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FULL LENGTH ARTICLE

A novel approach for reduction of total acidity in kerosene based on alkaline rich materials readily available in tropical and sub-tropical countries

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Abstract The inability of refineries in some nations globally to produce kerosene locally as an aviation fuel is due to its acidity. In this study the viability of selected alkaline rich ash materials (e.g. cocoa husk, cassava peels, etc.) readily obtainable in tropical nations were examined for their ability to remove the acids. Fresh acidic kerosene samples were equilibrated with different ashes in predetermined ratios, filtered and characterized alongside with non-treated reference samples. Results revealed that the physicochemical properties of non-treated and treated kerosene remained the same except for conductivity, total acidity and micro-separation. The total acidity was reduced to a lowest limit than 0.015 mg KOH/g required. Treatment studies with specific masses of ashes and kerosene reduced acidity to approximately 0.00 mg KOH/g. Overall these alkaline source materials should be seen as a promising and alternative option in the systematic reduction of acidity in kerosene for aviation use.

1. Introduction

Crude oil, petroleum, is a naturally occurring flammable liquid consisting of a complex mixture of hydrocarbons, comprising of liquefied petroleum gas (LPG), gasoline, kerosene, gas oil, etc. which are all energy sources. Kerosene, a fractional distillate (150–260 °C), constitutes one of the most important fuels mainly used for powering jet engines and to a lesser extent for domestic purposes [1,2]. Accordingly, kerosene is labelled as dual purpose kerosene (DPK). DPK can only be used as aviation fuel if it meets very stringent international standard specifications. Currently, aviation fuel is almost exclusively extracted from the kerosene fraction of crude oil, including

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both jet fuel for turbine engines and aviation gasoline for piston engines [3].

There are many different kinds of crude oil however, the cheapest and readily available are usually known to contain a high amount of acids [4] and hence when processed produces acidic kerosene which cannot be used as aviation turbine kerosene (ATK), a big worry among nations the world over, including Ghana. The acidic compounds found in kerosene fractional distillate which contribute to higher total acidity value are naphthenic acids, cresylic acids, mercaptans and hydrogen sulfides [5]. Thus the higher the acidity of crude oil, the higher the total acidity content of kerosene produced. This ultimately also affects the usage of kerosene as aviation fuel, as these acids tend to corrode the jet engines. Prominent among the acids that add to the total acidity of kerosene are naphthenic acids. Crude oil contains varied amounts of these acids possessing high corrosive potential toward metals under certain conditions, and therefore, is very treacherous to the aviation industry [3,6].

Naphthenic acids occur in a wide boiling range of crude oil fractions, 180–380 °C of kerosene or ATK, and diesel fractions, and are generally concentrated within petroleum distillates of boiling temperatures between 200 °C and 370 °C. Naphthenic acid corrosion control can be attained by various mitigation measures including pre-distillation and removal of naphthenic acids from the crude oil being processed; blending of acidic with non-acidic crude oils [7] or distilled fractions; neutralization by injection of soda or other neutralizers; use of corrosion inhibitors; and coatings, and limiting of fluid flow [1]. Caustic washing removes acidic components of the petroleum fractionate, including phenol and cresols (cresylic acid). In addition to reducing corrosion in the refinery, the caustic wash also improves the burning qualities, storage stability, and odor of the finished kerosene and diesel fuels. Besides the high cost of the caustic technology, there also exists some challenges relating to separation of the aqueous caustic phase from the organic kerosene phase [5]. These challenges have caused some refinery industries to resort to reliance on the type of crude which are free of acids or contain a minimal amount of acids, for example, sweet crude oil, light crude oil, etc. with the belief that kerosene produced from such crude brands through fractional distillation processes would meet the international standards for ATK. Non-caustic processes for the removal of naphthenic acids from petroleum distillates, including ammonia, triethylene glycol, ion-exchange resins, and aluminosilicate zeolites, have also been reported though not commercialized [4].

In view of these acids present in crude oil, refineries are constantly exploring diverse ways of removing or lowering the acidic content of petroleum products such as aviation kerosene to minimize the cost of production. Various methods have being explored viz absorption, extraction or destruction of naphthenic acids [1,8–10]. Despite these, many nations including Ghana are suffering because periodically the kerosene produced does not meet aviation fuel strict standards; hence kerosene is most often used for domestic purposes resulting in periodic shortages. This does not augur well for the aviation industry and businesses. Accordingly, there is the need for investigation into efficient and cheaper alternatives that can reduce acidity in petroleum refinery kerosene to the lowest levels.

For instance, Ghana produces high tonnage of dual purpose kerosene (DPK). Information from the Tema Oil Refinery (Ghana) indicates that out of 3500 metric tons of crude oil processed per day, 15% comes as DPK, about 648,000 L/day. The demand for aviation turbine kerosene on the Ghanaian market per month is about 12,000,000 L and that of domestic kerosene is about 5,000,000 L [11]. Unfortunately, there has been perennial shortages of kerosene particularly, aviation fuel, thus having adverse effects on both people and businesses in diverse ways. These shortages are as a result of Ghana's only refinery inability to supply kerosene to meet international standard requirements due to high acidic levels (predominantly naphthenic acids) which could also recur in other nations as well. However, the refinery's inability to reprocess the distilled DPK to obtain ATK is as a result of the highly expensive nature of the caustic treatment process. Hence, the kerosene produced is eventually converted to domestic use whose demand is far lower than the aviation industry.

Incidentally, most of the low-priced and readily available crude oil on the world market contains higher levels of acidity values which are beyond standard limits. In this work, focus is placed on lowering the total acidity (naphthenic acid, cresylic acids, etc.) content of kerosene via cheaper sources of alkaline/base materials, specifically ash, obtained from cocoa husk, coconut husk, plantain heels and cassava peels. These materials are all good candidates for washing kerosene to reduce acidic content. The maximum standard total acidity value of kerosene for aviation usage is currently 0.015 mg KOH/g as specified by the international standards [12].

2. Experimental

2.1. Sample collection

Apparently these source materials are very common, less in demand and readily obtainable in most tropical and subtropical countries like Ghana. In this case, the ash source materials including plantain peels, cassava peels and coconut husk were collected from Tema (Greater Accra Region), Kasoa and Bawjiase markets (Central Region). Cocoa husks and leaves were collected from Buoyem and Techiman (Brong Ahafo Region) Fig. 1. For kerosene, five fractional distillates (13 L each) from five different crude oil sources namely Bonny-light crude oil (Nigeria), Forcados crude oil (Nigeria), Coco crude oil (Congo), Medanito crude oil (Argentina) and crude oil blend were obtained from the Tema Oil Refinery Ltd (Ghana). All samples were collected in duplicates during the period of study, 2011–2012.

2.2. Chemicals, reagents, analytical equipment

All chemicals used were of analytical grade. Toluene, concentrated nitric acid (HNO_3 63.01% v/v), *p*-naphtholbenzein and fluorescent indicator solutions were obtained from BDH (VWR International Ltd, Poole, BH15 1TD, England). Iso-octane and propan-2-ol were obtained from Alpha Chemika, Mumbai-400 002, India. Potassium hydroxide pellets (KOH) and barium hydroxide [$Ba(OH)_2$] powder from Analar

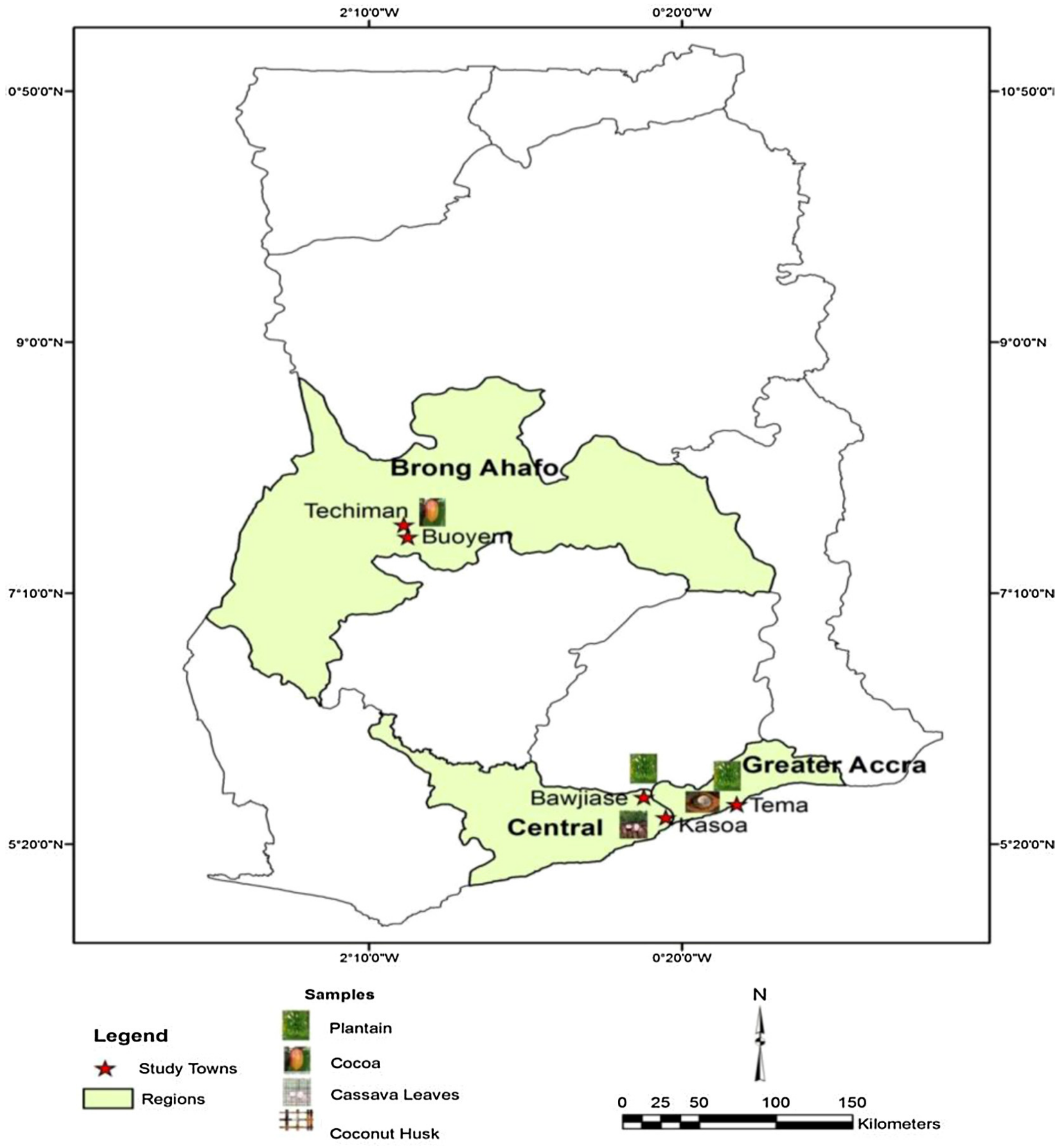

Figure 1 Map of Ghana showing sampling locations for alkaline based materials.

Normapur, Lutterworth, LE17 4XN, United Kingdom. Standard multi-element solution for calibration of Plasma CAL ICP-AES and MS, was obtained from SCP Science, Canada. Nitrogen gas (N_2, 99%) and argon gas were obtained from Air–liquid Ghana Limited, Accra, Ghana.

For sample distillation, the Herzog Walter, HERZOG GmbH, Lauda-Königshofen Model No. D97922 (Germany) was used. Sulfur levels in kerosene were determined using a Thermo Scientific, TS–UV Module, Model N. ECS 3000, Netherlands. Sulfur in oil with Horiba Sulfur-in-Oil Analyzer, Model No. SLFA-20, Japan. Flash Point Tester, Herzog Pensky Martens Model No. HFP 339. Smoke Point Tester, Stanhope-Seta. Kinematic viscometer, Ubbelohde viscometer, Herzog, Model No. HVU 480. Micro-separation was measured with Micro-separometer Model No. 1140 Emcee Electronic Inc., Venice, Florida, USA.

2.3. Preparation of local ash materials

Local raw materials such as cocoa husk, cassava peels, coconut husk, plantain peels and cocoa leaves were oven dried separately at a temperature of 105 °C for 120 h to remove moisture. Samples were then charred to remove carbonaceous materials under suction hood and then heated at 600 °C for 24 h in a muffle furnace to obtain the ash, which was cooled and subsequently stored in a desiccator.

2.4. Determination of metals present in ash

Metals in ash were determined following the ASTM method D5863. 1.00 g of ash was digested with 10 ml of conc. HNO_3, heated at 90 °C for 2 h, then allowed to cool, filtered and made up to 100 ml in a volumetric flask with de-ionized water. The resultant solution was analysed for various metals using ICP-AES.

2.5. Physicochemical analysis of fresh kerosene

A blend of all the five different kerosene samples was subjected to physicochemical analytical tests by the methods specified by the American Standard for Testing and Materials ASTM D1655 as follows:

2.5.1. Determination of total acidity

Total acidity test was carried out by ASTM method D3242. The total acidity of kerosene was measured using colorimetric titration involving *p*-napthol benzein as indicator. A known mass of kerosene was diluted with 100 ml of the titration solvent composed of isopropanol, toluene and water in a ratio of 49.5:50:0.5 by volume and titrated with 0.01 M of alcoholic KOH. Prior to the titration, N_2 gas was bubbled through the sample and titration solvents. A blank titration was also carried out with the titration solvent. The total acid was calculated based on the following equation:

$$\text{Total acidity} = \frac{(Vt - Vb) * M * 56.1}{W}$$

where Vt is the volume of KOH titrated to reach the equilibrium point, Vb is the volume of KOH for blank titration, M is the concentration of the KOH solution and W is the sample mass. The accuracy of the method is dependent on the mass of oil used.

2.5.2. Determination of electrical conductivity

In the determination of the electrical conductivity the sample was placed in a cell containing two electrodes. A voltage was applied across the electrodes and the resulting current was expressed as the conductivity of the sample (ASTM D2624).

2.5.3. Determination of smoke point

The sample was burned in a wick-fed lamp. The smoke point was the maximum height of flame that could be achieved without smoking (ASTM D1322).

2.5.4. Determination of water separation/Micro Separation (MSEP) index

Levels of MSEP of the kerosene sample were studied following ASTM method D3948. In this, the kerosene sample was mixed with water, forced through a fiber glass coalescing medium, and rated. The MSEP rating indicates the relative ease of coalescing water from the sample. The instrument was pre-calibrated with a water-free fuel sample.

2.5.5. Determination of freezing point

In the case of the freezing point, the sample was placed in a special jacketed tube fitted with a stirring rod and a thermometer. The tube was placed in a low-temperature bath and stirred as the sample cooled. Afterwards, as crystals of hydrocarbon appeared, the tube was removed from the cooling bath and allowed to warm up slowly with continuous stirring. The temperature at which the hydrocarbon crystals completely disappeared was the freezing point (ASTM method D2386).

2.5.6. Determination of copper corrosion

Using ASTM method D130, a polished copper strip was immersed in the sample for 2 h at 100 °C and then removed and washed. The condition of the copper surface was qualitatively evaluated by comparing it to standards.

2.5.7. Determination of particulate contamination

Using ASTM method D5452, the fuel was fed through a pair of matched-weight membranes with a pore size of 0.8 μm. The membranes were dried under standard conditions and weighed. The weight difference between the two was a measure of the particulate content of the sample.

2.5.8. Determination of Saybolt color

For the color of the kerosene sample, the ASTM D156 was applied, the Saybolt color chromometer method. The sample tube in the chromometer setup was filled with the kerosene sample. Then with the aid of an illuminating light, the color of the sample was established by matching with a whole color standard. Further verification was done by comparing to a reference standard color chart to establish the sample color.

2.5.9. Determination of naphthalene

In the determination of naphthalene, the ASTM D1840 method was adopted for the analysis. The sample was dissolved in isooctane (2,2,4-trimethylpentane) at a known concentration and the absorbance of the solution at 285 nm was measured to evaluate the naphthalene content.

2.5.10. Determination of distillation curve

In the distillation curve of the fuel sample, ASTM method D86 was employed. 100 ml of sample was placed in a round-bottomed flask and heated at a rate specified for a sample with its vapor pressure characteristics. Vapor temperatures were recorded when the first drop of condensate was collected (i.e. initial boiling point) till the final boiling point is attained.

2.5.11. Determination of aromatics

The aromatic content in kerosene was determined by ASTM method D1319. In this, an amount of kerosene sample was placed at the top of a special glass adsorption column packed with activated silica gel previously treated with fluorescent dyes. The hydrocarbons separate into bands of aromatics, olefins, and saturates because of their different affinities for the gel using 2-propanol under ultraviolet light.

2.5.12. Determination of density

The ASTM method D1298 was employed for the determination of the density of kerosene at 15 °C. The sample was transferred into a cylindrical container and a hydrometer was carefully lowered into the cylinder and allowed to settle. After the temperature of the sample had been equilibrated, the value on the hydrometer scale positioned at the surface of the sample and the sample temperature were recorded. The hydrometer value was converted to density at 15 °C using standard tables.

2.5.13. Determination of flash point

The ASTM D3828 method was adopted for this test. The sample was placed into a lidded cup and the cup heated to a fixed temperature. After a specified time, the cup was opened, a test flame applied, and an observation made whether or not a flash occurs. The test was repeated with a fresh sample at other fixed temperatures until the flash point was established with the required precision not greater than 0.5 °C.

2.5.14. Determination of kinematic viscosity

The ASTM method D445 was used for the kinematic viscosity. The kerosene sample was placed in a calibrated glass viscometer and held at a closely controlled temperature. The time required for a specific volume of the sample to flow through the capillary under gravity was measured. This time was proportional to the kinematic viscosity of the sample.

2.5.15. Determination of total sulfur

The total sulfur level in the kerosene sample was evaluated by ASTM D2622. The sample was placed in an X-ray beam and the intensity of the sulfur in the X-ray fluorescence was measured; this is used to calculate the sulfur content of the sample.

2.6. Treatment of fresh kerosene

500 ml of fresh acidic kerosene sample was treated with 10 g of cocoa husk ash by stirring together for 3 h and filtered to obtain "*treated*" kerosene (operationally defined). This was repeated for all other ash samples or materials.

2.6.1. Characterization of "treated" kerosene

Similarly, fifteen physicochemical analytical tests were conducted on the "*treated*" kerosene sample following the procedures described in Section 2.5 for fresh kerosene.

2.7. Determination of metals in fresh and "treated" kerosene samples

Metals in fresh and treated kerosene were determined following the ASTM method D5863. 40 g of fresh kerosene sample was weighed into a crucible and burnt off. 10 ml conc. HNO_3 was then added to the residue and heated at 90 °C for 2 h. This was allowed to cool, dissolved with deionized water and made up to 100 ml in a volumetric flask. The resultant solution was analysed for various metals using ICP-AES.

2.8. Experimental determination of interaction time and ash efficiency with kerosene

0.01 g each of ash material was agitated with 100 ml of fresh kerosene sample at different times: 5, 10, 20, 30, 40, 50, 60 and 70 min. Total acidity was then determined after each time. This procedure was repeated for different masses of ash material: 0.02 g, 0.03 g, 0.04 g and 0.05 g. Likewise, this same method was applied to different volumes of fresh kerosene sample, i.e. 200 ml, 300 ml, 400 ml, and 500 ml. However ash samples with minimal neutralizing potential could not show any appreciable acidity reduction after reacting with the 200 ml fresh kerosene sample; consequently the procedure of reacting with 300 ml, 400 ml and 500 ml fresh kerosene sample was limited to only cocoa husk ash material for this study.

2.9. Assessment of efficiency and effectiveness of the different ash materials

This was evaluated based on the graphs obtained from the optimum interaction times in Section 3.4, Figs. 2 and 3. From these graphs, the total acidity at the steady state was estimated. The estimated values were plotted as a function of the mass of ash per unit acidity. Based on the straight line graph obtained, the amount of ash needed to deplete 1 mg (KOH)/g of acidic kerosene was evaluated.

2.10. Determination of mix-ash efficiency on kerosene

The masses 0.01–0.05 g of mix-ash (cocoa husks 50% and cocoa leaves 50% i.e. ratio of 50:50) were weighed into a conical flask and 100 ml of fresh kerosene sample added. The mixture was stirred and total acidity of the resultant filtrate determined after 40 min of incubation (optimum interaction time). The experiment was repeated for ratios of 40:60, 30:70, 20:80 and 10:90 mix-ash materials.

2.11. Quality control and quality assurance (QA/QC)

For quality control and quality assurance purposes, reagent blanks, certified reference standards, replicated analyses and references were incorporated in the analytical scheme.

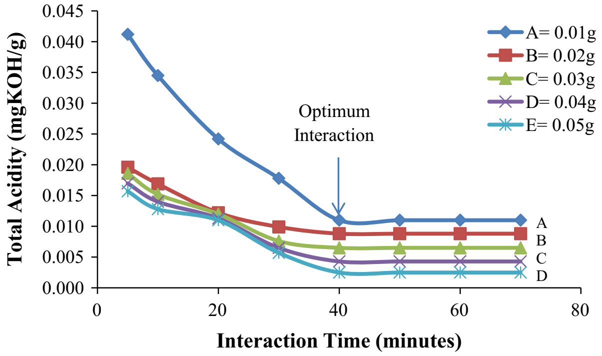

Figure 2 Depletion of total acidity versus time with cocoa husk ash.

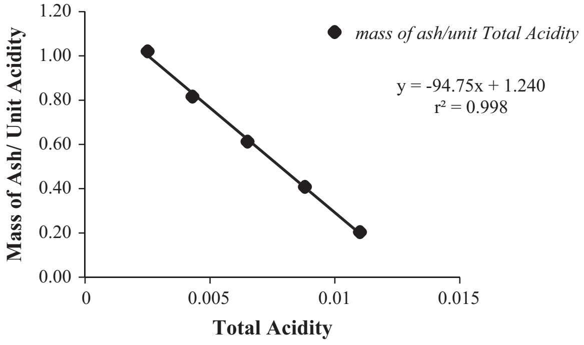

Figure 3 Effectiveness and efficiency of the cocoa husk ash-100 ml volume.

3. Results and discussion

3.1. Physicochemical properties of non-treated (fresh) and treated kerosene

Results of the physicochemical analyses of fresh and treated kerosene samples obtained from various crude oil blends are presented in Table 1. Results were the same no matter the type of crude oil used for the study. Of the sixteen parameters characterized, electrical conductivity, micro-separation index and total acidity were susceptible to change upon further treatment. In all, the fresh and treated kerosene distillates appeared clear and bright with densities of 825.30–825.50 kg/m^3 respectively. Parameters like aromatics, residue, densities, flash point, freezing point, smoke point, total sulfur, viscosity at −20 °C, particulate contamination and distillation curve were all within the standard limit specifications after distillation without treatment. Electrical conductivity on the other hand, was as usual poor just as it is for any crude oil samples. By the international specifications for kerosene as an aviation fuel, electrical conductivity should not be less than 50.0 pS/m, however, the untreated kerosene distillate recorded 3.0 pS/m while the treatment process improved the conductivity value to 44.0 pS/m.

On the contrary, micro-separation, a measure of the presence of surfactants in aviation fuels measured 95 in the untreated kerosene sample and 86 in the treated distillate as against a standard specification minimum of 70. It is noteworthy however, that the result of this test does not have any known relationship to the rate of water settling in tanks. This index also takes into account traces of refinery treating chemicals left in fuels and surface active substances added or picked up by the fuel during handling from production [13].

Three physicochemical parameters; electrical conductivity, water separation index and total acidity were affected significantly after the treatment process. Electrical conductivity of the treated kerosene was actually improved from 3 pS/m to 44.00 pS/m even without the addition of the static electricity dissipater compared to the fresh kerosene sample which was 3.00 pS/m. The improvement could be attributed to the presence of some of the ionic species that obviously found their way into the treated kerosene from the ash materials. However, ATK product for market which invariably required the use of additive to improve its electrical conductivity (> 50.00 pS/m), would only need a relatively smaller amount of such additive to effect the desired improvement. Therefore the ash treatment procedure does not only reduce total acidity but also renders the use of lesser amount of additive (i.e. conductivity improver) and eventually lowering the production cost of aviation fuel.

The total acidity is a significant parameter showing the gross acid content (water soluble and macromolecular organic

Table 1 Mean physicochemical data of treated kerosene, compared with fresh kerosene sample despite the class of crude oil and standard limits.

	Standard limits	Fresh kerosene sample	Treated kerosene sample
Appearance	Clear and bright	Clear and bright	Clear and bright
Aromatics, % volume	25.00 max	13.0	13.0
Copper corrosion	1b	1a	1a
Density at 15 °C, kg/m^3	775.0–840.0	825.3	825.5
Distillation			
Initial boiling point, °C		155.0	155.0
5% volume distilled at, °C		169.0	168.0
10% volume distilled at, °C		174.0	173.0
20% volume distilled at, °C		180.0	181.0
30% volume distilled at, °C		185.0	186.0
40% volume distilled at, °C		190.0	191.0
50% volume distilled at, °C		195.0	196.0
60% volume distilled at, °C		200.0	201.0
70% volume distilled at, °C		205.0	207.0
80% volume distilled at, °C		210.0	211.0
90% volume distilled at, °C		221.0	220.0
95% volume distilled at, °C		225.0	226.0
Final boiling point at, °C	300.0 max	238.0	239.0
Residue, %volume	1.5 max	0.8	0.8
Electrical conductivity, pS/m	50.0 min	3.0	44.0
Flash point, °C	38.0 min	52.0	53.0
Freezing point, °C	−47.0 max	−65.0	−65.0
Micro separometer	70.0 min	95.0	86.0
Naphthalenes, %volume	3.0 max	1.7	1.7
Saybolt color	+15.0 min	+30.0	+30.0
Smoke point, mm	19.0 min	23.0	23.0
Total acidity, mg KOH/g	0.015 max	0.05	0.002
Total sulfur, %wt	0.3 max	0.03	0.03
Viscosity @ −20 °C, cSt	8.00 max	3.5	3.5
Particulate contamination, mg/L	1.0 max	0.6	0.5

Min = minimum, max = maximum.

acids) in aviation fuel. The acidity expresses the content of macromolecular organic acids which normally contains naphthenic acids. The excessiveness of these acids may lead to serious metal corrosion as such levels of acidity must be kept low to forestall any such incident [14]. In this study, the total acidity of the treated kerosene was eventually reduced to almost zero i.e. complete neutralization. The treated kerosene gave a total acidity of 0.002 mg KOH/g, compared to 0.049 mg KOH/g for fresh kerosene, far lower than the guideline value of 0.015 mg KOH/g.

3.2. Metals in ash materials

Table 2 shows the concentration of metals in different alkaline ash materials used in the treatment of the various kerosene samples in the study. In all, very high levels of the macro elements were detected (Na, K, Ca and Mg). K levels were the highest in the different ash samples analysed. In terms of the ash materials prepared, cocoa husk ash was the richest in almost all alkaline and alkaline earth metals. The study therefore corroborated earlier findings by Afful and Dakubu [15]. Cocoa leaves ash on the other hand had the lowest levels of the alkaline and alkaline earth metals. Nonetheless, the levels of trace metals Cu, Fe, Mn, Ni and Zn were present in relatively higher amounts than those of Cr, As, Pb, V, Cd and Co. Arsenic, Pb and Co were not detected in the ashes of cassava peels, coconut husk plantain peels and cocoa leaves. Likewise Pb content in the cocoa husk, plantain peels and cocoa leaves ashes (2.80 mg/kg, 3.20 mg/kg and 15.40 mg/kg respectively) were very low and perhaps would not have any environmental consequences.

3.3. Concentration of metals in treated kerosene

Results of the metal concentration of fresh and treated kerosene samples is presented in Table 3. In general, very low concentrations of metals were observed in both fresh and treated kerosene samples. However, metal levels of treated kerosene samples were higher than levels detected in fresh samples. These low levels of metals in the kerosene samples could be due to the non-polar nature of kerosene. Even with the addition of about 223,000.0 mg/kg of K metal, only about 20.31 mg/kg was retained in the kerosene samples. It is also interesting to note that the metals Cr, As, Co and Ni were neither detected in the fresh nor the treated kerosene samples. However, in terms of Pb, 0.05 mg/kg was added to the initial level of Pb in the fresh kerosene samples. This finding therefore seems to suggest that the treatment process is clean, as little or no levels of metals leaked into the kerosene sample.

Table 2 Concentration of metals detected in the various ash materials (mg/kg).

Elements	Cocoa husk	Cassava peels	Coconut husk	Plantain peels	Cocoa leaves
K	223000.0	215200.0	208800.0	165600.0	11460.0
Na	467.00	2038.0	97720.0	3275.0	585.9
Ca	59830.0	57830.0	22960.0	64390.0	129400.0
Mg	44800.0	21420.0	25860.0	20160.0	43760.0
Cu	176.8	96.5	168.7	108.9	258.8
Fe	1430.0	17700.0	3492.0	24860.0	2342.0
Mn	964.4	852.2	199.0	753.4	4107.0
Ni	80.3	577.9	124.6	627.0	129.2
Cr	9.8	120.5	17.82	75.7	10.2
As	1.7	ND[*]	7.42	10.2	ND
Pb	2.8	ND	ND	3.2	15.4
V	82.7	154.5	126.4	207.1	199.6
Zn	397.3	1110.0	453.7	610.7	94.8
Cd	0.6	3.2	0.9	4.3	0.8
Co	21.9	20.2	ND	ND	53.5

[*] ND = not detected.

Table 3 Metal concentrations in fresh and treated kerosene samples (mg/L).

Elements	Fresh kerosene sample	Treated kerosene sample
K	0.44	24.75
Na	1.34	1.45
Ca	0.36	1.02
Mg	ND[*]	0.83
Cu	0.05	0.07
Fe	0.18	0.44
Mn	0.01	0.04
Ni	ND	ND
Cr	ND	ND
As	ND	ND
Pb	ND	0.05
V	0.02	0.07
Zn	0.05	0.08
Cd	0.01	0.01
Co	ND	ND

[*] ND = not detected.

3.4. Optimum interaction time of ash materials with kerosene for neutralization

As indicated in the methodology, optimum interaction time of ash material with acidic kerosene samples for effective neutralization was evaluated from the plot of the total acidity with time registered with the different ash samples. Since the reaction between the acid and the ash was on an equimolar basis, all the different ash materials reacted readily with the acidic kerosene. All the ash materials reacted to a steady state within 40 min of interaction. Plots obtained for cocoa ash husk are depicted in Fig. 2.

3.5. The efficiency of the different ash materials

The efficiency of each ash material was evaluated following the successful determination of the optimum time of interaction of each ash material with the acidic kerosene. Results obtained from each ash material are presented in Table 4. Prior to the determination of the efficiencies a second plot (Fig. 3) of total acidity at steady state with mass of ash was obtained from the plot of total acidity with time. The linear relationship obtained was extrapolated to obtain the mass of ash required to deplete the total acidity of 1–0 mg KOH/g. The result (Table 4) indicated that cocoa husk was the most efficient, requiring only 1.24 g of ash to deplete 100 ml kerosene to a total acidity of 1 mg KOH/g.

On the contrary, cocoa leaves ash required 14.8 g. The metal concentrations obtained in this study, also confirmed high levels of K, (23,000 pp) and Na (467 ppm) corroborating

Table 4 Mass of ash required to completely deplete acids in 1 mg KOH/g kerosene.

Ash material source	Required amount for total depletion (g)
Cocoa husk ash	1.24
Cassava peels ash	1.93
Coconut husk ash	2.02
Plantain peels ash	4.82
Cocoa leaves ash	14.85

Table 5 Mass of cocoa husk ash needed to react with a specific volume of acidic kerosene.

Volume of acidic kerosene/ml	Mass of ash needed
100	1.24
200	2.45
300	3.73
400	4.96
500	6.40

a previous study on inorganic contents of cocoa and plantain [15].

It can also be deduced from this study that the K content had some correlation with the efficiency of each ash material, ($r^2 = 0.99$, $p = 0.05$). Similarly attempts made to find the possible correlation for the other metals with efficiency, proved to be insignificant. Furthermore, the predominant alkaline medium mostly present in the ash materials was the oxides of K. However unlike Ca and Mg, the oxides of Na were very low for cocoa husk and cocoa leaves. Moreover, in spite of the close levels of K in coconut husk ash and cassava peels, these 2 ash materials had the lowest levels of efficiency.

Moreover, experiment conducted on cocoa husk ash alone showed that upon doubling the volume of acidic kerosene, there was a proportional increase in the amount of ash needed to do a complete depletion, tripling, quadrupling, etc. (Table 5).

3.6. The efficiency of the mix-ash materials

Table 6 shows the results of mix-ash efficiency on the depletion of acidic kerosene. The mixture was composed of the most and the least efficient ash materials in five different ratios. It indicated that a ratio 1:9 of cocoa husk ash and cocoa leaves improved the efficiency of the cocoa leaves ash by 27.80%. A 1:4 mix-ash ratio further improved the efficiency by 44.80% and that signifies that on situations where there are fewer amounts of the most efficient ash material, cocoa husk ash and a blend with cocoa leaves ash could act as a substitute. It stands to reason that in the instance where there is an insufficient supply of cocoa husk ash, a mix ash ratio of 1:4 cocoa husk ash and cocoa leaves ash could suffice.

Table 6 Efficiency of mix-ash material.

Mix-ash ratios cocoa husk ash: cocoa leaves ash	Mass of mix-ash per unit total acidity for complete neutralization (g)	Improvement on efficiency of cocoa leaves ash, %
1:1	3.992	73.10
2:3	5.012	66.30
3:7	6.430	56.70
1:4	8.199	44.80
1:9	10.730	27.80

4. Conclusion

Tropical alkaline rich ash materials could reduce acids found in kerosene for aviation use. Treating kerosene with various ashes obtained from cocoa husk, cassava peels, etc. gave results well within international standard specifications for ATK. The interaction of kerosene with different ash masses could also reduce and improve total acidity from 0.049 to 0.002. The optimum time of interaction was 40 min; cocoa husk ash was the most effective and efficient among all the ash materials employed. The investigations further demonstrated that cleaning acidic kerosene with these classes of bases is an option to be considered which could be economical.

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