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DEODORIZATION AND DEAROMATIZATION OF KEROSENE BY LIQUID EXTRACTION METHOD

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ABSTRACT

The odor in kerosene was removed by liquid extraction with concentrated sulphuric acid as the liquid solvent. Multistage, crosscurrent extraction process was used. The kerosene to sulphuric acid ratio and the number of liquid extraction stages required to completely remove the sulphur compounds causing the odor in kerosene were determined. Sulphur compounds determination was by the Nickel Reduction Method. The specific gravity, aromatic content, smoke point, flash point, mercaptan sulphur, initial and end boiling points and the k-factor of the kerosene were determined using standard procedures. Also the distribution of sulphur compounds in distillation fractions from raw and treated kerosene was studied.

It was found that the optimum kerosene to sulphuric acid ratio was 50:50% (v/v) based on total acid used while the number of liquid extraction stages required to completely remove the sulphur compounds causing the odor in kerosene was five. The material balance of the five-stage, crosscurrent extraction process was fully established. There were improvements in the properties of kerosene due to the removal of resinous, aromatic and asphaltic substances. It was proposed that deodorized kerosene with higher aromatic content could be produced by combining liquid extraction and distillation operations.

KEYWORDS: Kerosene, sulphuric acid, liquid extraction, deodorization, dearomatization.

INTRODUCTION

The odor in kerosene is caused by the presence of sulphur compounds. Extensive research has been carried out to identify the sulphur compounds in light refinery streams (Rall et al, 1962). Table 1 lists the types of sulphur compounds in crude oil and refinery streams. In addition, compounds such as hydrogen sulphide and mercaptans are acidic and corrosive and are highly undesirable in petroleum products. Acidic sulphur compounds are removed by chemical treatment during refining operations while non-acidic sulphur compounds are usually removed during refining operations by hydro treating processes (Hatch and Matar, 1981; Egorova, 2003; Internet #1). Also the presence of aromatics in kerosene is not desirable because they can cause unacceptable smoke points thus reducing the illuminating power of kerosene and increasing its char value (Graves and Brown, 1975).

Liquid extractions have been used to remove odour compounds and aromatics from kerosene. The removal of odour compounds from kerosene is termed deodorization and the removal of aromatics from kerosene is termed dearomatization. The currently available processes for liquid extraction of sulphur compounds and aromatics in kerosene are extractions using liquid sulphur dioxide, furfural, phenol and concentrated sulphuric acid (Mark et al, 1963). The choice of a particular solvent for the extraction depends on a number of factors. These include economic factors such as fixed capital cost, energy and maintenance costs and the recovery efficiency desired. The use of sulphuric acid has an edge over the other methods because of its low cost, availability and versatility (Nelson, 1978). A major problem associated with sulphuric acid treatment of kerosene is the handling of sulphuric acid sludge. Myers and Stegemayer (1954) pointed out that by-products such as resins, coke, drying oil, aluminium sulphate, hydrochloric acid and sulphuric acid for fertilizer production can be obtained from the sulphuric acid sludge. If by-product recovery is not desired the sludge is neutralized with lime, sodium carbonate or spent alkali solution before discharging into the sewers (Oliver, 1960).

Deodorized and dearomatized kerosene is used as an aviation fuel and as a solvent for insecticides, printing ink, paints and dry-cleaning purposes. There had been occasions in Nigeria when the petroleum refineries were down and not producing deodorized and dearomatized kerosene. On such occasions some insecticide spray manufacturers had used partially deodorized kerosene to produce insecticide spray which left the rooms and dresses in the wardrobes smelling kerosene after the use of the insecticide spray. It was such practices that provided the motivation for this study. The need was felt to embark on process development studies that will lead to the development of small-scale liquid extraction plant for the production of deodorized and dearomatized kerosene, using concentrated sulphuric acid as solvent. Sulphuric acid is again being manufactured in the country. Thus, it will be possible to have several small-scale plants in the country producing deodorized kerosene rather than just relying on the refineries alone. This is one example of the many possible downstream, small-scale, chemical plants from the petroleum refining industry.

In this study, the sulphur compounds causing the odor in kerosene were removed by liquid extraction with concentrated sulphuric acid as the solvent using multistage, crosscurrent extraction process. The kerosene to sulphuric acid ratio (based on total acid) and the number of liquid extraction stages required to completely remove the sulphur compounds in kerosene were determined. The sulphur compounds determination was by the Nickel Reduction Method. The raw and treated kerosene were characterized to determine the following properties: specific gravity, smoke point, flash point, mercaptan sulphur, aromatics content, initial and end boiling points and the k-factor (the characterization factor). Also the distribution of sulphur compounds in distillation fractions from the raw and treated kerosene was studied.

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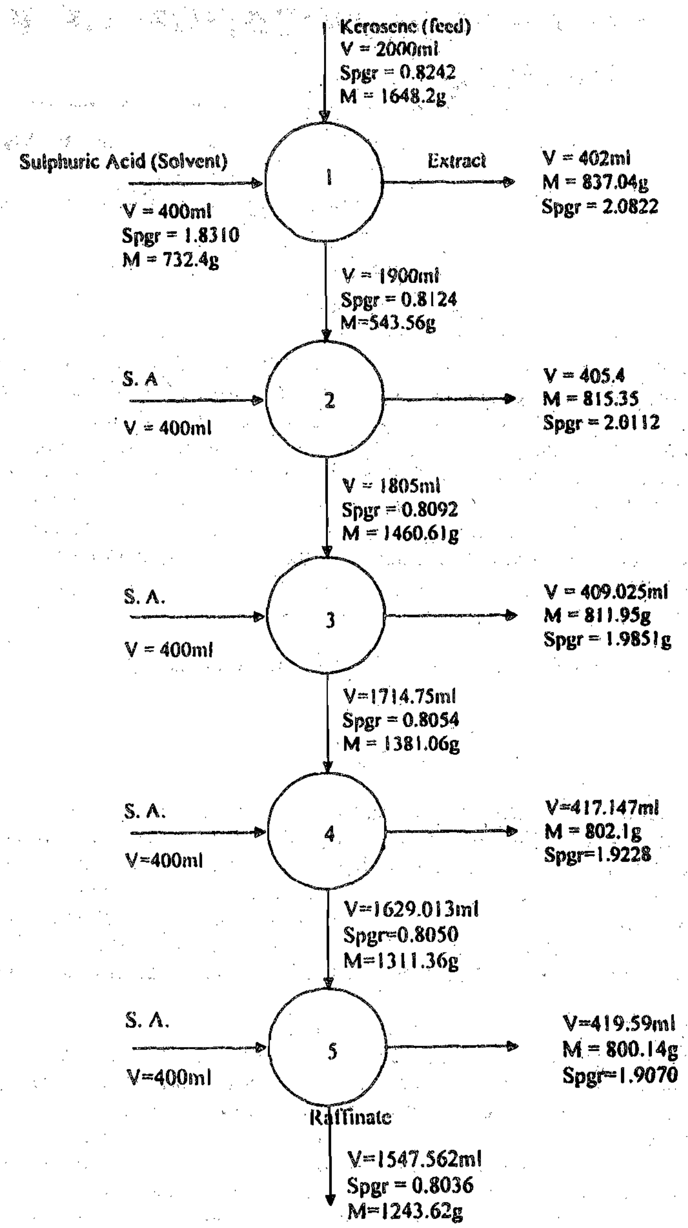


Fig. 1: Material Balance for the Stagewise Extraction of Impurities in Kerosene

MATERIALS AND METHODS

Materials

Kerosene: The kerosene was obtained from the Nigerian National Petroleum Corporation (NNPC) refinery, Port-Harcourt. The kerosene fraction was from Bonny Light Crude.

Sulphuric Acid: 98% concentrated sulphuric acid manufactured by BDH Laboratory Supplies was used.

Equipment

The equipment used for the stagewise extraction were: separating funnel, retort stand and clamp, beakers, funnel and filter paper (grade GF/A, size 110mm).

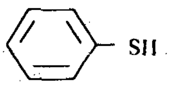
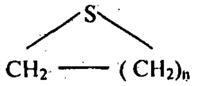
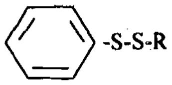
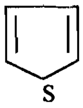
The equipment used for the characterization of kerosene were: the Nickel Reduction Method equipment for determining sulphur compounds; measuring cylinder, beaker and weighing balance for determining specific gravity; the Fluorescent Indicator Adsorption (FIA) instrument for determining aromatic content; the Smoke Point equipment for determining smoke point; the Tag Closed Tester equipment for determining flash point; the Potentiometric Method equipment for determining mercaptan sulphur; and the Distillation apparatus for determining Initial Boiling Point (IBP), End Boiling Point (EBP) and collecting distillation fractions at different percentage distillation.

Methods

1. Variation of kerosene to sulphuric acid ratio in single stage extraction.

The kerosene to sulphuric acid ratio in single stage extraction was varied as follows: 100:0, 90:10, 80:20, 70:30, 50:50, 40:60 and 30:70% (v/v). For each ratio, the aromatics and specific gravity of the raw or treated kerosene were determined. Experiments were carried out in duplicates. The optimum ratio was determined and used in the development of the stagewise extraction.

Table 1: Types of Sulphur Compounds in Petroleum and its Distillates

Type	Formula	Occurrence
Hydrogen sulfide	H_2S	*, **, ***
Mercaptans		
Aliphatic	R -SH	*, **, ***
Aromatic		***
Sulphides		
Aliphatic	R - S - R	**, ***
Cyclic		**, ***
Disulphides		
Aliphatic	R - S - S - R	**
Aromatic		***
Polysulphides	$R\text{-}S_n\text{-}R$	**, ***
Thiophene ad homologs		***

Occurrence: * – In crude oil, ** - In Straight Run Products, *** – In Cracked Products

Source: Hatch and Matar (1981)

2. Variation of number of stages in multistage extraction.

Using the optimum kerosene to sulphuric acid ratio, the number of liquid extraction stages required to completely remove the sulphur compounds causing the odor in the kerosene was determined by trial and error method. The multistage, crosscurrent extraction process was used. The acid used for each stage was calculated as follows:

$$\text{Acid required for each stage} = \frac{\text{Acid specified at the optimum kerosene to sulphuric acid ratio}}{\text{Number of stages}} \quad \ldots\ldots\ldots (1)$$

2000mls of kerosene (feed) was mixed with sulphuric acid (solvent) calculated from equation (1), in a separating funnel. The mixture was shaken for about 10 minutes and allowed to settle for 5 minutes in order to separate into layers. The acid sludge (the extract layer) settled at the bottom of the funnel while the treated kerosene (the raffinate layer) was on top. The designation of streams as feed, solvent, extract and raffinate was done using the conventional practice in literature (Treybal, 1981). The sludge was removed and the kerosene layer washed several times with 150ml of distilled water to remove the remaining acid in it. At the end of each wash, the pH of the wash water was tested to check if it was acid free. The water in the kerosene was separated by filtration using filter paper and conical funnel. The kerosene passed through the filter paper to the receiving beaker while the water was trapped in the filter paper in the conical funnel. The extraction was carried out for 2, 3, 4 and 5 stages until the sulphur compounds in the final product were removed. The volumes of the batch streams in and out of each stage were measured. The specific gravity of the kerosene feed and kerosene raffinate layer were measured.

3 Characterization of the raw and treated kerosene

The official methods of analysis (ASTM, 1960) were used for the determination of sulphur compounds, specific gravity, aromatics content, smoke point, flash point, mercaptan sulphur, and distillation ranges. Experiments were carried out in duplicates.

(i) Sulphur content by the Nickel Reduction Method

The kerosene sample was reacted with activated Raney Nickel to convert organically-bound sulphur to nickel sulphide. Hydrochloric acid was then added to liberate the sulphur as hydrogen sulphide. The hydrogen sulphide was absorbed in a sodium hydroxide – acetone solution and titrated with standard mercuric acetate using dithizone as the indicator. The equations for the reactions are:

$$S + Ni \longrightarrow NiS \qquad (2.1)$$

$$NiS + HCl \longrightarrow NiCl + H_2S \qquad (2.2)$$

$$CH_3COOHg + HS \longrightarrow HgS + CH_3COOH \qquad (2.3)$$

The sulphur in ppm was calculated using the equation:

$$\text{Sulphur content, ppm} = \frac{A \times T}{W} \times 1000 \qquad (3)$$

where A is the net volume of mercuric acetate solution used in titration, ml; T is the titer of the mercuric acetate solution, mg/ml; and W is the weight of sample, g.

(ii) Specific gravity by weight per volume method.

50ml of the kerosene sample at 25°C was measured out and weighed. The specific gravity was calculated as follows:

$$\text{Specific gravity} = \frac{\text{weight of samples}}{\text{volume of sample}} \qquad (4)$$

(iii) Aromatic content by Florescent Indicator Adsorption (FIA)

Approximately 0.75ml of the kerosene sample was introduced into a special glass adsorption column packed with activated silica gel. A small layer of the silica gel contained a mixture of fluorescent dyes. When the entire sample has been adsorbed on the gel, alcohol was added to desorb the sample and force it down the column. The hydrocarbons were separated according to their adsorption affinities into aromatics, olefins and saturates. The fluorescent dyes were also separated selectively with the hydrocarbon types. The boundaries of the aromatics, olefins and saturates zones were visible under ultraviolet light. The volume percentage of each hydrocarbon type was calculated from the length of each zone in the column.

(iv) Smoke Point.

A piece of dried wick was soaked in the kerosene sample and placed in the wick tube of the Candle. 20ml of the kerosene sample was introduced into the clean, dry Candle. The wide tube was placed in the Candle and screwed. The wick was cut horizontally and trimmed free of frayed ends so that 6mm of the wick projects from the end of the Candle. The Candle was inserted into the Lamp and lighted. The wick was adjusted so that the flame was about 10mm high and the Lamp was allowed to burn for 5mins. The Candle was raised until a smoky tail appeared. The height of the flame was estimated.

Table 2: Variation of aromatic content and specific gravity with kerosene to sulphuric acid ratio

Kerosene, % (v)	Sulphuric acid, % (v)	Aromatic Content⁺,% (v/v)	Specific Gravity
100	0	18	0.8242
90	10	17	0.8230
80	20	16	0.8226
70	30	15	0.8220
50	50	13	0.8210
40	60	*	*
30	70	*	*

⁺Mean values were rounded to the nearest whole numbers

*Treatment gave dark coloured kerosene

Table 3: Characterization of Raw and Treated Kerosene

	Raw Kero-sene	Treated Kerosene				
		Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Sulphur content, ppm	205.36	9.90	6.98	4.89	1.08	Nil
Specific gravity	0.8242	0.8124	0.8092	0.8054	0.8050	0.8036
Aromatic content⁺, %	18	14	11	8	6	4
Smoke point⁺, mm	25	26	27	30	35	39
Flash point⁺, °C	46	47	49	50	52	53
Mercaptan sulphur, ppm	0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Distillation Range						
IBP, °C	148	154	157	159	160	161
EBP, °C	244	248	245	246	249	250
k-factor	11.59	11.75	11.80	11.86	11.87	11.90

⁺Mean values were rounded to the nearest whole numbers

(v) Flash Point

The Flash Point cup was cleaned with kerosene, distilled water and dried with acetone or by blowing air through it. The cup was filled with the sample to the marked point and then dipped into the depression in the liquid bath below. The cover was placed properly and the thermometer inserted. The test flame was lighted and adjusted below the expected flash point. The flame was directed into the cup at intervals of 1°C rise in temperature until the flash point was reached.

(vi) Mercaptan Sulphur by Potentiometric Method

1.6g of sodium acetate was dissolved in 20ml of oxygen free water. The solution was poured into 975ml of isopropyl alcohol of 99% concentration. 4.6ml of glacial acetic acid was added to the solution. The dissolved oxygen was removed by purging the solution with a rapid stream of nitrogen, for 10 minutes. The sample was then titrated potentiometrically with silver nitrate solution using as an indicator the potential between a glass reference electrode and a silver/silver sulphide indicating electrode. Under these conditions, the mercaptan sulphur was precipitated as silver mercaptide and the end point of the titration was shown by a change in cell potential.

(vii) Distillation range

100ml of the sample was measured into the distillation flask. Two to three balls of anti-bubble chips were dropped into the distillation flask for the purpose of preventing overshoot of the light fraction. The thermometer, condenser and receiver were put in place to complete the distillation apparatus. The receiver was maintained at 13-18°C to reduce the rate of evaporation. All conditions being ensured, the first drop of the distillate was observed and the temperature of the thermometer recorded as Initial Boiling Point (IBP). After 95ml recovery, the thermometer reading was recorded as the End Boiling Point (EBP).

(viii) Calculation of k-factor

The k-factor is given by the equation: $\text{k-factor} = T_B^{1/3} / \rho$ ....(5)

where T_B is the average boiling point of a sample in Rankine and ρ is the specific gravity. The average boiling point of a sample was obtained by taking the average of the temperatures at which the 10, 30, 50, 70 and 90 percent distillation occurred.

4. Distillation and sulphur content analysis of kerosene fractions

The raw kerosene and the kerosene products from the extraction stages were distilled and various distillation fractions collected from them. These fractions were analyzed to determine their sulphur contents.

RESULTS AND DISCUSSION

1. Determination of optimum kerosene to sulphuric acid ratio in single-stage extraction.

Table 2 shows the variation of aromatic content and specific gravity with kerosene to sulphuric acid ratio. The optimum ratio is the one with the least aromatic content and specific gravity. It was observed that the aromatics decreased as the amount of sulphuric acid used for the extraction increased. However, increasing the amount of acid to 60% (v/v) and above gave dark coloured kerosene which implied that the kerosene was being denatured. Hence, the optimum kerosene to sulphuric acid ratio was found to be 50:50% (v/v).

It was also observed in Table 2 that the specific gravity of kerosene decreased with increase in severity of acid treatment. The decrease was due to the removal of aromatic hydrocarbons and resinuous and asphaltic substances (Lee, 1927).

2. Determination of number of stages and material balance in multistage extraction

Multistage, crosscurrent extraction was used to assure that the kerosene was not denatured. Multistage operation also improves the efficiency of removal of impurities. The initial volume of kerosene used was 2000ml and the total volume of acid required was also 2000ml based on ratio 50:50% (v/v) of kerosene to sulphuric acid. The complete removal of sulphur compounds was used as an index for determining the number of stages required. The number of stages required was found to be 5. The volume of acid used for each stage of extraction was therefore calculated as 2000/5 = 400ml.

The material balance of the stagewise extraction is presented in Fig.1. The volume and specific gravity of kerosene feed and kerosene raffinate layer were experimentally determined. The specific gravity of 98% fuming sulphuric acid was taken from literature. The volume of fresh acid (solvent) and the acid extract layer were also experimentally determined. The mass of kerosene feed, fresh acid and kerosene raffinate layer were calculated using the experimentally determined volume and specific gravity data. The mass of the acid extract layer for each stage was found by difference. It was then possible to calculate the specific gravity of the acid extract layer from the mass and volume data.

3. Characterization of the raw and treated kerosene.

The results of the characterization of the raw and treated kerosene from stage 1 to 5 are shown in Table 3.

There was a decrease in sulphur content from the initial value in the kerosene feed to zero in the final kerosene product from stage 5. As was stated earlier, the sulphur content was used to determine the required number of stages for the liquid extraction. Liquid extraction of kerosene with sulphuric acid completely removed all sulphur compounds detectable by the Nickel Reduction Method. The odor in kerosene from stage 5 was completely removed showing that the odor was caused by the presence of sulphur compounds.

There was a decrease in the specific gravity and aromatic content from the raw stage to stage 5 due to the removal of resinous, aromatic and asphaltic substances (Lee, 1927).

The smoke point and flash point increased from the initial kerosene feed to the final kerosene raffinate layer because of the improvement in the extent of the refinement.

Table 4: Distillation of kerosene samples and sulphur content analysis of fractions

Stage	% Distillation	Temperature, °C	Sulphur content, ppm
Raw Kerosene	30	201	125.00
	50	215	190.00
	70	222	136.36
	90	235	155.24
	EBP	244	125.00
Stage 1	30	202	6.3500
	50	213	4.2300
	70	221	0.2300
	90	232	0.0750
	EBP	248	0.0187
Stage 2	30	201	4.5100
	50	213	0.4500
	70	222	0.1130
	90	232	0.0280
	EBP	245	0.0125
Stage 3	30	202	0.9500
	50	214	0.2250
	70	221	0.0560
	90	233	0.0140
	EBP	246	0.0083
Stage 4	30	203	0.4500
	50	215	0.1125
	70	222	0.0280
	90	234	0.0120
	EBP	249	0.0040
Stage 5	30	203	Nil
	50	215	Nil
	70	223	Nil
	90	234	Nil
	EBP	250	Nil

Mercaptan sulphur was present in kerosene feed in trace amounts and it was reduced further by sulphuric acid treatment. The amount of mercaptan sulphur in the treated kerosene was low and perhaps did not contribute much to the odor.

There was an initial marked increment in the Initial Boiling Point (IBP) before it leveled off to a nearly constant value. This was due to the removal of most of the impurities from the kerosene sample.

The k-factor, which is also called the characterization factor, increased from the first stage extraction to the final kerosene product from stage 5. This was due to the improvement in the quality of the product from stages 1 to 5.

4. Distillation and sulphur content analysis of fractions

The sulphur content analysis of the distillation fractions of raw and treated kerosene from stage 1 to 5 are shown in Table 4. It was observed that the sulphur compounds were high and well distributed within the whole boiling point range in the raw kerosene. Also it was observed that in the treated kerosene from stage 1 to 4, the sulphur compounds were appreciably reduced and occurred mainly in the lower boiling fractions. This threw some light about the possibility of combining liquid extraction with distillation to produce kerosene of acceptable standard for some industrial applications like paints and printing inks. That is, instead of a five stage extraction one could use a two or three stage extraction followed by distillation in which only 30% of the feed is distilled off (carrying away most of the odor compounds) and the remaining undistilled 70% taken as the deodorized kerosene. The product from this process, though not completely deodorized, will certainly have a greater solvent potency than the product from the five stage extraction process. This is because the aromatic content will be higher and aromatics aid solvent potency.

CONCLUSIONS

The odor in kerosene was completely removed by liquid extraction with concentrated sulphuric acid as solvent using five-stage extraction process. The kerosene to sulphuric acid ratio (based on total acid) was found to be 50:50% (v/v). The material balance for the five-stage extraction process was established and this provides important process design and operating data. There were improvements in the properties of the treated kerosene due to the removal of sulphur compounds; resinuous, aromatic and asphaltic substances. Also the distribution of sulphur compounds in the distillation fractions of raw and treated kerosene samples showed that it could be possible to produce deodorized kerosene with higher aromatic content and solvent potency for paints and ink manufacturers by combining liquid extraction and distillation operations.

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