Effect of Petroleum Condensate/Gasoline Mixture on Automotive Engines

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Twelve combustible mixtures of condensate/gasoline were evaluated with the aim to delimit the extent at which the adulteration of premium motor spirit (PMS) with condensate samples becomes hazardous to spark-ignited gasoline engines. Results of the quality-assurance tests (low RON (research octane number) rating and low volatility corroborated by < 0.45 kg/cm^2 RVP (*Reid* vapor pressure) and high boiling-point (IBP (initial boiling point), FPB (final boiling point), and TR (total recovery)) ranges of atmospheric distillation) show that 16–100% (*v*/*v*) of condensate in the adulterated blends are undesirable for automotive engines. Such fuels may cause rough idling, detonation (pinging), and eventual knock of the spark-ignited engine. Continued availability of petroleum products in developing countries like Nigeria might discourage the uncanny practice of 'black marketers' who perpetrate the distribution of the 'killer products'. This might also boost the already impeded consumer trust on petroleum products.

1. Introduction. – 1.1. *Preamble.* In Nigeria, a considerable recoverable reserve of petroleum condensates (reservoired gases that condense to colorless or light yellow liquid hydrocarbons when produced) has been discovered in the Niger Delta, the most significant hydrocarbon province in the West African continental margin. Condensates from this region have been characterized as highly combustible, with an API (American Petroleum Institute) gravity generally higher than 55° at a temperature of 15.6 °C and normal atmospheric pressure [1]. They also have a gas/oil ratio (GOR) exceeding 5'000 standard cubic feet per barrel of oil (scf/bbl). They are mainly composed of saturated hydrocarbons in the light range (*i.e.*, butanes, pentanes, and hexanes). However, condensates with a high percentage of aromatic or naphthenic hydrocarbons have been found in the basins of the Gulf Coast, Canada, Russia, and Israel [2–5]. Such condensates are superior to the typical paraffinic type as gasoline feedstock. In Bangladesh, where seven condensate fields have been discovered, about 1'325 barrels are produced everyday from a total recoverable reserve of 64.7 million barrels. The condensate produced from the gas fields is transported through pipelines to the processing plants where they are refined for use.

Similar but different in the composition of condensates is 'gasoline' or 'petrol', a petroleum-derived liquid mixture consisting of mainly aliphatic hydrocarbons primarily used as fuel in internal combustion engines. Commonwealth countries, with the exception of Canada, use the term 'petrol' (abbreviated from 'petroleum spirit'), while the term 'gasoline' is commonly used in North America where it is often shortened in colloquial usage as 'gas'. Gasoline sales are usually reported by grades in accordance with their classification. Regular gasolines, *e.g.*, have an antiknock index (octane rating) higher than or equal to 85 and lower than 88. Midgrade gasolines have an octane rating higher than or equal to 88 and lower than 90; while premium gasolines have an octane rating higher than 90.

The adulteration of premium gasoline (= premium motor spirit; PMS) and kerosene (= dual purpose kerosene; DPK) with condensates has become a common enterprise in Nigeria. The country's harsh economic exigencies, accentuated by the periodic scarcity and hoarding of petroleum products, have indeed increased the illicit sales of adulterated fuels. This 'business', popularly known as 'black market', is carried out by miscreants whose primary motive is driven by their unscrupulous desire to make 'quick money' at the detriment of the unsuspecting consumer.

A major hazard of the adulteration of PMS with condensate includes the damage and ultimate knock of spark-ignited, gasoline-automotive engines. Another very disturbing effect of adulteration of petroleum products is the increasing cases of kerosene explosion amongst household users. Condensate-adulterated kerosene has been tagged the 'killer product' because of the high degree of burns associated with its explosion.

There are neither copious information nor empirical data on the adulteration of petroleum products by condensates. However, our group had earlier attempted to characterize some condensate samples from the Utorogu gas field in the Niger Delta, Nigeria [1]. The peculiar characteristics of this condensate, as well as the hue and cry associated with its combustible mix, have further stimulated the present research. In this work, we shall use bulk quality-assurance parameters such as the research octane number (RON), *Reid* vapor pressure (RVP), and gravity (API and specific gravities) to assess the quality of the condensate-adulterated gasoline. Our aim is to determine the extent at which such adulterations become hazardous to spark-ignited gasoline engines; by implication, we shall attempt to expose the defects of the adulterated product and, where there are none, to increase the quality assurance and trust of consumers.

1.2. *Antiknock Rating/Octane Number of Gasolines.* The antiknock rating is an important consideration in gasoline research. The antiknock rating of a gasoline can be measured by the two major methods, namely the research octane number (RON) and the motor octane number (MON). By definition, the octane number is the number which gives the percentage, by volume, of isooctane ($Me_3CCH_2CHMe_2$) in a mixture of isooctane and unbranched heptane ($Me(CH_2)_5Me$) that would have the same antiknocking capacity as the fuel under test. For instance, gasoline with the same knocking characteristics as a mixture of 90% isooctane and 10% heptane would have an octane rating of 90.

1.3. Reid *Vapor Pressure and Volatility Performance of Gasolines. Reid* vapor pressure (RVP) is a range of the vapor pressure of gasoline (in psi) at 100 °F (37.8 °C) in a bomb having a 4 : 1 ratio of air to liquid. The volatility characteristics of a gasoline are of prime importance to engine performance. Volatility characteristics of automotive gasolines are defined by the specifications of the American Society for Testing and Materials (ASTM) for automotive gasoline (D439). The ASTM specifications provide five volatility classes. These have varying limits of the maximum or minimum vaporization tendency to adjust for seasonal and geographical changes in the temperature and altitude in which the gasoline is to be used. These volatility characteristics have been established on the basis of broad experience and co-operation between gasoline manufacturer/suppliers and users of automotive vehicles and equipment.

2. Results and Discussion. – 2.1. *Atmospheric Distillation*. The results of the atmospheric distillation of the test gasoline *vs.* condensate/gasoline blends are given in *Table 1*. The pure gasoline (= premium motor spirit = PMS; unblended) had a 10 ml recovery temperature of 56 °C, which is far below the maximum temperature of 70 °C specified by the American Society for Testing and Materials (ASTM). The total recovery (TR) of 97 ml and 50 ml recovery at 104 °C as well as a final boiling point (FBP) of 198 °C (*Table 1*) obtained for PMS were also within the standard specifications. According to the ASTM, the limits specified for 50 ml recovery and the FBP should not exceed a maximum of 125 °C and 205 °C, respectively. Highlights of the result for the pure condensate showed a higher initial boiling point (IBP) of 42 °C; the FPB of 279 °C and the 50 ml recovery temperature of 131 °C obtained for the condensate exceeded the ASTM-specified maxima. These results show that the condensate will not ignite in an automotive combustion engine. In the same vein, the 25 : 75, 50 : 50, and 75 : 25 mixtures (*v*/*v*) of the adulterated condensate/gasoline blends exceeded the ASTM-specified maxima, which implies that these blends will also not ignite an automotive combustion engine. However, the 15 : 85 condensate/gasoline blend had a 50 ml recovery temperature of 106 °C and a FBP of 199 °C which are below the standard maxima; the 10 ml recovery was also below the 70 °C maximum (*Table 1*).

Table 1. *Recovery Temperatures at the Atmospheric Distillation of Pure Gasoline* (= PMS)[a]*, of Condensate, and of Adulterated Condensate/Gasoline Blends*

Volume distilled [ml]	Recovery temp. [°C] of PMS	Recovery temp. [°C] of adulterated consensate/PMS blends				
		Condensate	75 : 25 [%]	50 : 50 [%]	25 : 75 [%]	15 : 85 [%]
IBP[b])	35	42	41	40	39	39
5	49	69	62	58	54	52
10	56	80	73	69	62	61
20	68	97	88	83	74	72
30	78	108	101	97	87	83
40	91	118	114	109	101	93
50	104	131	127	121	113	106
60	119	146	138	144	125	123
70	133	163	154	152	139	137
80	154	193	178	171	157	153
90	173	242	219	206	182	175
95	190	277	258	231	209	192
FBP[c])	198	279	271	237	217	199
TR[d])	97 ml	97 ml	97 ml	96 ml	98 ml	98 ml

[a]) PMS = Premium motor spirit. [b]) IBP = Initial boiling point. [c]) FBP = Final boiling point. [d]) Total recovery.

The recovery temperatures for the 15 : 85 blend were closer to the ASTM maxima than those of the pure gasoline (control). However, the results show that an adulteration in this proportion, *i.e.*, a 15 : 85 blend, will auto-ignite without much damage to the automotive engine. In a situation of reduced gasoline supply and increased demand, an adulteration of pure gasoline by 15% of the Utorogu condensate (→ condensate/gasoline 15 : 85 (*v*/*v*)) might be used as a temporary relief.

2.2. Reid *Vapor Pressure* (RVP). The results obtained for the *Reid*-vapor-pressure evaluation of control samples (unblended PMS and condensate) and adulterated condensate/gasoline blends are collected in *Table 2*. The ASTM specifies a maximum RVP value of 0.6. A sample with an RVP value > 0.6 implies that it has very light ends and is too volatile, thus the sample will easily evaporate. Conversely, a sample with an RVP < 0.45 implies that the ends are heavy, and its use might cause auto-ignition problems (cold start), if not outright detonation of the automotive engine. This means that the mean RVP values obtained for the condensate (0.32), as well as the 50 : 50 and 75 : 25 condensate/PMS blends fall below acceptable standards.

Table 2. Reid *Vapor Pressure for Pure Gasoline* (= PMS)*, of Condensate, and of Adulterated Condensate/Gasoline Blends*

Test RVP[a]) samples	*Reid* vapor pressure [kg/cm^2]			
	IR[b])	SR[c])	FR[d])	MR[e])
Gasoline (= PMS)	0.48	0.49	0.51	0.49
Condensate	0.31	0.32	0.32	0.32
75 : 25 [%] Blend	0.26	0.29	0.30	0.28
50 : 50 [%] Blend	0.34	0.38	0.38	0.36
25 : 75 [%] Blend	0.44	0.48	0.48	0.47
15 : 85 [%] Blend	0.46	0.49	0.49	0.48

[a]) RVP = *Reid* vapor pressure. [b]) IR = Initial RVP reading. [c]) SR = Subsequent RVP reading. [d]) FR = Final RVP reading. [e]) MR = Mean RVP reading.

RVP is a measure of volatility, and the volatility of automotive gasoline must be carefully 'balanced' to provide the optimum compromise in the performance features that depend on the vaporization behavior. Gasoline that vaporizes too readily in pumps, fuel lines, and carburetors will cause decreased fuel flow to the engine, resulting in rough engine operation or stoppage (vapor lock). Conversely, gasolines that do not vaporize readily enough may cause hard starting and poor warm-up and acceleration, as well as unequal distribution of fuel to the individual cylinders, which may cause knock. Fuels that vaporize too readily also may cause, under certain atmospheric conditions, ice formation in the carburetor throat, resulting in rough idling. Results obtained from the RVP tests show that the Utorogu condensates and the adulterated 50 : 50, and 75 : 25 condensate/PMS blends might cause instant detonation of the spark-ignited automotive engine.

2.3. *Specific Gravity* (SG)/*API Gravity*. The specific gravity and weighted equivalent on the American Petroleum Institute (API) gravity scale of the control samples and adulterated condensate/gasoline blends are collected in *Table 3*. With reference to these results, the Utorogu condensate and the adulterated PMS samples had a specific gravity of 0.76–0.77 (*i.e.*, of 51.8–55.7° API gravity). A sample with a SG value higher than 0.7 will have a high burning rate and thus would be required in larger quantity. If it exceeds the 0.7 mark, it might result in an outright detonation (pinging) of the spark-ignited engine. Therefore, the results of the SG evaluation show that the condensate samples and blends with more condensate (50–75%) are not desirable for use in a spark-ignited gasoline engine.

Table 3. *Specific and API Gravities of Pure Gasoline* (= PMS)*, of Condensate, and of Adulterated Condensate/Gasoline Blends*

Test sample	Specific gravity	API gravity[a]) [degrees]	Test sample	Specific gravity	API gravity[a]) [degrees]
Gasoline (= PMS)	0.753	56.3	50 : 50 [%] Blend	0.763	53.9
Condensate	0.772	51.8	25 : 75 [%] Blend	0.758	55.2
75 : 25 [%] Blend	0.768	52.8	15 : 85 [%] Blend	0.756	55.7

[a]) API = 141.5/specific gravity (60°) – 141.5.

2.4. *Research Octane Number* (RON). The RON values of 10–90% condensate-adulterated samples and that of the pure-condensate and pure-gasoline samples are given in *Table 4*. The results of this RON test show that the PMS sample corresponded to 90.5% (by volume) isooctane and 9.5% (by volume) heptane, thus giving an RON of 90.5 which is within the premium gasoline rating. However, the RON values of the adulterated condensate/gasoline samples were in the range of 67–88. These results imply that the antiknock rating of the adulterated gasoline samples is low.

Table 4. *Research Octane Number* (RON) *of Pure Gasoline* (= PMS)*, of Condensate, and of Adulterated Condensate/Gasoline Blends*

Test sample	RON	Test sample	RON	Test sample	RON
Pure gasoline (= PMS)	90.5	70% Condensate	71.8	25% Condensate	83.8
Pure condensate	63.8	60% Condensate	74.5	20% Condensate	85.1
90% Condensate	66.5	50% Condensate	77.2	15% Condensate	86.5
80% Condensate	69.1	40% Condensate	79.8	10% Condensate	87.9
75% Condensate	70.5	30% Condensate	82.5		

The antiknock rating is perhaps the most important consideration in the quality evaluation of gasoline samples. Knock is a high-pitch, metallic-rapping noise associated with low octane rating of gasolines [6]. In other words, if the antiknock rating is too low, knock occurs. Heavy and prolonged knocking may cause power loss and damage to the engine. Engine power is a function of the fuel as well as of the engine design and is related to octane ratings of the fuel. Compression is directly related to power, so engines that require higher octane usually deliver more engine power. Many high-performance engines are designed to operate a high maximum compression and thus need a high-quality (high-energy) fuel usually associated with high octane numbers and, therefore, demand high-octane premium gasoline.

3. Conclusions. – Major criteria in the consideration of any gasoline as motor fuel or as a component of motor fuel are its volatility and knock performance. The basic measures of volatility are vapor pressure and distillation, while knock performance is measured by the octane rating. These parameters constitute the quality-assurance tests carried out in this work. An assessment of our results points to the undesirability of the adulterated Utorogu condensate/gasoline blends for a spark-ignited automotive engine, especially in the case of 16–100% (volume by volume) condensate/gasoline blends. This is due the low RON rating and low volatility corroborated by the < 0.45 kg/cm^2 RVP and high boiling-point (IBP, FPB, and TR temperature) ranges.

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Experimental Part

Materials and Methods. Premium gasoline (= premium motor spirit; PMS) was collected from the Nigerian National Petroleum Corporation (NNPC), while the petroleum condensate samples were collected from the Utorogu gas field of the Niger Delta, Nigeria.

Blending of the PMS/Condensate Samples. Test samples (condensate/PMS mixtures) were blended into 12 different proportions, *i.e.*, control (= pure PMS) 10, 20, 30, 40, 50, 60, 70, 75, 80, 90, and 100% (*v*/*v*) condensate/PMS. The blends and the pure samples were refrigerated at 35 °F (2 °C) to avoid evaporation of volatile components.

Evaluation of Condensate/PMS Samples by Atmospheric Distillation. A 100-ml portion of the test condensate/PMS sample was measured with a 100-ml graduated cylinder and was poured into a round-bottom boiling flask containing some boiling stones to prevent explosion. Readings were taken for the initial-boiling-point (IBP) temp., the 10-ml and 50-ml recovery temp., the final-boiling-point (FBP) temp., and the total-recovery (TR) temp.

Evaluation of Condensate/PMS Samples by Reid *Vapor Pressure* (RVP). RVP of the gasoline and blended samples were determined as described in the ASTM Test Method for Vapor Pressure of Petroleum Products (*Reid* Method; D323) [7]. The RVP machine was filled with 100 ml of the sample to be analyzed before being submerged into the RVP water bath. The RVP water bath was adjusted to boiling of the sample at 38 °C. The vapor escaping from the system was detected by the RVP scale and recorded in kg/cm^2. After taking the initial reading, the RVP machine was removed from the water bath, shaken for 2 min, and re-submerged into the water bath. A second reading was taken after 10 min and the process was repeated until no further increase in vapor pressure was detected.

Determination of the Specific Gravity of Condensate/PMS Samples. The specific gravity of gasoline and blended samples were determined by the ASTM Test Method (D1298/IP 160) [7]. A 400-ml graduated cylinder was filled with the sample to be analyzed. A hydrometer with calibrations of 0.70 or 0.75 was submerged into it. When the hydrometer was floating on the sample, readings were taken. A thermometer was then inserted into the graduated cylinder for 10 s, and the temp. was recorded. Specific-gravity values corresponding to the temp. in °F were read as values for the corrected SG.

Determination of the Research Octane Number (RON). A 400-ml portion of the test sample was introduced into a carburetor, and the RON machine was switched on. A midscale of the sample was established by its compression ratio. The compression ratio on which the sample was running was read from the micrometer gauge, otherwise known as the dial indicator. The highest compression ratio of the sample was obtained by gradually lowering or adjusting the carburetor readings. 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 so as to attain equilibrium conditions before the cylinder height was adjusted for a knockmeter reading between 45 and 47. After locating the fuel for maximum knock, the cylinder height was adjusted to a knockmeter reading of 50. The knockmeasurement instrument (the detonation pickup, detonation meter, and the indicating knockmeter) was adjusted as follows: The knockmeter needle was set at zero; the detonation-meter needle was at zero; the basic spread setting was in the range of 10 – 18 knockmeter divisions per octane number.

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