

Characterization Of Locally Refined Dual Purposekerosene(DPK) In The Niger Delta, Nigeria

Evbuomwan B.O and Alete O.G

Department of Chemical Engineering, University of Port Harcourt, Port Harcourt, Nigeria.

ABSTRACT: This paper examined the characterization of locally Dual Purpose Kerosene in the Niger Delta, Nigeria. Analysis was carried out to ascertain the impurities, stability and compatibility of locally refined kerosene product in Niger Delta, and the results obtained was compared with standard for filling station in Nigeria. The analysis conducted on the bunkering refined kerosene samples include metallic contents (sodium, magnesium and aluminum), elemental composition (sulphur) physiochemical properties (total acid number, diesel index, refractive index, flash point, viscosity, cloud point, density, and smoke point). and compositional ASTM procedural methods were used to determine the metallic, elemental and physiochemical properties, while gas chromatography with flame ionization detector (GC/FID) was used to determine the compositional total hydrocarbon content. The sodium, magnesium, sulphur, total acid number, refractive index, flash point, smoke point, carbon molecules, and total petroleum hydrocarbon exceeded standard limits. The GC results shows carbon molecules of diesel, wax and asphalt are found in locally kerosene sample, and the total petroleum hydrocarbon of the locally refined kerosene product is lower than the Department of Petroleum Resources requirement for kerosene.

KEYWORDS: Kerosene, refining, Physicochemical, Gas chromatograph, metals

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I. INTRODUCTION

Petroleum is a brown to black viscous liquid found beneath the sedimentary rock on the earth crust. It is sometimes found alongside with gases (associated natural gas) in free or dissolved form [1]. The crude oil composed mainly of hydrocarbons, but is also found with some impurities like sulphur, hydrogen sulphide (H₂S), ferrous (Fe), nickel (Ni), sand, and water (H₂O). The petroleum is generally believed to be derived from aquatic plants and animals which have existed millions of years ago whose remains mixed with mud and sand in layered deposits and transform geologically to sedimentary rock [2]. The petroleum migrates from source bed to more porous and permeable rocks (sandstone and siltstone) and it is entrapped in a reservoir after accumulation [3]. The crude oil is extracted from the ground after structural geology, sedimentary and reservoir analysis (porosity and permeability of geological structure) have been carried out [4]. The geological techniques only determines the existence of rock formation that are favourable for oil deposits, but drilling is the sure way to ascertain the presence of oil [5]. During drilling the oil is recovered by pressure created by natural gas or water within the reservoir or artificially by injecting water or steam into the reservoir to raise the pressure or injecting carbon dioxide, polymers, and solvents to reduce the crude oil viscosity [6]. After drilling, the crude oil is pumped through wellhead to a separator where gas and water are removed [1], and the crude oil is passed through pipelines, by ocean-going tankers or other form of transportation to the refinery, and it is stored in a storage tank to remove other impurities before distillation.

The petroleum is distilled in the refinery with equipment called fractionation tower or column, and the first step of distillation is the pretreatment which includes dehydration and desalting. The dehydration and desalting aims at removing water and salts from the feedstock before refining to avoid equipment corrosion and low standard products. Distillation separates the crude oil into fractions of different volatility, and other physical methods of separation used after distillation includes absorption, adsorption, solvent extraction, and crystallization [3]. The fractions obtained from the refinery include liquefied natural gas (LPG), gasoline (PMS), kerosene (DPK), diesel (AGO), bitumen, and asphalt. Some of the fractions may be subjected to conversion processes like cracking (thermal or catalytic cracking) and reforming depending on market demand. The carbon

contents of the fractions vary and make it useful for a particular purpose or the other [7]. According to [6], the fractions with carbon contents of C_1 to C_4 are gases, C_5 to C_7 are light naphtha, C_7 to C_{11} are gasoline, C_{12} to C_{15} are kerosene, C_{16} to C_{20} are diesel and lubricating oil, and above C_{20} are solids (paraffin wax, tar, and bitumen).

The gasoline (petrol) vapourizes easily and ignites very fast when close to source of ignition. The kerosene ignites slower than the gasoline, while the diesel ignites slower than the kerosene. The refining of the fractions in the refinery is by standard and specification [3]. The standard colour of kerosene is white, and kerosene is often referred to as the white product; its colour is measured by colorimeters. The fractions if not properly refined pose danger to the users, engines, and environment. The octane number of gasoline is used to measure the performance and quality of the gasoline, while the smoke point of kerosene measures the ability of kerosene to burn steadily and cleanly over a period, and cetane number determines the performance and quality of diesel. Kerosene is of two grades; the domestic kerosene also known as the house hold kerosene (HHK) and the jet kerosene which also known as the aviation technical kerosene (ATK). According to [8], kerosene is the main fuel used in cooking and lighting in Nigeria by majority of the third class citizens as substitute to electricity and gas. Other uses include fire breathing, fire juggling, fire dancing, antidote for snakebites, local insecticides on stagnant water, local disinfectant to treat cuts and burns, and solvent for removal mucilage and candle wax on glass, and lubricant for cutting glass and machining aluminum. Kerosene density varies between 0.74 and 0.85g/cm^3 and it is miscible petroleum solvent but immiscible with water [8]. The flash point of kerosene lie between 37°C to 65°C , the auto ignition temperature of kerosene is 220°C , and the volatility of kerosene is within the volatility of gasoline and diesel.

Kerosene is less volatile than gasoline, hence a lighted match thrown into a kerosene pool will quench. If not properly refined it produces unpleasant odour and emits fumes which are poisonous in sufficient concentration. Paraffinic feedstocks are usually used to produce kerosene of high quality that has decrease in smoke generation [9]. Other crude oils like asphaltic base, naphthenic oil or high sulphur oil require hydrotreating, acid treatment and water wash or extraction with caustic wash to remove aromatics and sulphur before satisfactory kerosene is obtained [10]. The chemical constituents of kerosene are n-dodecane ($n\text{-C}_{12}\text{H}_{26}$), alkyl benzene, and naphthalene. The chemical composition of kerosene dependence on the source and has a high number ($>100,000$) of isomers that possible.

Today, there is a total deviation in the traditional ways of obtaining these fractions through the activities of some locally refiners called bunkers in the south-southern part of Nigeria "Niger Delta". The refining method is totally different from the modern refinery methods and even worsted than the early refinery methods of 1880s that leave a lot of naphtha in kerosene produced [3]. The bunkering refined petroleum products contain a lot of impurities and unsaturated hydrocarbons, which cause cracking sound in vehicle engines; knocking of vehicles, motorcycles, and generators engines; corrosion and fouling of fuel tanks; burning of residential houses, properties, and end users; and pollution of the environment. The fact that major routes of refining are ignored; the refining is carried out without reflux, there is no heater and heat exchanger equipment, and there is no pump and cooler installations. The cook products are sold at very cheap price, and coupled with extreme poverty around the region, a lot of Niger Delta populace prefers its use to convectional refinery products.

The bunkering refining of the petroleum involves heating the crude oil on drums perforated at the top run with pipes to deliver the fractions to a receiver. Open fire is used as the source of heating the petroleum in the drums. The fractions obtained from the bunkering refinery include gasoline, kerosene, diesel, and residue. The residue is discarded to the immediate surroundings.



Plate 1: Locally refining of petroleum products in Niger Delta Nigeria.

The sources of petroleum pollution includes transportation of petroleum, operational discharge, oil well blowouts, leakage of oil storage tanks and pipeline, refinery effluents, natural oil seeps, industrial waste, urban rural run off, biosynthesis, atmospheric fallout, dry docking, terminal load, and accidental discharge of water oil. [11] report the causes of oil pollution in percentage as follows; 50% oil spill, 28% sabotage, 22% production operation. The effects of Bunkering refining (crude cooking of crude oil) include environmental effects, health effects, equipment effects, and economic effect. According to [12], the economic impacts of bunkering refining in Niger Delta are scarcely reported.

According to [13], beyond the economic consideration of petroleum theft in Nigeria, the environmental deterioration associated with bunkering oil refineries requires urgent attention. Sudden dramatic changes in environmental conditions of an area over a short interval can have serious and damaging effects on the living system there [14]. The land, water, and atmosphere of the region are affected. [15] reports change in physiochemical and microstructure of soil when oil contaminated soil is tested. [16] separately studied the effect of crude oil contaminated soil on cow pea and pepper and reported that crude oil hinder the growth of plants. The physio-chemical nature (P^H) of the soil is affected, and it affects the soil organisms and other soil properties [17]. According to [18], petroleum pollution affects the nutrient level and fertility status of soil, which leads to lack of mineral nutrients in the soil causing harmful effects like leaf chlorosis, necrosis, stunting growth in plant (led to reduction in accumulation of biomass). The oil in the soil create metabolic problem for plants due to aeration. Crude oil contamination of soil has been said to reduce germination, growth, and yield of plants. The gaseous pollutant (sulphur dioxide and nitrous oxides) enters the plants leaf via the stomata and affect palisade and mesophyll cells causing leaf collapse and loss of photosynthesis. Oil attenuate oxygen in water and coat breathing of aquatic organisms, it starves mangroves of oxygen by coating the breathing roots of the mangroves and scotch the tender structure of aquatic marophytes of fresh water vegetation.

According to [19], the intensity of hydrocarbon metabolization in soil is influenced by a number of factors like site specifics (soil properties, temperature, oxygen, pollution history, hydrogeology, and geochemistry) and contaminant specific (composition, concentration, age, and bioavailability). The water bodies (rivers, lakes, oceans, streams, and ponds) around the Niger Delta are been contaminated with hydrocarbons. Petroleum contains metals (sodium, magnesium, aluminum, etc) and other impurities which when discharged into water causes odour, taste, and colouring of water; hence making the water unfit for drinking. Only few of the host of toxic and hazardous chemicals already discharged in water may be removed by standard processes [20]. The water when drink can cause kidney failure and skin cancer (see plate 2).



Plate 2: Crude oil contaminated river via bunkering activities.

The kerosene tends to possess the properties of gasoline especially the flash point; as stick of matches is thrown a pool ignites. The kerosene has burn many people and houses in course of lighting stove or lantern in their houses, and the kerosene burn with a lot of smoke which darkens lantern globe, cooking pots and kettles. Kerosene bought from a local market through lantern fire explosion rendered a family in Akwa Ibom State, Nigeria homeless; burn money, wrapper, and scourge the chest of the house owner [21]. Also bunkering connected fire burned twelve houses and valuable items worth millions of naira in two separate fire incidents in

Bayelsa State, Nigeria [22]. The aim of this paper is to characterize the locally refined Dual Purpose Kerosene (DPK) in the Niger Delta region of Nigeria.

II. MATERIALS AND METHODS

Equipment and Reagents

The equipment used in the analysis include refractometer, Pensky Martens close cup flash point apparatus, u-tube viscometer and viscometer sucker, thermometer, hydrometer and graduated measuring cylinder, smoke point apparatus, aniline point apparatus, atomic absorption spectroscope (AAS), and gas chromatography (GC/FID). The reagents used are aniline, potassium hydroxide, phenolphthalein, blank (distilled water), sulphuric acid, nitric acid, hydrogen chloride, ammonia, sodium carbonate, ortho phosphoric acid, and di-phenol lamine, acetone, carbon disulfide, petroleum ether, helium gas, air, nitrogen, dichloromethane, methylene chloride, methanol, and anhydrous sodium sulphate.

Materials for the analysis

The materials used for the analysis is the locally refined kerosene fractions from bunkering refineries in Niger Delta, Nigeria. The samples for the analysis were collected through buying in 1.5 litres containers from well known locally refined petroleum product outlets in two locations in the Niger Delta, Nigeria.

Analysis of the samples

The analysis of samples was carried using three methods grouped as physiochemical techniques, atomic absorption spectroscope, and gas chromatography. The physiochemical parameter determined include refractive index, flash point, viscosity, cloud point, density, smoke point, diesel index, and total acid number; atomic absorption spectroscope determined sodium, magnesium, aluminum, and sulphur; and gas chromatography determined the total petroleum hydrocarbon. The various methods used were ASTM D1218, D93, D445, D2500, D1298, D1322, D4529 and D3339.

Atomic Absorption Spectroscope

The samples to be analyzed using the AAS apparatus was first digested and diluted using reagents such as sulphuric acid, nitric acid, hydrogen chloride, ammonia, sodium carbonate, distilled water, ortho phosphoric acid, and di-phenol lamine. The detection of the metals presence in the sample is based on wavelength.

Gas Chromatography (Agilent 6890)

Poured the sample into a one litre separatory funnel, and add 50ml of methylene chloride to the sample seal; shake for about 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extracted the sample by shaking the funnel for about two minutes with regular venting to release excess pressure. The organic layer was allowed to separate from water for a minimum of ten minutes; the methylene chloride extract was collected in a 250ml flask. Add second volume of methylene chloride to the sample bottle, both the separatory funnel and the column was rinsed with 20ml of the solvent into the extract. The extraction procedure were repeated a second time, and extracts combined in the Erlenmeyer flask. The extraction were performed the third time in the same manner as the preceding. Pour the combined extract through a drying column containing packed cotton wool anhydrous sodium sulphate and silica; connect the extract into the vial and concentrate with 1.0ml of the solvent and inject 1.0 μ L into the flame ionization detector gas chromatography for its PAH (polyaromatic hydrocarbon), TPH (total petroleum hydrocarbon), and BTEX (benzene, toluene, ethylbenzene, and xylene) analysis. The GC/FID is connected to a computer which interprets the result and plot the graph (chart) of the concentration of carbon per time.

III. RESULTS AND DISSCUSION

The results obtained after characterization of kerosene samples are presented in Tables 1 and 2, and Figures 1 and 2.

Table 1: Metallic/Elemental properties of the kerosene samples

Metallic/Elemental Test	Kerosene Kerosene		Average	Standard	Remark
	Sagbama LGA	Southern Ijaw LGA			
Sodium (%)	1.86	1.53	1.695	1.4max	Not acceptable
Magnesium (%)	0.98	0.94	0.96	0.8max	Not acceptable
Aluminum (%)	4.60	3.34	3.97	5.0max	Acceptable
Sulphur (%)	0.380	0.270	0.325	0.15max	Not acceptable

Table 2: Physiochemical properties of the kerosene samples

Physiochemical properties	Kerosene Sagbama	Kerosene Southern Ijaw LGA	Average	Standard	Remark
TAN (Mg KOH/g)	0.30	0.20	0.29	0.015max	Not acceptable
Diesel index	58.45	50.88 54.59	46min		Acceptable
Refractive index	1.44249	1.45001	1.44625	1.3360- 1.3966	Not acceptable
Flash point (°C)	73.40	68.10	70.75	45-65	Not acceptable
Viscosity (cst)	0.555	1.815	1.185	2.40max	Acceptable
Cloud point (°C)	-11.0	-7.0	-9.0	>-9	Acceptable
Density (g/cc)	0.810	0.815	0.8125	0.77-0.840	Acceptable
Smoke point (mm)	51.20	40.80	46	<22	Not acceptable

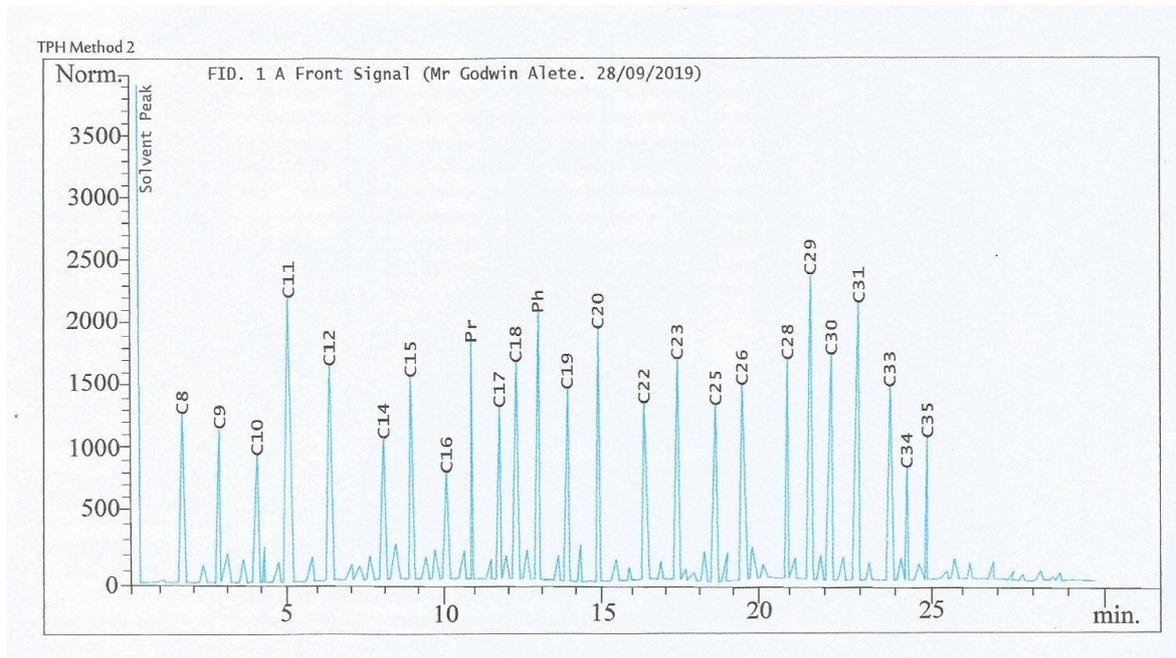


Figure 1: Chromatogram chart of the kerosene sample from Sagbama LGA

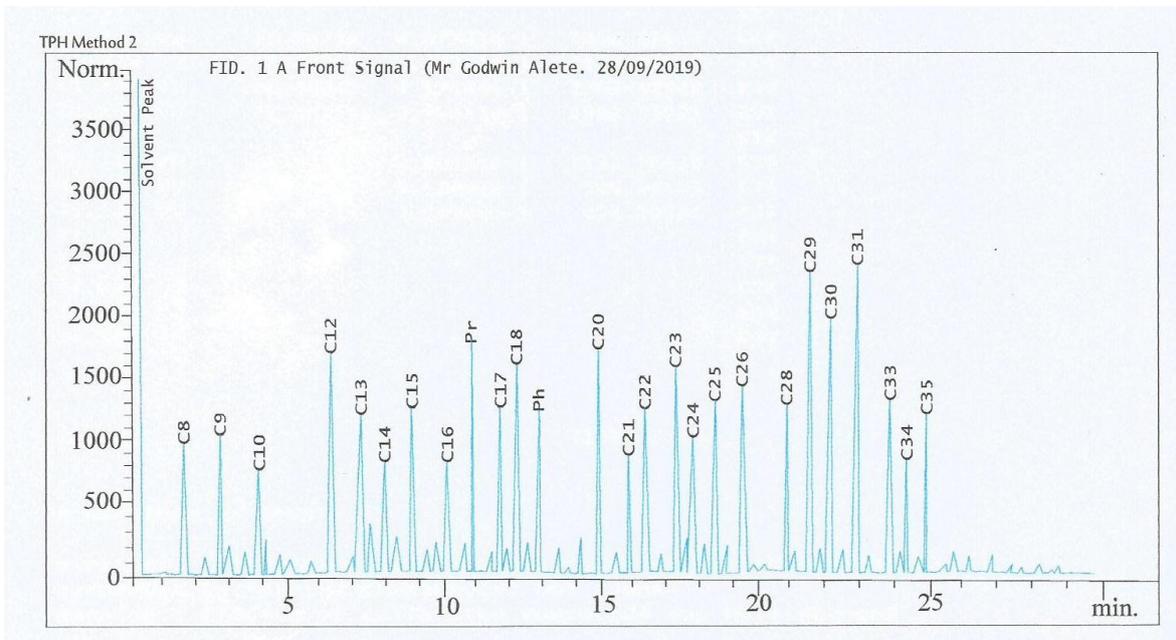


Figure 2: Chromatogram chart of the kerosene sample from Southern Ijaw LGA

Table 3: Chromatogram chart of the kerosene samples.

Carbon type present	Concentration of carbon type on each sample (ppm)	
	Kerosene Sagbama LGA	Kerosene Southern Ijaw LGA
C ₈	1236.83	968.31
C ₉	1141.17	1027.19
C ₁₀	864.36	734.02
C ₁₁	2102.78	–
C ₁₂	1514	1642.69
C ₁₃	–	1175.58
C ₁₄	975.52	710.11
C ₁₅	1463.91	1193.97
C ₁₆	705.31	758.16
Pr	1602.72	1713.12
C ₁₇	1131.9	1171.31
C ₁₈	1422.01	1491.05
Ph	1776.65	1125.76
C ₁₉	1248.01	–
C ₂₀	1516.73	1637.54
C ₂₁	–	746.25
C ₂₂	1180.51	1120.82
C ₂₃	1560.6	1481.53
C ₂₄	–	896.88
C ₂₅	1259.88	1195.15
C ₂₆	1386.32	1140.02
C ₂₇	–	–
C ₂₈	1519.34	1036.92
C ₂₉	2182.082	2129.05
C ₃₀	1529.89	1763.32
C ₃₁	1803.64	1982.59
C ₃₂	–	–
C ₃₃	1103.73	1131.3
C ₃₄	520.35	596.84
C ₃₅	793.09	821.11
TOTAL	33541.3	31390.6

There are some undesirable changes that occur in the original properties of petroleum product due to the presence of impurities, and the method of processing petroleum may cause production of low quality petroleum products. Table 1 shows the results obtained for sodium (1.695%), magnesium (0.96%), and sulphur (0.325%) in the two locally refined kerosene samples exceeded permissible standard specifications of kerosene products [23], while the aluminum (3.97%) is within the acceptable limit. The high levels of sodium, magnesium, and sulphur found in the kerosene samples implies that the kerosene samples can cause corrosion and fouling in stove, kerosene storage tanks and equipment and possess problem of environmental pollution and health risk to the Niger Delta populace when used.

In Table 2, the physiochemical properties of the kerosene samples for total acid number (average 0.29MgKOH/g), refractive index (54.71), flash point (70.75°C), and smoke point (46mm) exceeded permissible standard specifications of kerosene products [23], while the diesel index, viscosity, cloud point, and density are in acceptable limits; the deviation of total acid number, refractive index, flash point, and smoke point indicates; the high total acid number implies the kerosene has corrosion potential; the value of the refractive index signifies the kerosene contains impurity which will block engine filter if the kerosene is utilized in aviation. The kerosene having flash point of diesel fractions means it pose little fire hazard but will burn with incomplete combustion which in turn causes environmental pollution and health hazard; and the high smoke point value shows the kerosene will burn with black smoke.

Kerosene and diesel fuel are middle distillate with saturated species as the major components. Within the saturated constituents, the concentration of n-paraffins decreases regularly from C₁₁ to C₂₀[3]. The carbon molecule of kerosene is between C₁₁ to C₁₅[6]. From chromatogram charts of Figures 1 to 2, the GC/FID provided information with regard to the carbon molecules of the kerosene samples together with the concentration, but the Identification of product type (paraffins, naphthenes, and aromatic) is not shown; identification of product type in GC/FID is not straightforward (Speight, 2007). The chromatograms charts of Figure 1 and 2 as summarized in Table 3 show the peak value of carbon concentration per time. This indicates that compounds less than C₆ are not detected because they are highly volatile and interference can occur from the solvent peak, and shows that the carbon molecule of the samples ranges from C₈ to C₃₅. The kerosene from Sagbama local government has high carbon concentration of C₂₉, C₁₁, C₃₁, and C₂₃, while the kerosene from Southern Ijaw local government has high carbon concentration of C₂₉, C₃₁, C₃₀, and C₂₀. The high carbon concentrations (C₂₀, C₂₃, C₂₉, C₃₀, and C₃₁) in the locally kerosene fractions are not within carbon range of C₁₁ to C₁₅ for kerosene as provided by [6]. The kerosene samples are mainly composed of carbon molecules of diesel, wax, and asphalts. The Pr (pristane; 2,6,10,14-tetramethylpentadecane) and Ph (phytane; 2,6,10,14-tetramethylhexadecane) as shown in Table 3 are two isoprenoid species generally present in crude oils in sufficient concentration to be seen as irregular peaks alongside n-C₁₇ and n-C₁₈ peaks in gas chromatogram. The distribution of pristane and phytane relative to n-C₁₇ and n-C₁₈ are used to aid identification of crude oils and detect the onset biodegradation. In Table 3, the total petroleum hydrocarbon of the locally refined kerosene samples (33541.33ppm and 31390.63ppm) are higher than Department of Petroleum Resources (DPR) required value for total petroleum hydrocarbon. This shows that the kerosene is a pure diesel and unsuitable for use in a kerosene fed lamp and stove, hence the kerosene will burn with lots of smoke and incomplete combustion products when used.

IV. CONCLUSION

This research shows that the locally refined kerosene did not conform with the requirement for a standard filling station in Nigeria. The sodium, magnesium, sulphur, total acid number, refractive index, flash point, smoke point, carbon molecules, and total petroleum hydrocarbon exceeded standard limits. This has been attributed to either none purification of the products before refining, the refining techniques used, lack of reflux drum, lack of heat exchangers and pumps, the crude method of refining and handling the products, the type of crude oil used, none purification of the crude oil at the refining points, and lack of treatment of the products before sale.

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