

Fingerprinting of Some Petroleum Fractions Treated with Potassium Aluminium Sulphate

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Abstract This research investigates alteration in the composition of diesel and engine oil due to their treatment with 35g of Potassium Aluminium Sulphate, (KAl(SO₄)₂) for seven days at room temperature. Results reveal that after treatment, the Total Petroleum Hydrocarbon (TPH) of diesel increased from 7688.38mg/l to 12505.10mg/l whereas that of engine oil increased from 4967.48mg/l to 7700.47mg/l. This suggests that within these seven days, the salt was able to alter the composition of the samples by breaking down higher molecular weight hydrocarbon fractions within and above the C40 range to smaller molecular weight fractions within the C6 to C40 range. The TPH of the treated diesel oil was similar to that of kerosene after treatment and that of the treated engine oil was similar to that of the untreated diesel sample. Ratios calculated from fingerprints of the samples such as $n_{C_{20}}/n_{C_{24}}$, $n_{C_{18}}/n_{C_{24}}$, $n_{C_{18}}/n_{C_{20}}$, n_{C_7}/n_{C_9} , and $\sum K/\sum D$ for the treated diesel sample (0.76, 0.57, 0.75, 0.16, and 0.84) respectively were slightly similar to that of kerosene (0.65, 0.79, 1.20, 0.5, and 1.08), but different from that of the untreated sample whereas ratios like $n_{C_{10}}/n_{C_{11}}$, $n_{C_{11}}/n_{C_{12}}$, $n_{C_{14}}/n_{C_{16}}$, $n_{C_{11}}/n_{C_{20}}$ and $n_{C_{24}}/n_{C_{28}}$ for the treated diesel sample (0.53, 0.35, 1.02, 0.67 and 4.44) were similar to that of the untreated diesel sample (0.52, 0.36, 0.92, 0.46 and 5.47). None of the ratios for the treated engine oil sample were similar to either those of the untreated engine oil sample or those of diesel. Therefore, though the treatment of the samples with 35g of the salt caused alterations in the chemical composition of the samples, it did not totally transform them to the fraction obtained before them during distillation process.

Keywords Fingerprints, Diesel, Engine oil, Potassium Aluminium Sulphate, TPH, Composition, Ratios

1. Introduction

The Concise Oxford dictionary defines Petroleum (L. petroleum, from Greek: petra (rock) + Latin: oleum (oil) or crude oil as a naturally occurring, flammable liquid consisting of a complex mixture of hydrocarbons of various molecular weights and other liquid organic compounds, that are found in geologic formations beneath the Earth's surface[1]. Petroleum is recovered mostly through oil drilling. This latter stage comes after the studies of structural geology (at the reservoir scale), sedimentary basin analysis, and reservoir characterization (mainly in terms of porosity and permeable structures)[2],[3].

In its strictest sense, petroleum includes only crude oil, but in common usage it includes all liquid, gaseous, and solid (e.g., paraffin) hydrocarbons. Under surface pressure and temperature conditions, lighter hydrocarbons methane, ethane, propane and butane occur as gases, while pentane and heavier ones are in the form of liquids or solids.

However, in an underground oil reservoir the proportions of gas, liquid, and solid depend on subsurface conditions and on the phase diagram of the petroleum mixture[4],[5].

An oil well produces predominantly crude oil, with some natural gas dissolved in it. Because the pressure is lower at the surface than underground, some of the gas will come out of solution and be recovered (or burned) as associated gas or solution gas.

The proportion of light hydrocarbons in the petroleum mixture varies greatly among different oil fields, ranging from as much as 97% by weight in the lighter oils to as little as 50% in the heavier oils and bitumens. When it is refined and separated, most easily by boiling point, a large number of consumer products, from petrol, kerosene and diesel to lubricating oil, asphalt and chemical reagents used to make plastics and pharmaceuticals. Kerosene contains hydrocarbons with between 9 to 16 carbon atoms, diesel contains hydrocarbons with between 10 to 20 carbon atoms while engine oil contains hydrocarbons with between 24 to 38 carbon atoms[6].

The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel,

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copper and vanadium. The exact molecular composition varies widely from formation to formation but the proportions of chemical elements vary over fairly narrow limits as follows[7].

Four different types of hydrocarbon molecules appear in crude oil. These include: Paraffins, Naphthenes, Aromatics and Asphaltics. The relative percentage of each varies from oil to oil, determining the properties of each oil[5].

Potash alum (Potassium Aluminium Sulphate) is an inorganic salt with the molecular formula $KAl(SO_4)_2$. Potassium Aluminium Sulphate forms a solid, white powder at room temperature. It is a hygroscopic material which when exposed to air, hydrates (absorbs water). It is an important part of many products created by the pharmaceutical, cosmetic, and food industries because of its astringency property. It is also used in the manufacture of paper, dyes, glue, and explosives. Additionally, it helps in the water purification process, is used to speed up the hardening of concrete and plaster, and acts as a catalyst in various chemical reactions[8],[9].

Fingerprinting is a technique which involves the use of a gas chromatograph (GC –FID or GC-MS) for analysing samples for hydrocarbons fractions (TPH, PAH, and BTEX) present in them. This largely depends on the calibration of the equipment. A chromatogram which is obtained on completion of the analysis shows the components of the analysed sample and these components can be used in calculating various ratios. These ratios have a wide range of applications[10],[11].

In Akwa Ibom state, during scarcity of kerosene in the early nineties, diesel treated with Potassium Aluminium Sulphate was used as a substitute for kerosene. This paper therefore looks at the effect of treatment of diesel and engine oil with 35g of Potassium Aluminium Sulphate, $KAl(SO_4)_2$ for seven days and also tries to ascertain if this treatment makes the samples similar to the fractions obtained before them during the distillation process. 35g of the salt was chosen because reference [12] reported that it gave the best results in two days.

2. Materials and Method

2.1. Sample Collection

About 1000ml of Diesel oil was collected using a 500ml glass bottle from Onne port located in Port Harcourt, Rivers state, Nigeria while the inorganic salt, Kerosene and Engine oil were obtained from vendors in Uyo, Akwa Ibom State, Nigeria. On arrival at the laboratory, the diesel, kerosene and engine oil samples were stored in a refrigerator at 4°C till commencement of analyses while the Potash alum was stored in a cabinet.

2.2. Sample Preparation

Potash alum was dried at 80°C in the oven for about 12 hours. After drying the salt, it was kept in the desiccator for cooling before 35g of the salt was introduced into 50mls of

the diesel oil and engine oil in dry and clean 100ml bottles. The resulting mixtures were thoroughly shaken daily and allowed to react at room temperature in the Laboratory for seven days.

2.3. Oil Extraction and Gas Chromatographic Analyses

1g of each of the samples was weighed into well labeled clean and dry vials and 10mls of pentane was added to them. The samples weighed stirred using a magnetic stirrer for about 5 minutes before they were allowed to concentrate to 1ml. The extracts were fractionated into aliphatic fractions by adsorption liquid chromatography using a column of alumina and silica gel, while pentane was used as gradient solvent. The extracts were concentrated to 1ml and these were subjected to analyses[13],[14].

The TPH of the samples were determined using a Hewlett Packard 6890 gas chromatograph made by Agilent (USA) with the following operational conditions; flow rate (H_2 30ml/min, air 300ml/min and N_2 30ml/min), injection temperature (50°C), detector temperature (320°C). For signals, the GC was interfaced to a Hewlett Parker (hp) computer.

3. Results and Discussions

The treatment of the samples with 35g of Potassium Aluminium Sulphate altered the total petroleum hydrocarbon (TPH) of the samples within the seven days of treatment (table i). The results revealed that the TPH of the diesel increased from 7688.38mg/l to 12505.10mg/l whereas that of engine oil increased from 4967.48mg/l to 7700.47mg/l. This suggests that within these seven days, the salt was able to breakdown higher molecular weight hydrocarbon fractions within and above the C40 range to smaller molecular weight fractions which fell within the C40 range. This is corroborated by the increment and decrement in the concentrations of some of the fractions and the presence of C6 to C12 fractions in the fingerprints of the treated engine oil sample which was absent in the untreated engine oil sample. The similarity in the TPH of the treated engine oil and that of the untreated diesel also supports this. For instance, the concentration of the C6 and C18 fraction in the untreated diesel oil was 1711.61mg/l and 1507.06mg/l whereas after the treatment, it drastically reduced to 21.66mg/l and 891.65mg/l respectively, the difference between them being statistically significant at 95% confidence limit. On the contrary, the remaining fractions recorded increased concentrations. This also supports alteration in the composition of the sample. On looking at the total concentration of fractions within the diesel, engine oil and kerosene range in the samples, it revealed that the concentration of fractions in the kerosene range (table ii) for the treated diesel sample (8247.0 mg/l) was a little similar to that of kerosene (11361.95mg/l) but very different from that of the untreated diesel sample (2347.26mg/l). Also, the concentration of fractions in diesel range for the treated

engine oil sample was similar to that of the untreated sample. Statistical analysis (students' t-test) shows that the difference between the TPH of the treated diesel sample and that of kerosene was not significant at 95% confidence limit. For the treated engine oil sample, the result shows that the total

concentration of fractions within the engine oil range (6861.14mg/l) was still similar to that of the untreated sample (4349.52mg/l), thus suggesting that though the sample had undergone alterations in its composition, it still retained the characteristics of engine oil.

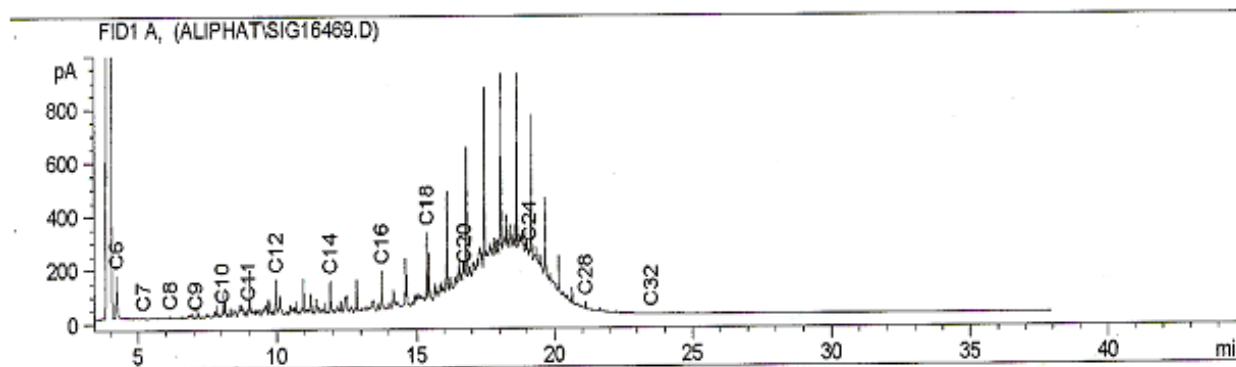


Figure 1. Fingerprint of diesel

Table 1. Effect of Potassium Aluminium Sulphate on some petroleum products

Hydrocarbon fraction	Diesel (mg/l)	Kerosene (mg/l)	Engine oil (mg/l)	Treated Engine oil	Treated Diesel
C6	1712	40.33	-	32.35	21.66
C7	7.18	87.09	-	43.49	15.85
C8	50.66	88.05	-	157.4	221.5
C9	25.09	174.4	-	7.99	97.22
C10	130.4	694.1	-	37.99	420.0
C11	248.8	2697	-	83.93	791.9
C12	690.7	2044	-	12.00	2233
C14	612.2	5612	8.98	30.41	2378.
C16	666.9	141.3	27.36	7.97	2327
C18	1507	6.81	149.56	157.4	891.7
C20	545.0	5.67	432.07	261.8	1187
C24	1258	8.66	1611	2668	1555
C28	229.8	24.96	953.4	2654	349.9
C32	4.74	2.62	1402	1137	12.43
C36	-	4.42	379.7	402.5	3.05
C40	-	-	3.79	6.62	-
Total	7688	11631	4967	7700	12505

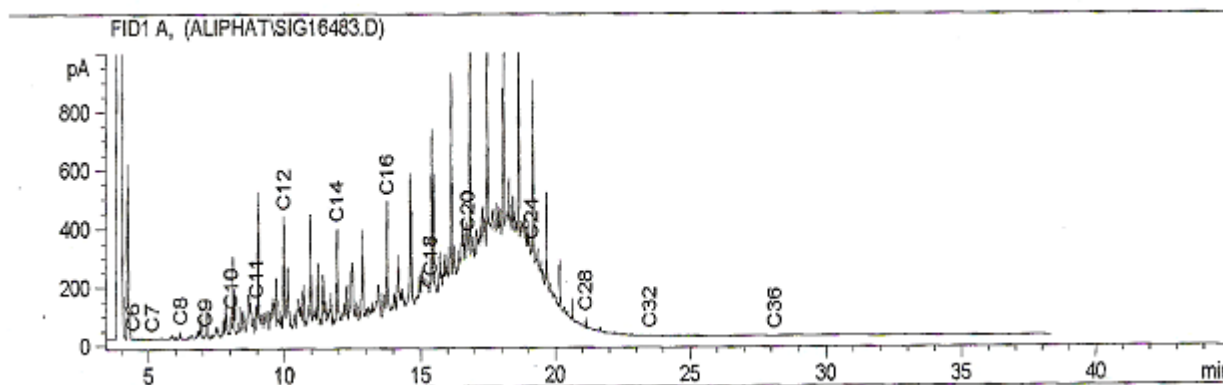


Figure 2. Fingerprint showing alteration in the composition of diesel after treatment with the salt

The fingerprints of the samples (Fig. 1, Fig. 2 and Fig. 3) also confirm alterations in the composition of the samples though the alterations did not make it very similar to kerosene which is the fraction obtained before it during the distillation process. Of all the ratios calculated using the fingerprints of the samples, only few of them were slightly similar while one ($nC_9/nC_{16} = 0.04$) was the same for the untreated and treated diesel sample. The nC_{20}/nC_{24} , nC_{18}/nC_{24} , nC_{18}/nC_{20} , nC_7/nC_9 , and $\sum K/\sum D$ ratios for the treated diesel sample (table 4) of 0.76, 0.57, 0.75, 0.16, and 0.84 respectively were slightly similar to that of kerosene (0.65, 0.79, 1.20, 0.5, and 1.08), but different from that of the untreated sample. These show that though the treated sample had not undergone enough alteration in composition to make it have the same properties as kerosene, it had some characteristics of kerosene. Reference[12] also reported that though the treatment of diesel with 35g of Potassium

Aluminium Sulphate had effects on the physicochemical characteristics of diesel oil, the treated diesel oil cannot be used as kerosene. The similarities in the TPH of the two samples confirm this. On the contrary, ratios like nC_{10}/nC_{11} , nC_{11}/nC_{12} , nC_{14}/nC_{16} , nC_{11}/nC_{20} and nC_{24}/nC_{28} for the treated diesel sample (0.53, 0.35, 1.02, 0.67 and 4.44) were similar to that of the untreated diesel sample (0.52, 0.36, 0.92, 0.46 and 5.47). These suggest that the treated diesel sample still had some characteristics of diesel[15]. On the contrary, for the engine oil, none of the ratios were similar to the ratios for either the untreated engine oil sample or the untreated diesel sample. This therefore suggest that the engine oil had undergone enough alteration to make it different from the untreated engine oil but the alteration was not enough to make it exhibit some characteristics of diesel oil. The presence of peaks within the C6 to C12 region affirms this.

Table 2. Ratios of selected hydrocarbon fractions of the samples

S/N	Ratios	Treated Diesel	Kerosene	Diesel	Treated Engine oil	Engine oil
1	$\sum K/\sum D$	0.84	1.08	0.56	0.33	0.05
2	$\sum E/\sum D$	0.20	0.003	0.35	12.39	7.04
3	$\sum K$	8247	11362	2347	180.3	36.34
4	$\sum D$	9808	10506	4271	553.5	618.0
5	$\sum E$	1921	40.66	1492	6861	4350
6	nC_7/nC_9	0.16	0.5	0.29	5.44	-
7	nC_9/nC_{16}	0.04	1.23	0.04	1.00	-
8	nC_{10}/nC_{11}	0.53	0.26	0.52	0.45	-
9	nC_{11}/nC_{12}	0.35	1.32	0.36	6.99	-
10	nC_{11}/nC_{14}	0.33	0.48	0.40	2.76	-
11	nC_{11}/nC_{20}	0.67	475.7	0.46	0.32	-
12	nC_{14}/nC_{16}	1.02	39.72	0.92	3.82	-
13	nC_{16}/nC_{18}	2.61	20.75	0.44	0.05	0.18
14	nC_{18}/nC_{20}	0.75	1.20	2.77	0.60	0.35
15	nC_{18}/nC_{24}	0.57	0.79	1.20	0.06	0.09
16	nC_{20}/nC_{24}	0.76	0.65	0.43	0.10	0.27
17	nC_{24}/nC_{28}	4.44	0.35	5.47	1.01	1.69
18	nC_{28}/nC_{32}	28.15	9.53	48.48	2.33	0.68

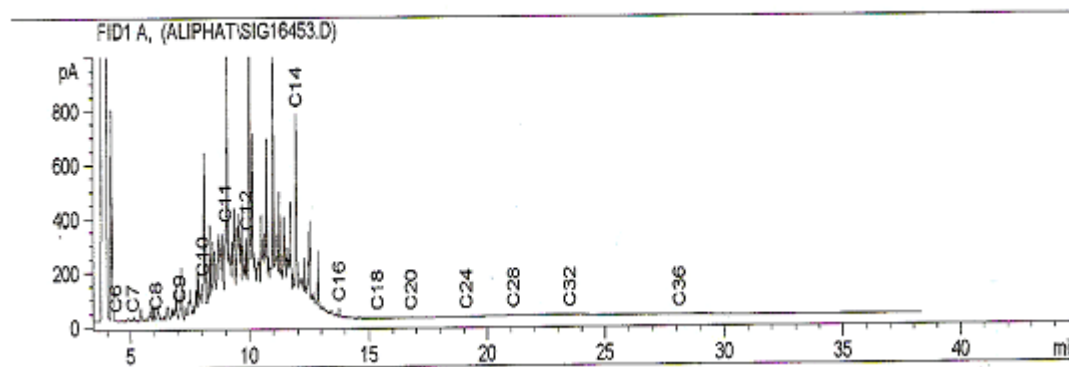


Figure 3. Fingerprint of Kerosene

4. Conclusions

The results obtained from the analyses of samples of diesel and engine oil treated with 35g of Potassium Aluminium Sulphate has shown that the treatment of the samples for seven days altered the TPH of the samples. Some of the fractions recorded increment in their concentrations whereas others had decreased concentrations. The C6 and C18 fractions drastically reduced after treatment of the diesel oil while the treated engine oil sample had peaks within the C6 to C12 region, though it was not present in the untreated sample. These suggest that the inorganic salt may have been able to breakdown (crack) the hydrocarbon fractions in the samples to fractions within above the C6 to C40 range, thus confirming the alteration in the composition of the samples. From the above, it could be concluded that though the treatment of the samples with the salt altered their compositions, the alteration was not enough to make the samples similar to the fractions obtained before them during the distillation process.

Where:

ΣK – sum of fractions within the kerosene range

ΣD - sum of fractions within the diesel range

ΣE - sum of fractions within the engine oil range

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