Adulterating the quality of automotive gas oil using dual purpose kerosene: Effects on compression ignition engines, humans and environment

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A R T I C L E   I N F O

A B S T R A C T

Five combustible mixtures of automotive gas oil and dual purpose kerosene were obtained from a retail outlet and blended into different automotive gas oil (AGO) and dual purpose kerosene (DPK) proportions (85:15, 75: 25, 50:50, 25:75 & 15:85% (v/v)). Samples were analyzed using densitometer, hydrometer, karl fischer titrator, pour and cloud point tester based on American Standard for Testing and Materials (ASTM) with the aim of delimiting the degree to which adulteration affects the quality of the pure sample, impact on the environment as well as the effects on compression ignition engines. Results obtained from the analyses of the blended ratios show the following parameters in the ranges; density (0.858–0.827g/cm^3); specific gravity@60 ^{0}F (0.859–0.828), kinematic viscosity (4.800–1.200 cSt), cloud point (7.000–2.000 ^{o}C), pour point (-15.000 – < -34.000 ^{o}C) and moisture content (500.000–1200.000 ppm). Results of the analyses showed that 85 % dual purpose kerosene in the blended mixture fell below American Standard for testing and materials (ASTM) and Department for Petroleum Resources (DPR) acceptable standard in terms of viscosity. A maximum of 15% dual purpose kerosene in the blended mixture fell within ASTM specification in terms of moisture content. Specific gravity, density, cloud point and pour point of all the bended samples were within specification. Adulterating automotive gas oil with dual purpose kerosene at (≥ 15:85 %) AGO:DPK ratio as well as the use of biomass as an alternative source of energy due to diversion of dual purpose kerosene for adulteration, results in the release of various types of harmful poly aromatic hydrocarbons to the environment through the exhaust of diesel engines and cooking respectively. It can also lead to reduction in compression ratio, power loss as well as wear and tear of engine parts.

Capsule Summary: Adulterating AGO with DPK above acceptable limit could result in heavy smoking of exhaust pipes thereby releasing polyaromatic hydrocarbons to the environment which can cause health effects like decrease in immune function, kidney and liver damage, lung abnormalities, cancer in humans and animals as well as various damages to engine parts.

INTRODUCTION

Adulteration is the introduction of a foreign undesirable substance to a substrate which affects the quality of the substrate (Patra and Mishra, 2001). Fuel adulteration involves blending expensive petroleum products such as gasoline premium motor spirit (PMS) and AGO with less expensive petroleum products such as condensates or used lubricants (Sukdev, 2002). The primary cause of adulteration is the intention of maximizing profit orchestrated by differential tax system. The fact that adulteration of PMS with AGO and that of AGO with DPK is difficult to detect, combined with the differential tax structure makes such adulteration financially rewarding, even though it is illegal (Osueke and Ofondu, 2011). The term DPK stem from the fact that the product can be used both as an aviation fuel and for domestic purposes (cooking) this is slightly different from HHK (Household Kerosene) which is basically used for domestic purposes (Gupta et al., 1992). Mixing specific amount of DPK with AGO does not lead to an increase in tailpipe emission but contributes to air pollution however high level adulteration could have adverse effects on compression ignition engines (Yadav et al., 2005). Unlike PMS, diesel engines do not use high voltage spark ignition plugs but compression ignition stroke (Mishra et al., 2008). An engine running on AGO compresses the air inside the cylinder to high pressure and temperatures. AGO is generally injected directly into the cylinder near the end of the compression stroke (Moon, 1974). The blending of DPK with AGO is widely and legitimately practiced by Oil Industry worldwide as a means of adjusting the low temperature operability of the fuel. This practice is not harmful or detrimental to tailpipe emissions provided the resulting fuel meets engine manufacturers' specification (Yadav et al., 2005; Chikwe et al., 2012). A thin line separates adulteration from blending. Blending in petroleum refining is the physical mixture of different liquid hydrocarbon components to form a desired product. Both blending and adulteration involves physical mixture, blending produces a desired product while adulteration leads to an undesired product (Wiziack et al., 2011). The undesirability of adulteration is observed from the deviation in the quality assurance parameters of the product. Quality assurances parameters of petroleum products are parameters that determine the suitability of the product for specific purposes (George, 1993; Onojake et al., 2013).

Adulterating AGO with DPK results in heavy smoking of vehicle exhaust thereby releasing poly aromatic hydrocarbons (PAHs) to the environment. The movement of PAHs in the environment depends on properties such as how easily they dissolve in water, and how easily they evaporate into the air (Yadav et al., 2005). PAHs in general do not easily dissolve in water. They are present in air as vapors or stuck to the surfaces of small solid particles. They can travel long distances before they return to earth in rainfall or particle settling (ASTDR, 1995). Some PAHs evaporate into the atmosphere from surface waters, but most stick to solid particles and settle to the bottoms of rivers or lakes. In soils, PAHs are most likely to stick tightly to particles. Some PAHs evaporate from surface soils to air. Certain PAHs in soils also contaminate underground water (Yadav et al., 2005). PAHs have a lot of adverse effects on humans, plants and animals. PAHs can cause various forms of cancer, decrease in the immune system, kidney and liver damage. They have been proven to cause tumors in animals, birth defects and decreased body weights as well as toxic effects on the antioxidant of plant metabolism (ASTDR, 1995).

Since DPK is mostly used by low income earners, its diversion for the purpose of adulteration drastically reduces its availability to the end users who turn to biomass for the purpose of cooking, leading to an increase in indoor air pollution and consequent adverse effects on the environment (Dhole and Ghosal, 1995). Biomass refers to organic matter derived from living organisms basically plants or plant-based materials that are not used for food or feed. Using biomass as a fuel produces air pollution in the form of carbon monoxide, carbon dioxide, nitrogen oxides, volatile organic compounds (VOCs), particulates and other pollutants at levels above those from traditional fuel sources such as DPK or natural gas (Zhang and Smith, 2007). Utilization of wood biomass as a fuel can also produce fewer particulate and other pollutants than open burning as seen in wildfires or direct heat applications. Black carbon which is a pollutant created by combustion of biofuels, and biomass is the second largest contributor to global warming (Springsteen et al., 2011). The use of biomass for cooking can also lead to deforestation owing to the fact that the woods will definitely be harvested faster than the trees can grow. Deforestation has many negative effects on the environment; the most dramatic impact is a loss of habitat for millions of species. Seventy percent of Earth's land animals and plants live in forests, and many cannot survive the deforestation that destroys their homes (Baxter, 2005). Deforestation also drives climate change. Forest soils are moist, but without protection from sun-blocking tree cover, they quickly dry out. Trees also help perpetuate the water cycle by returning water vapor back into the atmosphere. Without trees to fill these roles, many former forest lands can quickly become barren deserts (Heinimö and Junginger, 2009). Trees also play a critical role in absorbing the greenhouse gases that fuel global warming. Fewer forests mean larger amounts of greenhouse gases entering the atmosphere and increased speed and severity of global warming (Springsteen et al., 2011).

Adulterating AGO with DPK can also lead to consistent engine knock in both automotive and generator engines, insufficient supply of engine power, slow rate of deflagration experienced by most consumers of the product, clogging of fuel filters, injectors and slow speed of engines (Patricia et al., 2012). The Standards Organization of Nigeria (SON) surprised the public with its discovery that fuel retail outlets in the country, for the sake of making excessive profit, do adulterate petroleum products. In a survey carried out by SON, the result of which was presented to stakeholders, the

organization revealed that more than 60 per cent of the over 2,000 retail outlets in Nigeria have automotive gas oil adulterated with kerosene to about 77 per cent (NNPC, 2008).

The aim was to delimit tolerable levels of admixing the adulterant (DPK) in the petroleum product (AGO) hence determine the extent at which such adulterations affect the quality assurance parameters of AGO and by implication to examine how hazardous the adulterated product can affect compression Ignition engines and the environment.

MATERIAL AND METHODS

AGO also known as Diesel oil was obtained from the Nigerian National Petroleum Corporation (NNPC) and this was used as the control sample labeled Y. Another sample of AGO labeled Z was obtained from a retail outlet within Port Harcourt metropolis. DPK which serves as the adulterant was also obtained from NNPC. Test samples (AGO/DPK mixtures) were blended into five (5) different proportions (85:15, 75: 25, 50:50, 25: 75 & 15:85% (v/v)). The different blends and the control samples were kept in the refrigerator to avoid the evaporation of the volatile components prior to laboratory analyses. Analyses of the properties of the blended samples were carried out three times per blended sample, and the results compared with those obtained from the control sample. A summary of results are shown in Table 1.

Density and kinematic viscosity were measured using SVM 3000 densitometer, cloud and pour points were measured with Normalab cloud and pour test Cabinet, Specific gravity was measured with the hydrometer method, while moisture content was measured using Coulometric karl fischer titrator according to ASTM.

Determination of density and kinematic viscosity

The cells of the equipment were thoroughly cleaned. 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, dynamic viscosity readings were displayed and the readings recorded (ASTM D4052-96 2002).

Determination of cloud point

The test sample was poured into the test jar to the level mark. The test jar was closed tightly by the cork carrying the test thermometer. The test jar was inserted in the jacket of the cooling bath maintained at a temperature of 0 +/- 1.5 ^{0}C. At each test thermometer reading that is a multiple of 1 ^{0}C 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 ^{o}C. The cloud point is the temperature at which cloud is observed basically from the bottom of the test jar (ASTM D5771 2002).

Determination of pour point

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 ^{0}C 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 (ASTM D97 – 06 2012).

Determination of specific gravity

The specific gravity of AGO and blended samples were determined by the ASTM test Method (D1298/IP 160). A 400 ml graduated cylinder was filled with the sample to be analyzed. A hydrometer with calibrations of 0.80 or 0.85 was submerged into it. Readings were taken as the hydrometer floats on the sample. A thermometer was then inserted into the graduated cylinder for 10 seconds and the temperature recorded. Specific gravity values corresponding to the temperature in ^{0}F were read as values for the corrected specific gravity (ASTM D287 2002).

Determination of moisture content

Test sample was agitated vigorously to obtain a homogenous solution. This is important because only a small quantity of 0.1 ml test solution is required for the analyses to prevent the coulomat from easy contamination. Karl Fischer titrator is operated with a central processing unit, a keyboard and monitor. The analyses commences by clicking the start key on the monitor with the mouse which results in the stirring of the coulomat by a magnetic stirrer giving rise to the conditioning of the equipment. Once analysis was completed, results were shown on the monitor (Tavčar, 2012).

RESULTS AND DISCUSSION

The quality assurance parameters of AGO and different ratios of AGO/DPK blended samples are shown in Table 1. 15:85 AGO/DPK sample (the most adulterated) was labelled as X, The control sample of pure AGO indicated as Y was obtained from NNPC while AGO sample from a retail outlet was indicated as Z.

One of the effects of blending AGO with DPK is the change in the appearance (color) of the resultant AGO/DPK blended sample. Product color is a common concern for refiners with a number of petroleum products including AGO, Kerosene (DPK and HHK), Lubricating base oil etc. (Cammy, 1986). The issue of AGO product color is now a cause of concern especially with the introduction of Ultra low Sulphur Diesel (ULSD) as the typical ULSD unit cycle length may be limited by color change of the product (Yadav et al., 2005). It is well known that the color of petroleum products is affected by the reaction conditions in the hydrotreater especially temperature and hydrogen partial pressures (Moon, 1974).

Table 1: Quality assurance parameters of AGO and AGO/DPK blended samples

Sample	Appearance	Dens. @ (g/cm^3)	Spec. grav.	Kin. Vis. (cSt)	Cloud point (^{0}C)	Pour point (^{0}C)	Moist. Cont. (ppm)
Y	Dark Yellow	0.8697	0.8708	4.2	4	-3	180
Z	Dark Yellow	0.866	0.867	5.3	1	-10	450
85:15:00	Greenish Yellow	0.858	0.859	4.8	7	-15	500
75:25:00	Light Brown	0.8578	0.853	4.2	5	-27	620
50:50:00	Light Yellow	0.85	0.851	3.8	3.5	-32	740
25:75	Light Yellow	0.832	0.833	2.6	3	<-34.000	836
15:85 (X)	Light Yellow	0.827	0.828	1.2	2	<-34.000	1200
ASTM SPEC.		0.82-0.87	0.82-0.87	1.6-5.5	+2 to -6	+3 to -6	<500

It is also generally accepted that the species responsible for color change in petroleum products are poly aromatic hydrocarbons (PAH). Some of these PAHs are green, blue and fluorescent in color which is apparent even at very low concentrations of these species (Mai et al., 2008). From Table 1 it can be deduced that the color of the AGO/DPK blended samples changes as the concentration of the DPK increases. The color change ranges from dark yellow to greenish yellow to light brown down to light yellow. The Table also shows that as low as 15% DPK added to 85% AGO transformed the color of the resultant blend from dark yellow to greenish yellow indicating that some PAHs must have been introduced into the AGO sample. These species can polymerize to form condensed aromatic structures which tend to be green to yellow/brown in color and can also form sediment through oxidation and free radical reactions resulting to product instability (Dhole and Ghosal, 1995). Studies show that PAHs such as Anthracene, fluoranthene and their alkylated derivatives could be responsible for color change in AGO (Boyle and Thomas, 1988). Apart from the environmental implications of these PAHs when released through diesel smoke at high concentration, their presence could also be catastrophic to the compression ratio of diesel engines (Seifert and Teeter 1970).

The density of a sample can be defined as the weight per unit volume of the sample in other words it is the ratio of the weight to the volume of a given sample. The density of AGO varies depending on the type and the environmental conditions (Grigor'ev and Ovchinnikov, 2010). The density of AGO reduces with increase in the volume of DPK added. Department of Petroleum Resources (DPR) specifies a density range of 0.8700 – 0.8200 for AGO. Table 1 shows that AGO/DPK samples have densities in the range of 0.858 -0.827. Based on this, it can be deduced from the above results that all the AGO/DPK blended samples meet specification with respect to density.

The specific gravity and weighted equivalent on the American Petroleum Institute (API) gravity scale of the control samples and adulterated AGO/DPK blends were collected in Table 1. With reference to these results, AGO/DPK blended samples have specific gravity in the range of 0.85-0.82. Since the density is directly proportional to the Specific gravity, an increase in the volume of DPK added results in a decrease in the specific gravity. Based on ASTM Standard, all the AGO/DPK blended samples shown in the above results were within specification.

Viscosity is a measure of a liquid's resistance to flow. High viscosity means the fuel does not flow easily. The dynamic (shear) viscosity of a fluid expresses its resistance to shear flow where adjacent layers move parallel to each other with different speeds, while the kinematic viscosity (also called "momentum diffusivity") is the ratio of the dynamic viscosity to the density of the fluid. Fuel with the wrong viscosity (either too high or too low) can cause engine or fuel system damage. Low viscosity fuel will increase gear train; cam and follower wear on the fuel pump assembly because of the higher injection pressure (Linus et al., 2011; Onojake et al., 2012). Fuel atomizes less efficiently and the engine will be more difficult to start. Low viscosity fuel may not provide adequate lubrication to plungers, barrels and injectors, and its use should be evaluated carefully (Ogali et al., 2012). The viscosity of the fuel affects atomization and fuel delivery rate. The viscosity of diesel fuel is normally specified at 40 ^{0}C. Fuels with viscosities over 5.5 centistokes at 40 ^{0}C are limited to use in slow speed engines, and may require pre-heating for injection (Chikwe et al., 2012). For some engines, it is advantageous to specify a minimum viscosity because of power loss due to injection pump and injector leakage. Maximum viscosity, on the other hand, is limited by considerations involved in engine design and size, fuel temperature and the characteristics of the injection system (Moon, 1974). Table 1 shows that the viscosity of AGO/DPK blended samples ranges between 1.20 to 5.30 cSt. Department of Petroleum Resources (DPR) specifies a viscosity range of 1.60 – 5.50 cSt for AGO. Sequel to this, it can be deduced from the above results that all the AGO/DPK blends except 15:85 (AGO/DPK) blend met ASTM Specification. The viscosity reduces with increase in the

Table 2: Correlation of the quality assurance parameters of AGO and 15:85 AGO/DPK blended sample

Parameter	X	Y	X – Mx	Y - My	(X - Mx)²	(Y– My)²	(X–Mx)(Y-My)
Density (g/cm³)	0.827	0.8697	-194.316	30.287	37758.514	917.305	5885.243
Spec. Gravity	0.828	0.8708	-194.316	-30.286	37758.125	917.239	5884.999
Kin. Vis. (cSt)	1.2	4.2	-193.943	-26.957	37613.693	726.666	5228.059
Cloud Point (⁰C)	2	4	-193.142	-27.157	37304.025	737.489	5245.123
Pour Point (⁰C)	-34	-3	-229.142	-34.157	52506.285	1166.684	7826.763
Moist. Content (ppm)	1200	180	1004.858	148.843	1009738.6	22154.313	149566.256

Mx: Mean of X = 195.142, My: Mean of Y = 31.157, $\sum$(X – Mx)(Y – My) = 179636.444, $\sum$(X – Mx)² = 1212679.238, $\sum$(Y-My)² = 26619.696.
Pearson correlation coefficient (R) = 0.9998, Coefficient of determination (R²) = 0.9996

volume of DPK added. It can also be observed from the results that DPK reduces the viscosity of the AGO obtained from the retail outlet towards the viscosity of the control sample. Table 1 shows that 25% v/v DPK blended with AGO (retail outlet) gave the same viscosity as that of the control sample.

Cloud point is the temperature at which haziness is first observed at the bottom of the test jar containing the sample. It can also be said to be the temperature at which wax crystals become visible (ASTM D5771 2002). Table 1 shows that AGO/DPK blended samples have cloud points within 8 to 3 ⁰C. The Table also shows that addition of DPK to AGO obtained from the retail outlet reduces its cloud point to that of the control sample hence blending AGO with DPK can be used in adjusting the temperature operability of the fuel however caution must be applied to ensure that other parameters do not go out of specification. The above results show that all the AGO/DPK blended samples were within ASTM Specification in terms of cloud point, however AGO blended with higher concentrations of DPK will cloud faster in cold weather conditions. Diesel fuel is prone to waxing or gelling in cold weather; both are terms for the solidification of diesel oil into a partially crystalline state. Below the cloud point the fuel begins to develop solid wax particles giving it a cloudy appearance (Bahari et al., 1992). The presence of solidified waxes thickens the oil and clogs fuel filters and injectors in engines. The crystals build up in the fuel line (especially in fuel filters) until the engine is starved of fuel thereby affecting engine power performance, this also negatively affects the engine carburetor, cause total engine damage and may lead to heavy smoking of vehicles which in turn have adverse effect on humans and their immediate environment (ASTM D4539–10 2002; Onojake et al., 2013).

Pour point is the temperature at which diesel fuel becomes so thick that it will no longer pour from a container. At this temperature the fuel essentially becomes unpumpable. Pour point is typically well below the temperature at which the fuel will plug a fuel filter, therefore pour point is only a useful measure for fuel handling properties but not a good indicator of vehicle operability (ASTM D97–06 2012). Table 1 show that the higher the volume of DPK added to AGO the lower the pour point. Pour point of AGO is the quality assurance parameter with the highest deviation after being blended with DPK. AGO blended with high volume of DPK will not flow at very low temperatures that is why most diesel vehicles are equipped with filter heaters (Ogali et al., 2012).

Moisture content of a sample refers to the percentage of water within the sample. Each Petroleum product has a tolerable level of moisture content (Azernikov, 2008). The maximum allowable moisture content for AGO according to DPR and ASTM is 500 ppm and this is referred to as water in solution or dissolved water which is different from suspended water caused by adulteration. Table 1 shows that moisture content increases with increase in the volume of DPK added. DPK has a higher water tolerance than AGO being a product obtained from fractional distillation of petroleum at temperatures of 150 ⁰C to 275 ⁰C which is quite lower than that of AGO (200 ⁰C to 300 ⁰C), it therefore requires less refining than AGO (Bahari et al., 1992). The deviation in moisture content of

Table 3: Pearson's correlation coefficient matrix for quality assurance of AGO and AGO/DPK blended samples

Parameter	Moist. Cont. (ppm)	Cloud Point (⁰C)	Pour Point (⁰C)	Spec. Grav.	Kin. Vis (cSt)
Moist. Cont. (ppm)	1				
Cloud Point (⁰C)	-0.32	1			
Pour Point (⁰C)	-0.89	0.14	1		
Spec. Grav.	-0.95	0.23	0.9	1	
Kin. Vis (cSt)	-0.85	0.31	0.72	0.9	1

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AGO due to addition of DPK is only second to the pour point. There are various reasons why AGO may contain dissolved water. Among them are; condensation of water in fuel tanks, components in the diesel fuel which help to retain the water in solution and fuel temperature. AGO with dissolved water within specification (<500ppm) does not pose problems as this will typically produce satisfactory results (Patricia et al., 2012). Table 1 show that only 85:15 AGO/DPK blended sample meet DPR and ASTM specifications with respect to moisture content.

Pearson's correlation analysis was adopted to analyze the relationship between the quality assurance parameters of 15:85 AGO/DPK blended sample (X) being the most adulterated AGO sample and control sample (Y) obtained from NNPC as shown in Table 2. Table 2 shows that a strong positive correlation was obtained from the statistical analyses carried out which means that a high X variable went with a high Y variable and a low X variable went with low Y variable. Table 3 shows the Pearson's correlation coefficient matrix of the quality assurance parameters of AGO and AGO/DPK blended samples, illustrating the correlation between individual parameters to each other. The Table shows that similar parameters are positively correlated, also all other parameters are positively correlated to each other except with the moisture content. The Moisture content is negatively correlated to other parameters. A negative correlation implies that a high X variable will lead to a low Y variable. Pearson's correlation coefficient can be calculated with the Eq. 1. The automotive fuels are susceptible to adulteration, which lead to affect the engine, human being and the environment and hence adulteration must be monitored by authentic analytical techniques to avoid negative impacts (Abreu et al., 2015; Correia et al., 2018; de Oliveira et al., 2004; de Souza et al., 2014; Kalligeros et al., 2005; Mendes et al., 2017; Onojake et al., 2012; Romanel et al., 2018; Silva et al., 2013; Squissato et al., 2018; Teixeira et al., 2008; Vempatapu and Kanaujia, 2017).

$$R = \frac{\sum (X-Mx)(Y-My)}{\sqrt{\sum (X-Mx)^2 \sum (Y-My)^2}} \qquad (1)$$

CONCLUSIONS

The quality assurance parameters considered in this study are very key in choosing AGO suitable to the environment as well as compression ignition engines. Blending different volumes of DPK in AGO results in the release of different poly aromatic hydrocarbons which is noticed through the color change of the resultant mixture. Adulterating AGO with DPK above acceptable limit could result in heavy smoking of exhaust pipes thereby releasing poly aromatic hydrocarbons to the environment, it also increases the use of biomass for cooking due to diversion of DPK resulting to air pollution. Health effects from chronic or long term exposure to PAHs may include decrease in immune function, kidney and liver damage, lung function abnormalities as well as various forms of cancer in humans and animals. PAHs also have toxic effects on the antioxidant components of plant metabolism (ASTDR, 1995). Blending AGO with DPK resulted in products that meet specification in terms of specific gravity, density, cloud point and pour point. However the kinematic viscosity of adulterated AGO with DPK could lead to reduction in compression ratio, power loss as well as wear and tear of engine parts. In addition to adjusting the temperature operability of AGO as seen in the results obtained in the cloud and pour points of the different AGO/DPK blended samples, blending AGO with controlled/specific amount of DPK can also be used in adjusting the viscosity of AGO especially those with high viscosities obtained from retail outlets. The use of high concentration of DPK in AGO is not favorable in temperate regions due to the tendency to form wax (cloud point) which could lead to clogging of filters. Moisture content in AGO above ASTM specification causes explosion of fuel injector tips, excessive injector wear, power loss, corrosion of engine system parts and eventual engine or fuel system damage (Patricia et al., 2012).

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