Comparative study on characterisation of atmospheric and vacuum oil residue from KRPC, Kaduna, Nigeria

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Abstract
This Study focused on Characterisation of Atmospheric and vacuum oil residue samples using FTIR technique and Physico-Chemical Analysis. A total of ten Oil residues samples were used in this study, five each from atmospheric and vacuum distillation. The samples were obtained from Kaduna Petroleum and Refining Petrochemical Company (KRPC), a subsidiary of Nigeria National Petroleum Corporation (NNPC).The samples were characterized by FTIR, Total Nitrogen and Sulfur Content. The FTIR spectra reveal that both residual samples showed the presence of C-H stretching of aliphatic alkanes at 2925 and 2850 cm-1, the very sharp and broad peak at 3600 cm-1 as observed in Sample of Vacuum residue is attributed to O-H stretching of alcohol which makes it distinct from other spectra. These spectra results agrees with many other studies on Nigerian crude oil residue. The result for total nitrogen and sulphur content show that both residues fall above the range for sulphur expected in Nigerian Crude oils and Products, i.e. 0.05-0.30w/% as well as the range of nitrogen normally reported for Nigerian Crude oil i.e. 0.1 to 0.7w%,therefore there is need for denitrogenation and desulfurization of these residues before refining.

Keywords: FTIR, atmospheric residue, vacuum residue, krpc, nnpc

Introduction
The chemical composition of heavy oils and residue is, in spite of the large volume of work performed in this area, largely speculative [4]. Indeed, the simpler crude oils are extremely complex mixtures of organic compounds. In fact, the composition of petroleum can vary with the location and age of the field in addition to any variations that occur with the depth of the individual well. Two adjacent wells are more than likely to produce petroleum with very different characteristics [6].

On a molecular basis, petroleum contains hydrocarbons as well as the organic compounds of nitrogen, oxygen, and sulfur; metallic constituents may also be present, but only to a minor extent. While the hydrocarbon content of petroleum may be as high as 97% (as, for example, in the lighter paraffinic crude oils), it is, nevertheless, the non-hydrocarbon (i.e., nitrogen, oxygen, and sulfur) constituents that play a large part in determining the nature and, hence, the process ability of the feedstock [3].

1.1 Sulfur compounds in crude oil residuum
Sulfur compounds are perhaps the most important non hydrocarbon constituents of petroleum and occur as a variety of structures. During the refining, a great number of the sulfur compounds that occur in any particular petroleum are concentrated in the residua and other heavy fractions. The relative importance attached to sulfur compounds in petroleum may, at first, seem unwarranted, but the presence of sulfur compounds in any crude oil can only result in harmful effects. For example, the presence of sulfur compounds in finished petroleum products such as gasoline will cause corrosion of engine parts, especially under winter conditions when water containing sulfur dioxide (from the internal combustion) May Collect in the crankcase [1].

1.2 Nitrogen compounds in crude oil residuum
The presence of nitrogen in petroleum is of much greater significance in refinery operations than might be expected from the small amounts present. Nitrogen compounds can be responsible for the poisoning of cracking catalysts, and they also contribute to gum formation in such products as domestic fuel oil. The trend in recent years toward cutting deeper into the crude to obtain stocks for catalytic cracking has accentuated the harmful effects of the nitrogen compounds that are concentrated largely in the higher-boiling portions [1].

2. Materials and Methods
The petroleum products used in this research work were residues from atmospheric and vacuum distillation obtained from Kaduna Refining and Petrochemical Company (KRPC), a subsidiary of NNPC, Nigeria

2.1 Reagents
All the reagents used in this work are of Analytical grade

2.2 Sample Collection
Ten Crude oil Residues samples were collected from oil movement unit of Kaduna Refining and Petrochemical Company (KRPC), a subsidiary of NNPC.2L of each oil were obtained, the samples were put in a clean sample bottles and kept away from sunlight. Atmospheric residue samples were collected first from the same pool and Vacuum Residue Samples were then collected a week later.

2.3 FTIR Analysis

A drop of the liquid residua sample was placed on the face of a highly polished salt plate (KBr), then the second plate was placed on top of the first plate so as to spread the liquid in a thin layer between the plates and the plates were clamped together. The liquid was finally wiped off out of the egde of the plate. The sandwich plate was then mounted onto the sample holder and IR spectra was generated.

2.4 Total nitrogen content

The procedure involved measuring Petroleum Residue sample ($1cm^3$) into a round bottomed flask. Then Na_2SO_4 (5g) was added followed by $CuSO_4$ (0.23g) and concentrated H_2SO_4 ($12.5cm^3$), The mixture was heated at a temperature of 350^oC until the digestion was completed and digest turned green and clear. The flask and the content were then allowed to cool and the solution was transferred into a standard flask ($250cm^3$). A portion of each digest ($5cm^3$) was pipetted into a micro-Kjeldahl unit and an excess of aqueous NaOH (40%) was added to make the solution strongly alkaline and force ammonia out of the solution, which was distilled into prepared boric acid indicator ($5cm^3$) in a titration flask and added up to $45cm^3$ of distillate ammonium borate contained therein. The Solution was then titrated with 0.01MHCl to regenerate the bluish colour of the boric acid at the end point. The percentage nitrogen in the sample was calculated by using the equation:

$$\% \text{ Nitrogen in the sample} = (0.01 \times 0.014)gN2 \times 250 \times \frac{100}{5} \times \frac{t}{W} \ldots \ldots \ldots .2.1$$

Where t= titre value of 0.01M HCl used in the titration.
w= weight (ml) of the sample taken for the analysis

2.5 Total Sulphur Content

The procedure involved measuring the petroleum products sample (1.5g) into round bottomed flask ($500cm^3$) and adding distilled water ($250cm^3$) to it. Then solid KOH (5g) and solid $KMnO_4$ (15g) were measured and added to the mixture in the flask together with anti-bombing chips. The mixture was refluxed for 6 hours and allowed to cool then concentrated HCl ($150cm^3$) was added slowly through the condenser. The flask was heated until its contents turned colour less, cooled and the condenser washed into the flask with a little distilled water. The content of the flask was collected into a beaker ($500cm^3$) washed with distilled water and filtered into a beaker. The filtrate was boiled with Concentrated HCl ($10cm^3$) and hot barium chloride ($100cm^3$) with stirring. This resulted in deposition of a fine white precipitate of barium sulphate after heating the beaker on the water bath for 5hr. the precipitate was filtered and washed with hot distilled water to remove chloride ions. The filter paper containing the precipitate was deposited on a weighed small porcelain crucible and heated strongly on a hot plate until a white powder was left. A drop of concentrated HCl and a drop of concentrated H_2SO_4 were added and the crucible was reheated until a white powder was left. The crucible was cooled and weighed and the weight of barium sulphate determined by the equation.

Calculation of total Sulfur Content
Mass of $BaSO_4$ precipitated, mB (g) = (Mass of $BaSO_4$ in the sample – mass of $BaSO_4$ in the blank) Gravimetric factor of $BaSO_4$ = 0.137
Mass of sulphur in $BaSO_4$ precipitated (mS) = 0.137g × mass of MB Mass of sampled analyzed = 1.5g

$$\% \text{Sulphur} = \frac{ms}{1.5g} \times 100 = \frac{0.137 \times mB \times 100}{1.5g} \ldots 2.2$$

3. Results

Table 1: Functional Groups of Atmospheric Oil Residue by FTIR Method

Atmospheric Oil Residue	Characteristics frequencies	Bond
A	1650	C=C Stretching
	2850	C-H scissoring and bending
	2925	C-H stretching
A	2850	C-H Scissoring and bending
	2925	C-H Stretching
A	1650	C=C Stretching
	2850	C-H scissoring and bending
	2925	C-H stretching
A	2850	C-H scissoring and bending
	2925	C-H stretching
A	2850	C-H scissoring and bending
	2925	C-H stretching

Table 2: Functional Group of Vacuum Oil Residue by FTIR Method

Vacuum Oil Residue	Characteristic Frequency	Bond
V	1650	C=C Stretching
	2850	C-H scissoring and bending
	2925	C-H stretching
V	1650	C=C Stretching
	2850	C-H scissoring and bending
	2925	C-H stretching

V	1650	C=C Stretching	
	2850	C-H scissoring and bending	
	2925	C-H stretching	
V	2850	C-H scissoring and bending	
	2925	C-H stretching	
V	2850	C-H scissoring and bending	
	2925	C-H stretching	
	3600	O-H Stretch H-bonded	

Table 3: Physicochemical Analysis of Atmospheric Residue

Samples	Total Nitrogen Content %	Total Sulfur Content %
A	0.99	1.16
A	0.86	0.36
A	0.99	0.86
A	1.12	1.09
A	1.03	0.77
Average	0.99	0.84

Table 4: Physico Chemical Analysis of Vacuum Residue

Samples	Total Nitrogen Content %	Total Sulfur Content %
V	1.03	0.68
V	0.99	0.25
V	0.95	0.14
V	1.95	0.59
V	0.99	0.84
Average	1.03	0.50

4. Discussion
Ftir analysis: The Results of FTIR Analysis as summarized in Table 3.1 and 3.2 for atmospheric residue and Vacuum residue samples. It was found that both residue showed the presence of C-H stretching of aliphatic alkanes at 2925 and 2850 cm-^{1},there was no visible peak representing the O-H and N-H vibrations while the carbonyl stretching of C=O was also not depicted. The very sharp and broad peak at 3600 cm-^{1} as observed in Sample of Vacuum residue is attributed to O-H stretching of alcohol which makes it distinct from other spectra. These spectra results agrees with many other studies on Nigerian crude oil Residue. The FTIR results reveals that atmospheric and vacuum residue sample contain both saturated and unsaturated classes of organic compound.

Physico-chemical analysis: Physico -Chemical Analysis gives information about the nature of products as well as the relative purity of the products.

Results of Physico chemical Analysis as summarized in Table 3.3 and 3.4. From the result, it was found that both residues fall above the range for sulphur expected in Nigerian Crude oils and Products, i.e. 0.05-0.30w/% as well the range of nitrogen normally reported for Nigerian Crude oil i.e. 0.1 to 0.7w%. The values for both nitrogen and sulfur content differs from previous studies reported by [1]. The difference May depend on the source, Process, conditions and final treatment of the petroleum products in the refining industry.

The nitrogenous and Sulfur compounds in petroleum are important impurities because they have deleterious effects on Quality of finished products and environment. They Poison cracking and reform catalysts during petroleum refining, causes instability of finished products, promote sediment and impart colour and odour. The combustion of liquid fuels containing Nitrogen compounds produces oxides of nitrogen which are potential health hazard [2].Therefore there is need for treatment of these residues (denitrogenation and desulfurization) before refining.

Conclussion
Infrared Spectra obtained for all the samples bear a good degree of resemblance to the results of earlier works with some minor differences, Moreover, there is need for treatment of the residues (denitrogenation and desulfurization) before refining.

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