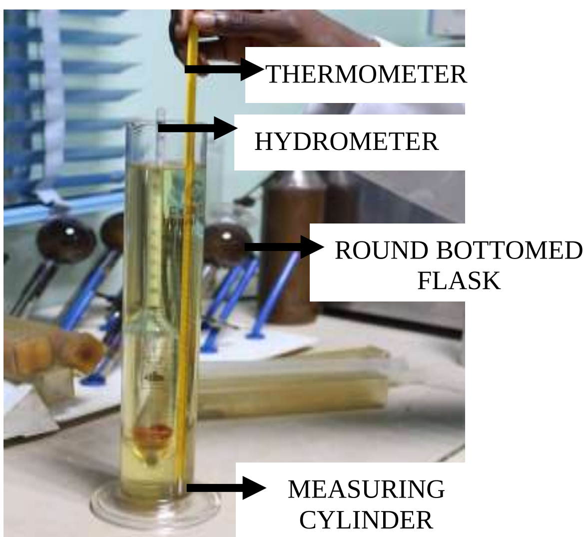

Figure 5: Measuring Cylinder

Test Methods

ASTM D86 Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure:

Based on its composition, vapor pressure, expected IBP and/or FBP, the sample is placed in one of four groups. Apparatus arrangement, condenser temperature,

and other operational variables are defined by the group in which the sample falls. 100-ml of the sample is distilled under prescribed conditions for the group in which the sample falls. The distillation is performed in a laboratory batch distillation unit at ambient pressure under conditions that provide one theoretical plate fractionation. Systematic observations of temperature readings and volumes of condensate are made. The volume of the residue and the losses are also recorded.

Determination of the initial and final boiling point of the samples will be conducted according to the ASTM-D86 standard test method (ASTM, 2006b). The gasoline sample (100mL) was added into a round bottom flask. The distillation machine was switched on and the temperature was adjusted to 300◦C. The initial boiling point (IBP) temperature of the gasoline samples were recorded immediately when the first drop of gasoline entered the measuring cylinder. The temperature of the distillation machine was increased to take the final boiling point (FBP) reading. Also,the total recovery (TR) temperature was recorded.

RESULTS

Distillation Profile for AGO Samples

Distillation (or volatility) characteristics of a diesel fuel exert a great influence on its performance, particularly in medium- and high-speed engines. Distillation characteristics are measured with a procedure (ASTM D-86, IP 123) in which a sample of the fuel is distilled and the vapor temperatures are recorded for the percentages of evaporation or distillation throughout the range. The volatility requirement of diesel fuel varies with engine speed, size and design. However, fuels having too low volatility tend to reduce power output and fuel economy through poor atomization, and those having too high volatility may reduce power output and fuel economy through vapor lock in the fuel system or inadequate droplet penetration from the nozzle. In general, the distillation range should be as low as possible without adversely affecting the flash point, burning quality, heat content, or viscosity of the fuel. If the 10% point is too high, poor starting may result. An excessive boiling range from 10% to 50% evaporated may increase warm up time. A low 50% point is desirable in preventing smoke and odor. Low 90% and end points tend to ensure low carbon residuals and minimum crankcase dilution. The temperature for 50% evaporated, known as the mid-boiling point, usually is taken as an overall indication of the fuel distillation characteristics where a single numerical value is used alone. For example, in high-speed engines, a 50% point above 575°F (302°C) probably would cause smoke formation, give rise to objectionable odor, cause lubricating oil contamination, and promote engine deposits. At the other extreme, a fuel with excessively low 50% point would have too low a viscosity and too low a heat content per unit volume. Thus a 50% point in the range of 450–535 F (232–280°C) is most desirable for the majority of automotive-type diesel engines. This average range usually is raised to a higher temperature spread for larger, slower-speed engines. Although determining the volatility of diesel fuel is usually accomplished through a boiling range distribution (ASTM D-86, IP 123).

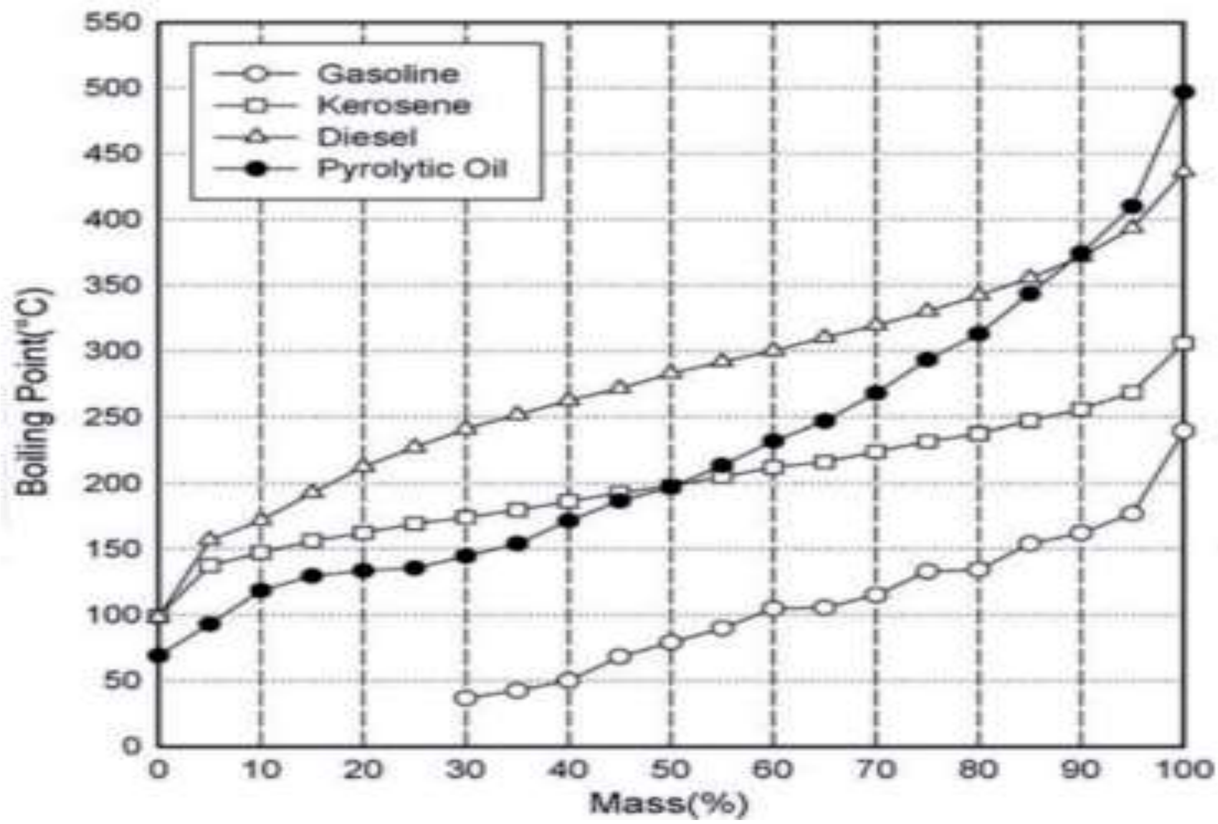

Figure 9: Distillation Profile Of Different Petroleum Products.
DOI: http://dx.doi.org/10.5772/intechopen.90639

Distillation Profile for HHK Samples

Table 1: Distillation Profile Results for HHK Samples From Illegal Refining Source and Certified Suppliers

Distillation Profile (%)	HHK Illegal Source 1(℃)	HHK 2 (℃)	Standards (℃)
IBP	55	153	
5	120	163	
10	143	177	175-205 max
20	152	179	
30	168	185	
40	188	189	
50	203	193	
60	220	180	
70	235	196	
80	257	225	
90	275	230	
95	290	237	
FBP	330	266	250-300 max
% Recovery	97%	99%	
% Loss	2%	Nil	0.5-1.5 max
% Residue	1%	1%	

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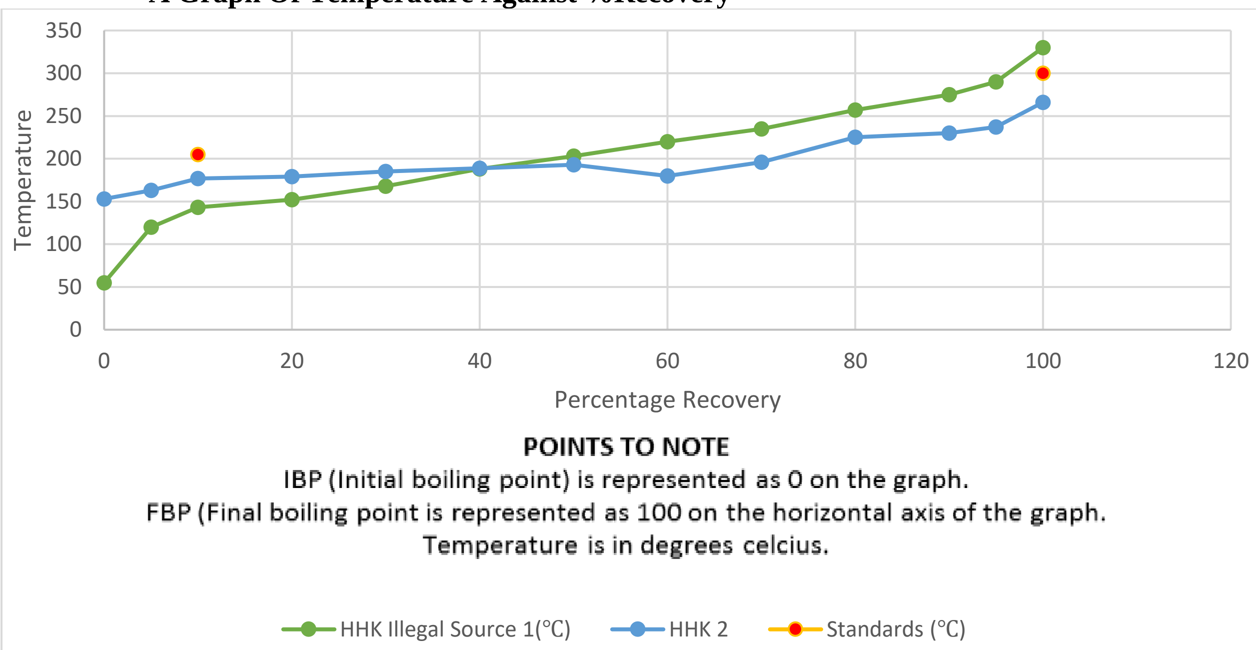
Figure 10: Distillation Profile Results for HHK Samples From Illegal Refining Source and Certified Suppliers.

A Graph Of Temperature Against %Recovery



Flash Point for HHK Samples

The flash point of fuel is the temperature to which the fuel must be heated to produce an ignitable vapor-air mixture above the liquid fuel when exposed to an open flame. The flash point test is a guide to the fire hazard associated with the use of the fuel and can be determined by several test methods, but the results are not always strictly comparable. The minimum flash point is usually defined by the Abel method (IP 170), although the Pensky–Martens method (ASTM D-93, IP 34) may also be specified. In practice, flash point is important primarily for fuel handling. A flash point that is too low will cause fuel to be a fire hazard, subject to flashing test methods and possible continued ignition and explosion. In addition, a low flash point may indicate contamination by more volatile and explosive fuels, such as gasoline. Flash point is significant for safety in handling and use but not directly related to engine performance.

Other Analysis Results for HHK Samples

Table 4.4: HHK Flash Point, Density and API Analysis Results for ATK Samples from Illegal Refining Source and Certified Suppliers

	HHK Sample 1	HHK Sample 2 (g/ml)	Standard
Flashpoint	31°C	45°C	38°C-45°C(max)
Density@60°F	0.8130	0.7830	0.779-0.829kg/m³
API	42.55	54.0	

Flash point is basically volatility test and indicates how flammable a product is. Lower flash point values indicates that the samples in question will be more flammable compared to it's standard. This is mostly caused by contamination with more volatile components.
House hold kerosene are products that should be home friendly and low flash point of this product will make it unsafe for use as the flammability of such products will automatically increase.

Density (Specific Gravity)

Density (or specific gravity) is an indication of the density or weight per unit volume of the diesel fuel. The principal use of specific gravity (ASTM D-l298, IP 160) is to convert weights of oil to volumes or volumes to weights. Specific gravity also is required when calculating the volume of petroleum or a petroleum product at a temperature different from that at which the original volume was measured. Although specific gravity by itself is not a significant measure of quality, it may give useful information when considered with other tests. API gravity (ASTM D-1298, IP 160) is an arbitrary figure related to the specific gravity in accordance with the following formula: °API = (141.5/ (specific gravity @ 60/60°F)) - 131.5.

CONCLUSION

Previous studies have shown that Nigerian refined gasoline has a low octane rating, which can negatively impact engine performance Faruq et al. (2012). However, the results of the current research indicate that the Nigerian refined gasoline samples met ASTM standards for octane rating, in contrast to the findings of Faruq et al. (2012). Additionally, the flash point of kerosene was found to be low, which is consistent with the research of Evbuomwan and Alete (2020). This is believed to be a result of a lack of purification and poor refining techniques, as well as a lack of equipment and proper handling methods.

Godwin et al. (2020) also investigated the properties of artisanal and regular gasoline samples from Eastern Obolo Creek and Mkpat Enin, Akwa Ibom State, Nigeria. The findings of this study suggest that artisanal refined gasoline may have been poorly refined or adulterated, which could cause issues in automotive engines. The results of this research align with the understanding that artisanal refined petroleum products often do not meet the necessary standards.

This research work has also shown that adulteration of petroleum products has become prevalent in our times. Subsidy and price differential among HHK, PMS and AGO encourages diversion, scarcity, adulteration and consequently, explosions that have continually negatively affected individuals, homes and industries. Adulteration of petroleum products could be deliberate or inadvertent. Most of those involved in adulteration do it for economic gains. Adulterated petroleum products had been implicated in most explosions that were recorded in Nigeria. Each time such explosion occurred, the victims were usually abandoned both by the governments and the NNPC.

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