# KEROSENE DESULPHURIZATION BY ACID TREATMENT

*BY*

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### M.ENG/SEET/2003/1022

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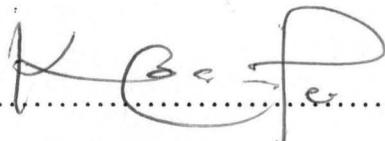form for another degree nor diploma at any University or any institution.

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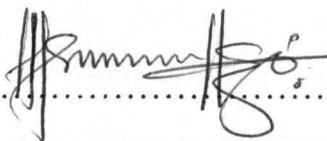
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# CERTIFICATION

This thesis titled, **KEROSENE DESULPHURIZATION BY ACID TREATMENT** by **Ndagana, Gimba Mohammed** (M.Eng/SEET/2003/1022) meets the regulations governing the award of the degree of M.Eng of the Federal University of Technology, Minna and is approved for its contribution to scientific knowledge and literary presentation.

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# DEDICATION

I sincerely dedicate this research work to Almighty God for his guidance, protection and grace upon my life from the very beginning to the end of this programme.

I equally dedicated the research work to my wonderful parents Alh. Zubairu K. Mohammad and Hajiya Hassana Zubairu, my beloved wives (Fatima and Amina Gimba), twin partner, brothers, sisters and the rest family members, May God Almighty bless them and see them through in what so ever good they are doing, Amen.

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I sincerely have to honour the unremitting effort of my parents Alhaji Zubairu and Hajiya Hassana for their motivation, moral support and financial support, which brought me to this cadre today. By God's grace they shall live and reap the fruit of your labour on me.

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# ABSTRACT

This work used Chemical Engineering Unit Operations and processes to carry out desulphurization of kerosene using different concentrations of tetraoxosulphate (VI) acid (75, 80, 85, 90 and 95 percent) at various contacting times of 10, 20, 30, 40, and 50 minutes. The amount of Sulphur removal was determined for each concentrated acid with time using Sulphur in oil Analyzer. The result shows that the highest amount of total sulphur content removal was achieved with 95 percent of tetraoxosulphate (VI) acid at the best contacting time of 30 minutes.

Characteristics of treated kerosene like flash point, smoke point, specific gravity and colour of some treated samples were determined to check the consistency of treated kerosene grade.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| ASTM | American standard for testing and measurement |
| bbl | Barrel |
| Ib | pounds |
| IP | Institute of Petroleum |
| $^0$f | Degree Farhenheight |
| $^0$C | Degree Centigrade |
| g | Grammes |
| mm | Millimeter |
| w | Weight of sample |
| % | Percent |
| wt% | Weight percent |
| Mg/kg | Milligramme per kilogram |

| | |
|---|---|
| ADU | Atmospheric Distillation Unit |
| IBP | Initial boiling point |
| ML | Millilitre |
| Kg/cm2 | Kilogramme per Cubic Centimeter. |
| DMF | Dimethyl Formamide |
| DMSO | Dimethyl Sulforide |
| D | Drum |
| IS | International Standard |
| ISO | International Standardization Organization |
| BP | Boiling point |
| MEA | Methyl ethyl amine |
| DEA | Diethyl Amine |

# CHAPTER ONE

## 1.0    INTRODUCTION

This section deals with a brief background leading to the choice of the project topic.

## 1.1    Background of Study

Kerosene is a crude oil fraction distilled between $150^0$C and $280^0$C. Kerosene was the major refinery product before the automobile was invented, is now used for illuminating and heating purposes. Kerosene consist of paraffin, naphthalene and aromatic. The presence of aromatic compound in Kerosene is responsible for the odour and mostly the poor combustion which has often prevent against its uses. It must be free of aromatic and unsaturated hydrocarbons and sulphur compounds because they burn with a smoky flame and cause incrustation of the wick. The desirable constituents of Kerosene are saturated hydrocarbons. Therefore, cracking processes are not adopted for manufacturing kerosene; it is prepared from straight run distillates. The same applies to other illuminating oils, such as mineral seal oil and railroad long-time burning oil, which are higher quality products than those intended for general illuminating and heating purposes.

Kerosene has been associated with smokiness and sootiness that blackens cooking utensils, heating appliances and heat exchanger. This sootiness also prevent heat transfer and reduces the heating efficiency due to the soot that has been deposited on the components. Smokiness associated with kerosene is due to the aromatic compounds present and has led to eyesight problems in rural areas where its

consumption rate are high, and the dwelling place is poorly ventilated (Onuoha, et al 2002). Some crude oils, like those from the Pennsylvanian oil fields, contain kerosene fractions of excellent quality. Other crudes of conventional California and asphalt-base type must be thoroughly refined to remove aromatic hydrocarbons and sulphur compounds. In the past the kerosene fraction from such crude oils was treated with huge quantities of fuming sulfuric acid to convert it into a marketable product. This resulted in high reagent and oil losses and was often economically prohibitive.

During recent years, the field of use for kerosene has grown more and more. Nowadays, it is used for burners, heaters and stoves with highly effective result.

The general applications of kerosene are the following:

i)      Domestic applications: Lamps, Heaters, Stoves.

ii)     Fuel for agricultural tractors (Horticultural sprays)

iii)    Fuel for aviation; for Jet engines and turbines.

iv)     Special applications in the petrochemical industry; solvent for paints, thinners, varnishes.

The properties of kerosene vary according to market requirements, the type of crude and chemical or physical treatment the crude undergoes. The kerosene used in agricultural tractor motors do not have the same properties as those used in illumination and aircraft engines.

The fuel specifications for jet engines and fuels for turbine engines make it possible to classify kerosene in three groups:

i)    Gasoline type jet engines;

ii)   Kerosene type fuels;

iii)  Fuels with a high ignition point for aircraft engines.

The chemical composition of kerosene depends on the basic crude oil and the different processes used to refine it. Generally, the standard methods used do not alter the paraffin /naphtha ratio and the direct distillation products contain practically no unsaturated hydrocarbons.

Kerosene also contains other products besides hydrocarbons: These are sulphuric and nitrogeneous compounds as well as oxygenated products.

Sulphuric compounds in kerosene distillates may contain from 0.05 to 0.3% of sulphur under the form of different organic compounds. Some of the compounds are produced during distillation at a high boiling point starting from sulphuric compounds present in the basic crude. Sulphuric compounds are mercaptans, sulphides, bisulphides and thiophenes.

The content of nitrogeneous compounds in most crudes is low. Basic and not basic compounds can be found in distillates. The presence of nitrogenous compounds in kerosene is of importance from the colour stability point of view.

Oxygenated compounds in kerosene distillates may contain compounds of the acid type such as phenols. In the same way, phenolic compounds are very important from the colour stability point of view.

The characteristics odour of kerosene are caused by odour producing agents which include: sulphur, sulphides, polysulfides, mercaptan, thiophene etc.

Mercaptans and disulphides are found in the gasoline fraction of some crude, but their concentration in higher boiling distillates are normally negligible because a gasoline would be unsuitable for use if it can corrode the metallic part of the fuel system of the engine, it must be substantially free from corrosive compounds both before and after combustion. Corrosiveness is usually due to the presence of free sulphur and sulphur compounds which burns to form sulphurdioxide, this combine with water vapour formed by the combustion of the fuel to produce sulforous acid which may oxidize to a slight extent to sulphuric acid. Both acids are corrosive towards iron and steel. And would attack the cooler parts of the engine exhaust system and its cylinder as they cool off after the engine is shut down.

Hydrogen sulfide and mercaptan sulphur are most undesirable contaminants because apart from their corrosive nature, they possess an extremely unpleasant odour.

It is therefore essential that before kerosene is put to those aforementioned uses, the sulphur and mercaptan contents have to be removed or reduced to an acceptable level of which could no longer given unwanted odour or affect the process of combustion where necessary. (Ebewele, 1995)

Much have been written about mercaptan and total sulphur removal from kerosene with the use of different routes, modes of operation, and operating conditions, (Walker and Kenny (1956), Yabroit and Bodor (1930), O'Donnel and Jan. P. (1944), Sierra A. V. (1953), Deleany et al (1949), Happel, Genly and Kelly (1942), to mention only a few).

The choice of concentrated tetraoxosulphate (VI) acid for the treating process have the advantage of reducing the sulphur content of the kerosene. concentrated tetraoxosulphate (VI) acid would be employed in this process because it is the most generally applied among the chemical refining agents. It is also cheap, it's action can be controlled by varying its concentration, temperature and time (Nelson, 1958)

## 1.2   Aim and Objectives of Study

The overall aim is to verify the effectiveness of concentrated tetraoxosulphate (VI) acid in the desulphurization of Kerosene using different concentrations and times.

The objectives are;

1.   To determine total sulphur content of kerosene using sulphur in oil analyzer.

2.   To develop process flow diagram which depicts chemical engineering unit operation and processes (reactions) for the desulphurization of kerosene using concentrated tetraoxosulphate (VI) acid.

3   To find the effect of concentration and time on the sulphur removal from kerosene.

4   To find out which concentration and time has the best efficiency in terms of sulphur removal.

5   To determine the properties of treated kerosene.

## 1.3    Relevance of Study

The relevance of this study is to establish that before kerosene can be put into those aformentioned uses, the sulphur containing compound constituents have to be removed or reduced to an acceptable level of which could no longer give unwanted odour or affect the process of combustion where necessary.

# CHAPTER TWO

## 2.0 LITERATURE SURVEY

This section deals with a brief historical development leading to the choice of the project topic.

## 2.1 Historical Development of Kerosene

In the early days of petroleum Industries, natural petroleum was broken into three major fractions, viz; low boiling (inflammable gasoline), less inflammable (kerosene) and residue (high boiling). The main use then was for lighting and heating without any additional purification. Later batch still was invented for distillation of petroleum and illuminating kerosene was the only target produce. The light gasoline fraction and also the main part of the heavy residue were burned because no use was found for them (Ebewele, 1995).

The kerosene fraction obtained was found to possess obnoxious odour and produce smoking flames due to the presence of certain impurities present. The removal of small amount of impurities by treatment with sulphuric acid, caustic soda, etc has been and continues to be practiced (Nelson, 1958).

Kerosene was formerly known as coal oil because a similar product was being distilled from coal. It was revealed that kerosene was first processed by researchers in Europe and North America. They learned how to extract it from coal tar shale. But in 1859, the first successful petroleum well was drilled in the United State of America. This resulted in large scale petroleum production and provided an abundant source of kerosene (John, 1959).

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The average composition of kerosene is 85 percent of carbon, 15 percent of hydrogen, with traces of non-hydrogen compounds such as nitrogen, oxygen and sulphur compounds.(Adeniran, 2000)

In 1945, another major used was discovered which is the use of kerosene as a jet engine fuel. Due to its properties kerosene is used in jet fighters, cargo planes, aeoplanes, etc. This type of kerosene is referred to as Aviation Turbine Kerosene (ATK). Its analysis are of various types and must meet the specification required such as Electrical Conductivity, Flash point, water separation index, specific gravity, API gravity were tested which are carried out on to actually get the specific product needed. (Adeniran, 2000)

Later in the 1970s, when oil lighting was replaced by electric lightening, kerosene was then principally used as a domestic heating fuel and for solvent applications. When it is used as a domestic heating fuel, the type of kerosene is known as the house hold kerosene (HHK) and is used for cooking, fuel in heaters and also in lanterns for lighting. It is also very important in the lives of the rural dwellers in the developing countries. In the sense that it is mainly used as a means of cooking fuel and used for lighting in case of disruption in the supply of electric power.

Another use of kerosene is the use of the product as a solvent. Thick solution or compounds can be dissolved by the addition of kerosene to it so as to make of a fluid for easy usage which has been extensively used as petroleum spray oil in herbicides, insecticides and fungicides.

As earlier said, kerosene is drawn off as one of the side streams in a distillation column. The fraction contains mainly three types of hydrocarbon, VIZ: paraffins, naphthalenes and aromatics. It may also contain small quantities of olefins, if cracking occurred in the furnaces. Also contaminants are present in the kerosenes obtained such as sulphur water, oxygens, mercaptans etc. This type of kerosene is referred to as Straight Run Kerosene (SRK).

The kerosene obtained is later purified with some purification processes such as Hydrotreatment introducing hydrogen into the feed going into the reactor in the presence of a catalyst and MEROX sweetening removal or dissolving of sulphur containing compound to make them inactive in the kerosene.(Adeniran,2000)

After the hydrotreatment and the merox sweetening processes, we have obtained what is known as hydrotreated kerosene which is carried out in the kerosene hydrotreating unit (KHU) in the refinery. The kerosene is then stored and it is disposed for various uses. The adulteration of the product can then be assessed by carrying out analysis on the product being produced. Stage by stage samples are taken to see whether the product meets the standard specifications.

## 2.2    Tests and Properties of Kerosene.

The properties which are cordially judged for kerosene of all grades by refineries and government agencies are shown in Table 2.1 (enterprises,2006).

### 2.2.1. Flash point.

This is defined as the minimum temperature at which the vapours from oil sample will give a momentary flash on application of a standard flame under specific

**Table 2.1: Standard Physical Literature Value of Kerosene.**

| S/N | PROPERTY | LIMIT | UNIT |
|---|---|---|---|
| 1 | Specific gravity at room temp | 0.825 max | Kg/1 |
| 2 | Smoke point | 22 min | Mm |
| 3 | Colour (Saybolt | 20 min | - |
| 4 | Flash point | 115 min | $^{0}$F |
| 5 | Total sulphur | 0.15 max | % wt |
| 6 | Copper Corrosion (3hr at 50$^{0}$C) | No. 1 strip max | - |
| 7 | Odour | Marketable | - |
| 8 | Char value | 15 max | mg/kg |
| 9 | Distillation recovered at 200$^{0}$C | 20 min | % VOL |

test conditions. Abel (P:21; IP 170 /59) Pensky-Martens (P:21; IP 34/58) Cleveland are the test apparatuses frequently used for the purpose. Significance of the flash point is that it can predict the possible fire hazards during transportation, storage and handling. Early tendencies were to incorporate more volatiles in kerosenes, thus inviting unusual fire hazards. This necessitated a strict vigilance by way of fixing flash point. The flash point of marketable kerosene should be above $42^{0}$C and is determined by Pensky – Martens Apparatus (P:21; 1P 34/58) and Test.

Pensky – Martens Apparatus consists of a cylindrical cup made of brass of approximate dimensions $50.8\pm1.27$mm X $55.88\pm1.27$mm (height inside) with a

thickness at the bottom 2.41±0.64mm. Inside the cup at two – third rds heights from the bottom, there is a sudden and slight tapering up to the top of the cup. This looks like a ring and guides as a filling level for the sample. The top position acts as a vapour – air chamber.

The cup is provided with acid, and the lid is actually made of two metal discs, sliding over the other. The lid also includes (a) stirring device (b) two flame holders, one test flame and other pilot flame (c) provision for thermometer (d) spring handle. By turning the spring handle, it is possible to slide one lid over the other whereby the exactly cut chords align with each other, exposing air – vapour mix of the cup to flame. Infact, there are three chord openings, central one is meant for flame introduction, while the other two act as air introducers. When the handle is turned test flame is also simultaneously lowered into the central chord opening to explode air – vapour mixture. The test flame is issued from an opening of 0.69mm diameter. The whole cup is heated by air-bath, which is primarily heated by electric power.

The test sample is filled up to the mark, and the temperature of the oil is slowly and uniformly raised at a rate of $3^0C$ per minute. Test and pilot flames are lighted. Occasional stirring is done. The spring handle is rotated at every $1^0C$ rise in temperature; till a bluish light flash is noticed . Heating should be maintained at the prescribed rate.

Abel flame meter is used for highly volatile samples, whose flash point shall be less than $40^0c$. Pensky – Martens closed cup can be used for medium flash liquids, when a high flash point liquid is to be tested open cup flash meter is convenient.

Flash point is essentially dependent upon the light end characteristics of a fuel. Approximate relationship between flash point and IBP – 10% boiling range is given by (Nelson, 1958) as Flash Point $= 0.64T^0C - 61.95$.

Flash point is regarded as vapour property hence the ambient pressure directly influences the flash point. Thus one is reminded to note the ambient pressure before such a test is conducted. Correction for pressure may be accorded by applying the following relation:

Flash point $T^0C =$ Flash point $(t^0C) + \dfrac{760 - p}{30}$ at 760mmHg observed at PmmHg

Where P is the pressure in millimeters at the time of observation.

**Flash point at $T^OC$** = Corrected flash point.

**Flash point at $t^oC$** = Observed flash point.

760 = Constant term in MMHg.

**2.2.2 Fire point** This closely follows the flash point. The test is carried out in open cup rather than a closed one. Cleveland apparatus (ASTM D 92) offers the advantage of open flash point and fire point. Fire point temperature is noted when the oil vapours can burn continuously for 5 seconds when tested in flash point apparatus and it occurs after the flash point, by $3 - 4^0C$. For domestic needs a very high flash point above $50^0C$ is also not desirable. The easy ignition is credited to volatiles only and decreased in volatiles enhances the flash point causing difficult in ignition.(Bhaskara,1984)

### 2.2.3 Smoke point

It is an indication of clean burning quality of kerosene. Illumination depends upon the flame dimension although it is not related to flame height. Many paraffins may be gifted with better flame heights but illumination may be poor.

Smoke point is defined as the maximum height of flame in millimeters at which the given oil will burn without giving smoke. Thus smoke point test enables the burning quality to be measured by adjusting the wick height to give proper non-Smokey flame. Illumination is supposed to be characteristic of the components of fuel usually not measured. Different flame heights are obtained due to the presence of different components such as obtained due to the presence of different components such as paraffins, naphthenes and aromatics.

Aromatics contribute smoke, hence removal of aromatics increase smoke point. Smoke point may be predicted approximately by knowing the group composition of oil given as smoke point = 0.48p + 0.32N + 0.20A where P,N,A are % paraffins, maphthenes aromatics in the sample. A dogma of high point meant a better quality fuel is not always acceptable as it can not specify any illumination characteristics. In recent literature stress is given to this luminosity number (ASTM D 1740) and prescribed as a test for kerosene. This indicates luminosity of the flame and accompanying radiation problems in combustion chambers. Smoke point apparatus with modifications to include a photo electric cell can measure the flame radiations. Luminosity number is expressed just like octane number. The constituents taken here are tetralin (O luminosity number) and iso octane (100

luminosity number). The blend of these two should match with the luminosity of fuel(Bahaskara,1984).

## 2.2.4 Burning quality test.

This indicates the ability of kerosene to burn steadily and clearly over a long period. Kerosene is tested by burning in a standard wick lamp for a period of 24 hours, in a room free from air currents. The average rate of burning, change in shape of flame, the density of chimney deposits are the prime factors by which the quality of kerosene is assessed. A good quality kerosene (after burning for 16 hours) should present the chimney as clean as possible (only slightly clouded) and the wick should not have any appreciable hard incrustations with as large flames as in the beginning (Allinson, 1973).

The continuity of the initial illumination over long periods in a lamp rests on the normal flow of kerosene to the wick end. Quantity of oil available at the tip of wick depends on the height of wick over liquid surface, texture of wick and properties like viscosity and surface tension of oil. Even though surface tension of different oils (kerosenes) may not vary much, viscosity varies. Stabilization of flame is governed by viscosity. A good oil of 650 c.c. must burn at least for 120 hours(Bahaskara,1984)

## 2.2.5  Sulfur content

High sulfur content is inimical due to its combustion products when large amounts of such fuel is burnt, accumulation of these oxides results, offering wayward problems of corrosion and pollution. Total sulfur can be estimated by Bomb method.

Maximum permissible amount of sulfur is 0.13%; in all kerosene(John and Sons,1993)

## 2.2.6 Aniline point.

This test indicates qualitatively the amount of aromatics present in kerosene. Aromatics of this boiling range present in the fuel cause abnormal ignition delay. For this reason an estimation of aromatics is essential. One such method is aniline point which, can predict the suitability of oil. Aniline point is defined as the minimum temperature at which equal volumes of anhydrous aniline and oil mix together.

Aniline being an aromatic compound freely mixes with aromatics; so a low aniline point indicates, low kerosene index (because of high percentage of aromatics) (Bhaskara,1990)

## 2.2.7  Volatility

The nature of distillation range estimated is of significance with regard to burning characteristics. It can control the flash point and viscosity.  Ten percent boiling point reveals the flash point which in turn, indicates the ease of ignition; specially when kerosene is used in pump stoves; this plays a very important role in continuous support of flame.  Mid boiling range contributes towards viscosity. Often flare up in oil heaters is observed if mid-boiling range is not properly constituted. Sixty percent distillation at $200^0$C ensures steady performance of oil in heaters. Minimum of 15% distillation at this temperature is enforced to guarantee adequate volatility (Allison, 1973).

### 2.2.8 Flammability

For safety reasons' mainly in view of the fire danger which is incurred in the use of oils of low flash point in lamps, the law demands that the flash point of kerosene marketed in the United Kingdom (U.K) should not be below $75^0F$ ($25^0C$) as determine by the ASEL instrument.(Pery and Chiton, 1992).

### 2.2.9 Colour

This property has little significant in indicating performance quality, but it is included in most specifications for the consumer information and it is desirable to producers of kerosene of uniform colour. The colour of an oil serves as an indication of the throughness of the running process. Colour is determined by ASTM D116 (Nelson, 1958) . It is measured in Saybolts. Standard specification of kerosene is between 16 to 25 Saybolt number which correspond to prime white to water white on the Saybolt chrome (John, 1959).

### 2.2.10 Calorific value

This is the quantity of heat released by a quantity of kerosene. It is burned completely with oxygen and the products of combustion returned to ambient temperature. The heating value of any fuel, or sources of energy is the amount of useful heat which can be extracted from it. This knowledge of the calorific value of the fuel and the efficiency of the heating equipment are essential to compare the merits and running cost of different fuels and energy sources (Barnett and Shipman, 1984).

A high calorific valve is obviously desirable in an oil used for heating purposes. Calorific value does not, however, vary greatly in one range of paraffinic type kerosene, but acid treatment improves this by reducing the sulphur and aromatic content of the oil. It may be determined by 1P 12 or ASTM D24 (Britain, 1975)

## 2.2.11 Specific gravity (Relative density)

Specific gravity is the ratio of the mass of a given volume of liquid at a specified temperature to the mass of an equal volume of pure water at the same or different temperature. Both reference temperatures shall be explicitly stated.

Specific gravity has no relation to burning quality, but serve as useful aid in checking consistency of production of a particular grade. The specific gravity of a kerosene changes slightly on acid treatment and reduces with the extent of sulphur and aromatic removal. It may be determined by the hydrometer method ASTM D1298 -1D160 (Britain, 1975).

## 2.2.12 Pour point

This is the lowest temperature at which kerosene flows when it is chilled without disturbance under specified condition (Adeniran, 2000).

The criteria of pour point fixation depends upon two factors namely climatic conditions and storage (handling). Fuel, at minimum ambient temperature must be free flowing. In India, pour point is fixed at $5^0C$ however in the Himalayan belt, where the climate persists at sub – zero level, this may not be satisfactory; hence low pour point oils are essential. It is also observed that at close approach of pour point

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(within 2 to $3^0C$), the viscosity increases very much, the result of which is high pumping costs.

## 2.2.13 Viscosity

It is the internal resistance of a fluid to flow. It is regarded as internal friction in the liquid and is attributed to the liquid particles. The higher the viscosity of a liquid, the lower its mobility of fluidity. The viscosity of a liquid petroleum product is influenced by the presence of resinous substances(Adeniran,2000).

## 2.3 Types of Kerosene

Generally, we have three broad types of kerosene viz:

i)      Domestic kerosene

ii)     Aviation turbine kerosene (ATK)

iii)    Dual purpose kerosene

## 2.3.1 Domestic kerosene

This kerosene popularly known as household kerosene (HHK) became the most major petroleum products and widely used initially for illumination and subsequently for heating. While modern technology has diminished its importance of kerosene, it is being utilized as a primary source of light in less developed countries and for stand by on emergency lighting in the more advanced areas of the world; because it is cheap, durable and flexible. It is also used for refrigeration and cooking.(Adesola, 2003)

## 2.3.2 Aviation turbine kerosene

This type of kerosene is a modified development of the illumination kerosene originally used in gas turbine engines. They are mainly produced by straight distillation of petroleum and used in air-craft flying at supersonic speed. Supersonic aircraft in the future will require large quantities of optional quality fuel that can be obtained all over the world even at great distances from refineries.

The various grade of fuel differ in their fractional composition and the overall marcaptan sulphur content. The freezing point for most ATK must not exceed $-60^0C$. The amount of aromatics are also limited because they do not burn as clean as other type. High aromatic content can cause smokiness and carbon deposition in the engines. They also degrade elastomers in the fuel system and increases the luminosity of the combustion flame which can adversely affect the life of certain design combustion chamber (Adeniran, 2000).

### 2.3..2.1. Aviation fuel properties

The main properties of fuel used by jet and turbine engines are the following:

### Volatility

Jet aircraft fly at a very high altitude (10,000 to 30,000 feet) where the resistance to the air is less and the overall performance of the aircraft is higher. When the altitude increases, the atmospheric pressure diminishes.The evaporation temperature also decreases. The evaporation temperature favors the occurrence of dangerous phenomena such as the formation of bubbles of vapour in the engine

supply circuit and the loss of fuel under the form of vapour through the respiration pipes.

The formation of bubbles of vapour is extremely dangerous as they may lead to engine break – down. Losses due to respiration cannot however be ignored since they may be the cause of a fire.

The negative effect of a diminuition in pressure at a high altitude is partially compensated by the diminution in the air temperature by about $50^0C$ (at 10,000 meters). In this way, the fuel cools at certain points of the supply circuit and the secondary tanks which is shown by a diminuition in its vapour pressure. In practice, the effect of a diminuition in pressure is often more important than a diminuition in temperature.

**Behaviour at a low temperature**

As already mentioned above, jet aircraft fuel must maintain its properties at a very low temperature. A low temperature may cause three phenomena:

- The crystallization or freezing of certain hydrocarbons

- An increase in the viscosity of the fuel;

- The separation of water under the form of frozen crystals.

The crystallization or freezing phenomenon is extremely complex and cannot be calculated empirically.

The freezing point of fuel varies between 40 to $65^0C$ according to its specifications. If the fuel crystallizes, its consumption diminishes due to *the partial*

blocking of the supply circuit filters. In this case the engines run the risk of stopping completely.

Aeroplane manufacturers attempt to solve these problems by means of special insulation devices or thermal regulation apparatus and by defining very strict specifications.

The viscosity of the fuel increases as its temperature diminishes: the hydraulic conditions of the supply circuit are modified and the pumps use a much higher power: these phenomena may reduce the correct performance of the engine.

Figure 2.1 shows the variations in water solubility in kerosene (in ppm – weight) according to the temperature.

We can see that the maximum water content increases at the same time as the quantity of aromatics in the fuel. According to the specifications, the refineries should produce kerosene with practically no water.

Treatment by percolation or filtration in the sun improves the product properties when they have to be further stored, distributed and delivered without contaminants.

The presence of defreezing agents give a further safety margin. Sometimes a supplementary laboratory test is required, for the purpose of ensuring that the fuel has a low tendency for absorbing water or that there are no accidental quantities of sensitive organic substances, even only in traces, which cause the formation of emulsions.

## Thermal stability

Kerosene may be used as a source of heat to keep the lubricant or the hydraulic control system fluids cool. Due to the high temperatures some hydrocarbons are modified producing lacs or semi-solid rubber which are deposited on the walls thus reducing performance and blocking the tubes and filters of the supply circuit.

The presence of olefins are very dangerous but the paraffinic hydrocarbons are also able to react (because of a peroxide formation process). In the same way, the presence of sulphur and organic nitrogen should be avoided.

The suppliers specifications impose limits to existing and potential gums but they are not sufficient to define the thermal stability of the product.
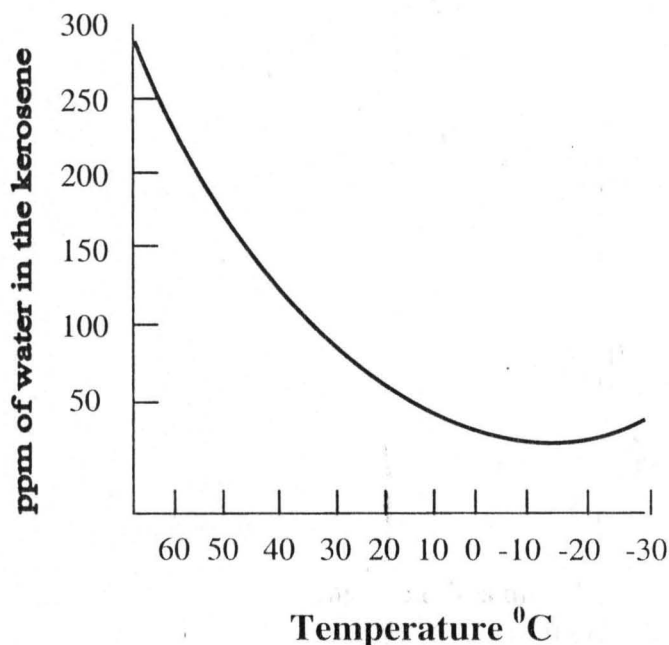
Fig. 2.1 Shows the Variation in water solubility in kerosene (in ppm weight) according to the temperature.

There is a standardized apparatus available called the ASTM CRC Fuel Coker which simulates flight conditions. This apparatus is used in controlling the currents and test research. The standard test conditions for fuel are the following:

Preheating temperature:     $300^0$ F $(148.9^0C)$

Filter temperature:         $400^0$ F $(204.4^0C)$

Fuel consumption:           6 1bs/hour  (about 2.72kg/hour)

Duration of the test:       6 hours

The visual calculation of the deposits is converted into a numeric classification. The standard scale ranges from 0 to 4. It is called the Preheating Deposit Code Number – P/H rating. The 0 corresponds to an absolutely clean surface. The 4 corresponds to a surface covered with a light – brown coloured film (hazel colour). The standard suppliers specifications impose a thermal stability corresponding to a P/H rating below 3 and a loss in load through the filter not higher than 330 – 254mm of mercury.

**Corrosiveness**

The corrosiveness of a fuel for aircraft turbine engines is controlled by limiting the sulphuric compound contents, mainly the mercaptans and limiting the total acidity. Nowadays, the acidity in fuels for aircraft turbine engines is only limited relating to the total acidity (0.03mg K0H/g) to avoid corrosion attacks. In the majority of cases, the mercaptan contents is limited to maximum of 0.001% in weight, expressed in sulphur.

The problems caused by an attack of sulphuric compounds on the silver and copper parts of the fuel pumps are caused by the use of a fuel which even though it complied with the specifications of the copper lamina test when it was new, deteriorated afterwards.

The problem of fuels which were transformed beyond the specification limits during storage is not a recent problem.

It is sure that an increase in corrosiveness may arise from the action of bacteria which reduce the sulphides. This is the reason why instructions were given that there must never be water in the bulk storage tanks used for aviation fuel. Despite this precaution, there are still a large number of cases where fuel is corroded (copper lamina test). Studies are therefore still being carried out on the treatment of residues (which cannot always be avoided) to kill the sulphur bacteria. Attempts are also made to purify the fuel using simple methods when it does not comply with the specifications.

Apart from the inherent corrosiveness in the structure and composition of the fuel itself, sometimes corrosion is found in the pipe-lines, the tanks and the distribution circuits owing to the presence of water in the fuel. The specifications of certain fuels for aviation turbine machines sometimes contain a list of homologated corrosion inhibitors.

### 2.3.3  Dual purpose kerosene (DPK)

This type of kerosene is not common as the other two types.  It is the type of kerosene which could be used either as an Aviation Turbine Kerosene (ATK) or

Household Kerosene (HHK). It is not all the oil producing nations that produce dual purpose kerosene, but it is very useful in order to meet the market demand for each of the type of product. It's properties comprise that of the Household kerosene and Aviation Turbine Kerosene.(Adeniran, 2000).

## 2.4 Importance of Kerosene

Kerosene or paraffin oil as it is often called in the United Kingdom was for fifty years the most important petroleum product. It has found many uses over the years and its output has grown steadily (Adeniran, 2000).

The low cost of domestic kerosene has rapidly attracts the attention of users when compared to other cooking source such as cooking gas and electricity. Kerosene has also solved the problem of deforestation, which also increases the dependence on its consumption (Onuoha, et al, 2002)

Kerosene has the following applications as:

- It is used as a carrier in Aerosal industries.

- It is used as carriers in the production of disinfectants.

- It is used as carriers in the production of insecticides.

- It is used as a solvent in the production of electrical cables.

- It is used in the production of polishes as components of silicone car and window polishes.

- It is used as rolling oil and in preparation of aluminum paints

- It is used as volatile lubricant for cutting tools, lubricant for rolling processes and it is a blending component for some lubricants.

- It is used as a solvent in degreasing and cleaning of machineries which may have attracted dirt. And it can also be used for delicate machines such as clocks.

- It is also used in industries which produces wood preservations and also to remove stains.

## 2.5   Treatment of Kerosene

For kerosenes (illuminating oils) a single treatment technique like desulphurization is not sufficient; as the illuminating quality of kerosene is not improved in this operation. Smoke point improvement is achieved by removing smoke causing ingredients, namely aromatics. Formulations of good kerosene touch a maximum limit of 20% aromatics. Aromatics in the kerosene range are preferably of single ring structures with side chains. Although a good number of solvents are pressed into service, still the universal replacement of the old process has not been ventured, for almost all solvents do have their inherent difficulties in recovery procedures. Solvents, like dimethyl formides (DMF) (Venkateswarun, 1972), dimethyl (Derandran, 1976), sulfoxide (DMSO) (Choffee, 1966), diethylene (Rao, 1978), glycols (Johnson, 1954), sulfolane (Broughton, 1967) are no doubt good and conducive as far as their extraction part is concerned; but hydrolysis in presence of water during recovery techniques is the intriguing problem. Genuine quests are in progress round the globe for better methods. Solvents like ethylene glycols are best suited for extraction of light aromatics like benzene, toluene and xylene, from reformed stocks, but not for kerosenes.

Infact kerosene quality may not be exposed by smoke point alone, it should be supplemented by flame luminosity. A look a the Table 2.2 would reveal that glycols may not be good solvents for improving smoke point, but the treated stocks posses a good luminosity compared to conventional solvents. Hence, while extraction of smoke causing ingredients is desirable, at the same time retention of illumination contributents like napthenes is foremost(Bhaskara, 1984).

Some of the methods available for treatment of kerosene are discussed in following sections.

### 2.5.1  Liquid sulphur dioxide extraction of aromatics

The oldest process for the removal of aromatics is liquid sulphur dioxide extraction invented by Edeleanu (1905) and since that time it continues to enjoy a commanding position.

Fig. 2.2a illustrates the process. Kerosene is first deaerated by exposing to vacuum. Any moisture in kerosene is removed by passing through a tower of adsorbent (I), (usually calcium chloride serves the purpose). The charge is then passed through a heat exchanger (2), cooled by raffinate and further chilled by liquid sulphur dioxide (3) to bring down the temperature to $8^0$C. The cold stock is fed into Extractor (a) where counter current extraction takes place. Liquid sulphur dioxide being heavier, the extract is obtained from the bottom of the extractor. Raffinate and extract are separately processed for pure streams in two sets of evaporators. Raffinate stream. through a heat exchanger (4) fed with treated and hot kerosene enters first unit of the evaporation system ($b_1$). The evaporators resemble more or less distillation units;

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## Table 2.2: Smoke Point and Luminosity Index.

| Solvent | Temp of extraction ($^0$c) | Solvent to feed ratio | Improvement in smoke point | | Luminosity index* | Calorific value kj/gm at $30^0$C |
|---|---|---|---|---|---|---|
| | | | Without dilution (%) | With dilution (%) | | |
| DMF | 25 | 2 | 11 | 10(10%) | | |
| | 40 | 2 | 14 | 12(10%) | (32) | 46.85 |
| | 60 | 2 | 12 | 11(10%) | | |
| DMSO | 30 | 2 | 12 | 13(5%) | | |
| | 50 | 2 | 12 | 13(5%) | (38) | 44.17 |
| | 70 | 2 | 12 | 13(5%) | | |
| Ethylene-Glycol | 30 | 4 | 4 | 4(5%) | (40) | |
| | 50 | 4 | 5 | 5(5%) | | |
| Diethylene-Glycol | 30 | 4 | 6 | 6(5%) | (42) | 37.16 |
| | 50 | 4 | 6 | 6(5%) | | |
| Raw Kerosene | (Smoke point = 8) | | | | (13) | 46.85 |
| Tetralin | (Smoke point = 9) | | | | (0) | 46.85 |
| i-octane | (Smoke point = 35) | | | | (50) | 47.44 |

*Luminosity is determined at highest smoke point elevation only

operate in series, under decreasing pressure. First evaporator ($b_1 - 1$) is operating above the critical pressure of sulphur dioxide, but below critical temperature. In evaporators, pressure ranges from 6 to 15 atmospheres. This permits the temperature during operation to reach as high as $80^0C$ to $110^0C$ without vaporizing sulfur dioxide. Heating is mainly done by steam in an outside boiler (5), and in this process some sulphur dioxide is expelled in vapor phase (or in liquid phase). The raffinate is now taken to low pressure evaporator ($b_1 - 2$) where most of the sulfur dioxide is vaporised and taken for compression system. The column is usually atmospheric and the temperature here will be $20^0C$ more than that of the first evaporator. Condensation of sulfur dioxide does not take place, hence only gaseous sulphur dioxide escapes. The bottoms of the evaporator through reflux (6) heater are now fed to third stage ($c_1$) unit where the pressure is maintained at 25mm to 190mm mercury, and that keeps the temperature around $15^0C$. sulphur dioxide from this unit is recovered by vacuum system ($d_1$) and then sent into the compression system ($d_2$) along with other streams of sulphur dioxide. Sulphur dioxide is compressed to above critical pressure and then cooled by a train of heat exchangers (e) fed with cold water at $20^0C$ which liquefies sulphur dioxide. The liquid sulphur dioxide is stored in tank (f) and self evaporation can bring the temperature of sulphur dioxide to $-10^0C$.

The same type of evaporation cycle is executed for recovery of sulphur dioxide from extract. The entire operation should be conducted in moisture free situation.

Depending upon the stock, the amount of solvent to feed varies. When smoke point elevation of kerosene is done then liquid sulphur dioxide to kerosene ratio is
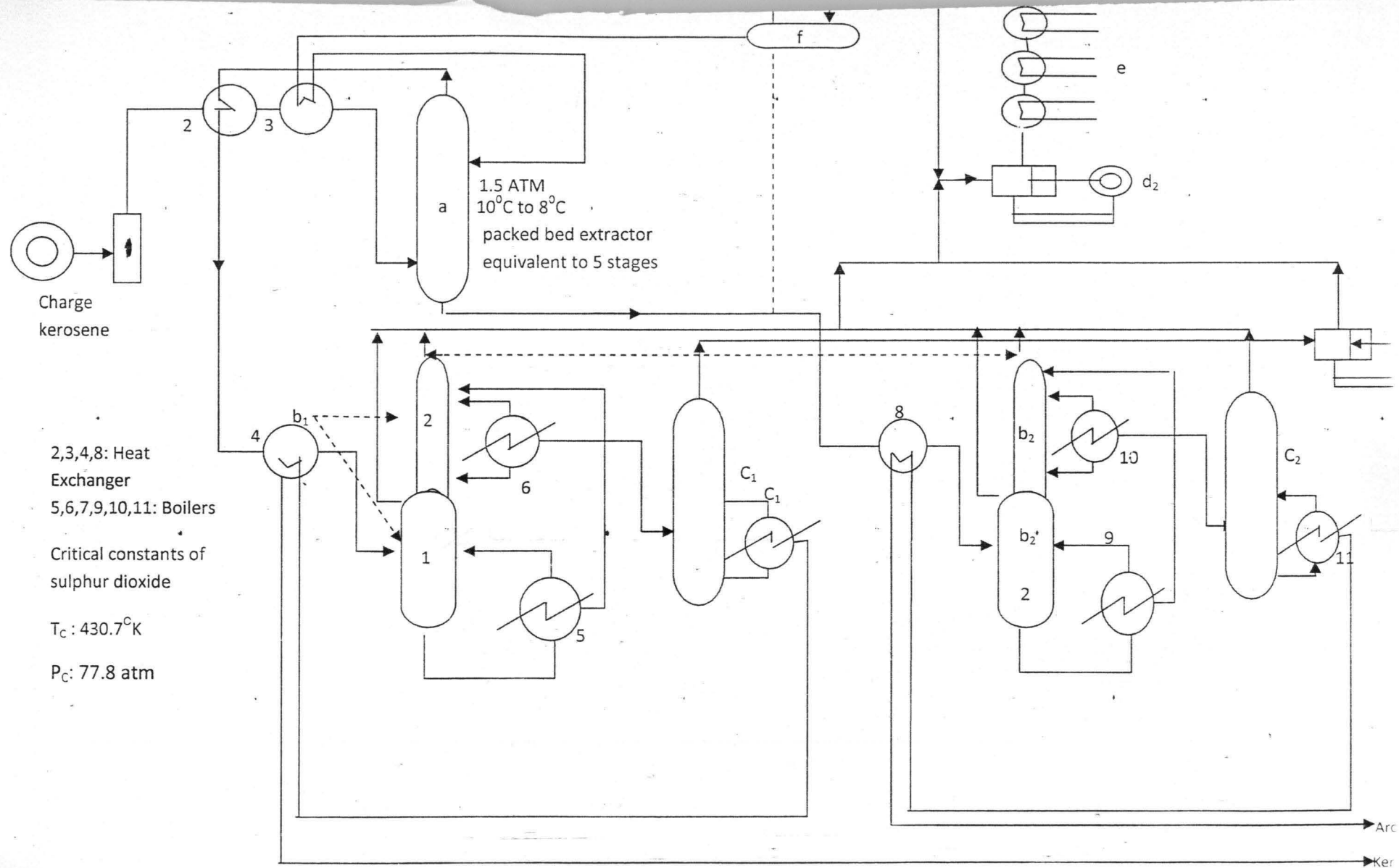
FIG. 2.2a Liquid $SO_2$ Extraction Process

2, 3, 4, 8: Heat Exchangers

5,6,7,9,10,11 are Boilers

Text labels within the figure:

f

1.5 ATM
$10^0C$ to $8^0C$
packed bed extractor
equivalent to 5 stages

a

e

$d_2$

Charge kerosene

2, 3, 4, 8: Heat Exchanger

5,6,7,9,10,11: Boilers

Critical constants of sulphur dioxide

$T_C : 430.7^0K$

$P_C$: 77.8 atm

$b_1$

$b_2$

$b_2'$

$C_1$

$C_2$

Arc

Ker

30

kept in the range of 1 to 1.5, and when diesel stocks are used a ratio of 1 to 1.4 is preferred. Sulphur dioxide extraction is quite convincing for lighter fractions, while for lube oils the solvency power of solvent is very much less, hence a mixture of benzene and sulphur dioxide is employed. A good recovery of 90 to 95% aromatics is possible leaving less than 2% aromatics in treated stocks (Wilkenson,et al, 1953). A smoke point elevation of 10 to 15 units is frequent in this operation. With lube oils the treating temperature is kept above the the pour point of the oil. The loss of solvent is considerably low (about 0.2%), and that really maintains the economy of process.

Information on liquid sulphur dioxide treatment of lubes and kerosenes is presented in Table 2.3 (Bhaskara, 1984).

| Table 2.3 | Kerosene | Lubes |
|---|---|---|
| Sulphur dioxide volume | 100% | 180% |
| Treating temperature | $-10^{0C}$ | 40 to $60^{0C}$ |
| Raffinate yield | 75% | 63% |
| Sulfur in feed | 0.15% | |
| Sulfur in finished product | 0.026% | |
| Smoke point (Feed) | 24mm | |
| Smoke point (Finished product) | 45mm | |
| Feed viscosity index | - | 55 |
| Product viscosity index | - | 9 |

New aromatics (Bhaskara, 1990) extraction process uses N – formylmorpholine solvent. This has been suggested to be quite competitive with present processes, has a greater flexibility to feed stocks and keeps abreast with the developments. Extraction of aromatics
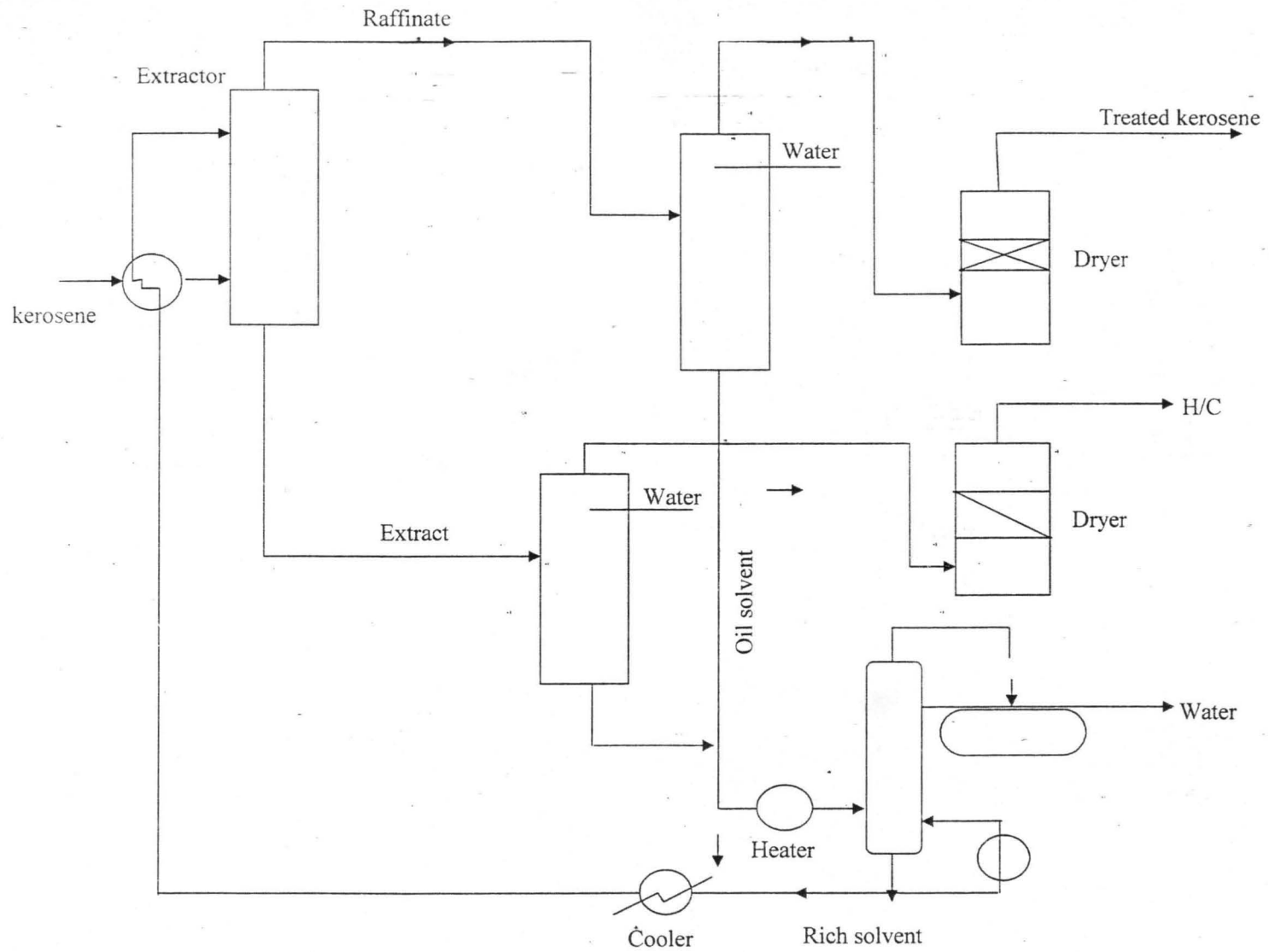
Figure 2.2b Improvement of Smoke Point with Solvents (DME & DMSO)

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by other solvents like DMF, DMSO and glycols is presented in Fig. 2.2b. It is apparent from the flow sheet, that solvent from the rich phase is separated by water washing and later by distillation. The hydrocarbon phases obviously contain some moisture and have to be dried separately; steam stripping may not be satisfactory because of the close boiling ranges of solvent and stock.

## 2.5.2  Sweetening treatments

Some of the methods available for this treatment are discussed below.

### 2.5.2.1.1  Merox sweetening

Mercaptan oxidation (Merox) process is most appealing as it is suitable for treating LPG, gasolines and kerosenes. This process has shown commendable abilities in ablating mercaptans in the form of harmless disulfides. All modern refineries in India are bent upon using this process. C/S and merox solution (catalyst cobalt salt) in caustic solution are contacted in extractor (1). Sweetened product from the top of extractor goes into merox separator (3) where a fresh gust of air comes in contact with Merox solution. Merox is regenerated here and the solution is transferred to a settler (4). The phases are separated in this horizontal settler (4), and the heavy merox is obtained from the bottom of the tank. This merox being regenerated is fed back to extractor along with fresh merox. The extract containing mercaptans is oxidized by blowing air in towers (2). Disulfides are separated in settler (5) by decantation and regenerated merox is collected for circulating into extractor.

A reduction of 90% sulfur is possible in this operation. When LPG is treated, the sweetened gas is passed through a mist eliminator to remove the merox

entrainments. Merox operations can be conducted in fixed beds also, where the catalyst is spread on charcoal.The flow sheet diagram of merox process is shown in Figure 2.3.

## 2.5.2.2 Mercaptan dissolving processes

In this process, the kerosene is being treated simultaneously with solutizer solution and shipped to regenerate the solution, except in tannin solutizer process in which air blowing is employed.

The solution may consist of caustic soda together with solubility promoters, such as salts of isobutyric acid, alkyl-phenols, metrand, cresols and solutizer solution are separated, and they later recycled and used again.

More computer mercaptan can be obtained by this process, the oxidation process first described are being abandoned mainly because of the reduction in octane number that occurs. The catalytic process has found to give the highest octane cracked gasolines the cost mount rapidly because the catalyst employed must be regenerated frequently.

## 2.5.2.3 Caustic washing methods

This involves bringing the kerosene in contact with sodium, calcium, or magnesium hydroxides for the removal of hydrogen sulfide and mercaptans. This result in saving in chemicals in subsequent treatment as the solution is being recycled. Caustic solution ranging from 5 to 15 percent are employed. Here, mercaptan in one alkali are oxidized to disulfides which can be withdrawn as a light liquid layer.
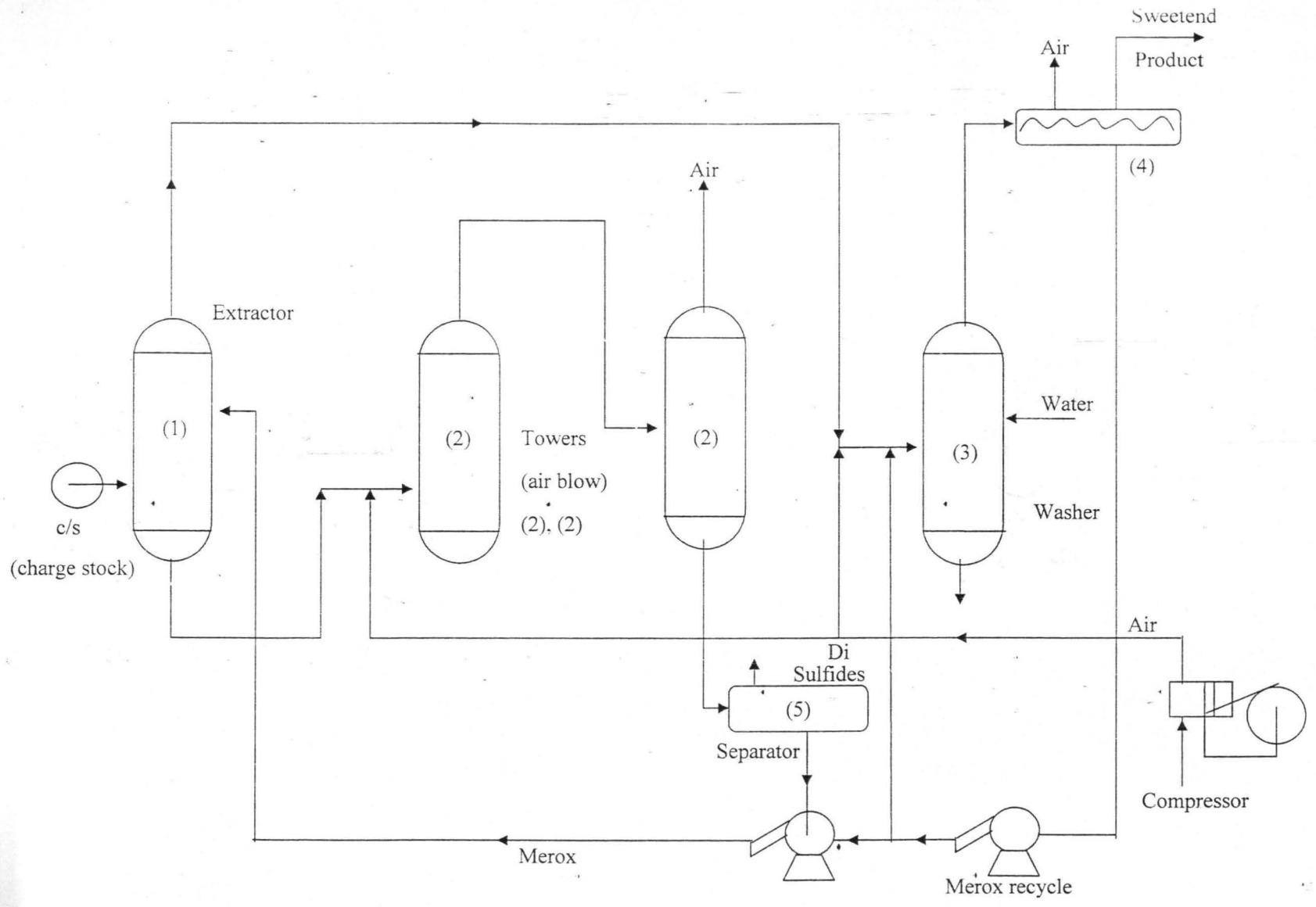
Figure 2.3 Merox Process

A solutizer process developed by Yabroff, D.I which permit more complete removal of mercaptan by caustic solution. Here, an organic agent is used to increase one solubility of mercaption in one caustic solution. The low molecular weight mercaptan such as methyl and ethyl mercaptan are dissolved by caustic alone, but solutizers must be added in order to remove the mercaptan having three or more carbon atoms to the molecules.

The unisol or methanol process employ at the centre of a packed treating column. Small amount of methanol are lost with the gasoline, and the methanol must be distilled after it (and the mercaptans) has been stripped from the caustic.

Tannin can be used with solutizer process and perhaps other solution – promoter processes. It is unique because the solutizer solution can be regenerated by air blowing rather than steam stripping. This keeps temperature low and reduces utility costs.

### 2.5.3 Doctor treatment

In this process the kerosene is contacted with a little sulfur and with alkaline sodium plumber solution, this process also removed elementary sulfur from the oil. Stability of colour is great improved by though separation of chemicals during settling and washing. Spend doctor solution is often recovered or used over again by adding more litharge (leadoxide) to the solution and carrying the sulfide in suspension. The process can be described by the following equations.

$$2RSH + N_{A2}PBO_2 \text{--------} \rightarrow (RS)_2PB + 2NaOH \text{-------} (2.2)$$

$$(RS)_2PB + S \text{ --------------} \rightarrow (RS)_2 + PBS\text{----------------(2.3)}$$
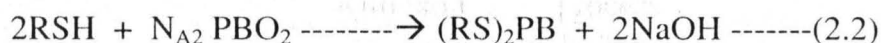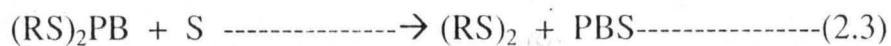
**Overall Reaction**

$$2RSH + S + N_{A2}PBO_2 \text{ --} \rightarrow PBS,(R_2S_2) + N_{A2}S + 2H_2O \text{ --- (2.4)}$$ in the over all reaction lead sulfide is acting as a catalyst to cause the two doctor reaction to occur simultaneously as shown above in equation (2.4)

The sweetening process of kerosene above are not entirely satisfactory proceed which has been developed within the fuels (Nelson, 1958). A satisfactory process has been developed within the group in for raw fuel and a small quantity of sulfuric acid are intimately mixed. The acid sludge is then separated and recycled, a very small percentage of fresh acid being injected into the recycled acid stream to maintain one desired acid strength. In addition to the sweetening effect the sulfuric acid treatment has a beneficial effect on other properties, such as colour and dun-forming characteristics.

Doctoring is principally based upon the following criteria.

1. Oxidising mercaptans to disulfides

2. Physical extaction

3. Catalytic conversions in presence of hydrogen.

4. In-situ destruction of sulfur bearing compounds

All the above methods are in practice, although the last mentioned method is universally acclaimed. Depending upon the commercial or chemical importance of a product the severity of treatment also increases (Bhaskara, 1984).

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### 2.5.3.1 Oxidising mercaptans to disulfides:

This is perhaps the oldest sweetening technique involving conversion of active mercaptans to inactive disulfides. Disulfides in gasolines are found to be harmless compared to sulfides; however for pollution considerations both are equally harmful. Important sweetening reagents are chlorides and hypochlorite of copper and iron and lead dioxide and lead sulfide. The reagents react with mercaptans in the following way:

<div align="center">Reaction</div>

$$4RSH + 4CuCl_2 \text{ ---------------}> 2R_2S_2 + 4C_uCL + 4HCL \text{ --------------- (2.5)}$$

<div align="center">Regeneration</div>

$$4C_uCL + 4HCL + O_2 \text{ ---------------}> 4CuCL_2 + 2H_2O \text{ ------------------- (2.6)}$$

$$Na_2PbO_2 + 2RSH \text{ -----------------}> (RS)_2\,Pb + 2Na(OH) \text{ -------------- (2.7)}$$

$$(RS)_2\,Pb + S \text{ ------------------}> R_2S_2 + PbS \text{ ------------------------------- (2.8)}$$
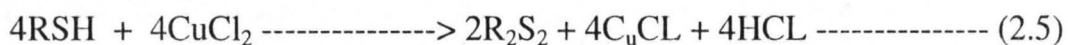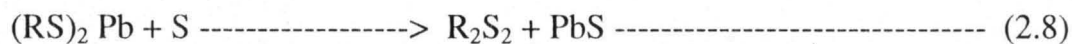
The reagents are often regenerated back. Regeneration of copper chloride is achieved by blowing air in contact with Hydrochloric acid. In case of lead doctoring the resulting lead disulfide is converted to lead sulfide by addition of fresh sulfur. Evidently for a fraction that contains free sulfur, this lead process is remarkable. Lead sulfide is converted back to lead plumbite by oxidizing the slurry with air at $80^0C$. If the free sulfur is in excess of equivalent mercaptan, fresh additions of mercaptan is essentials to consume the sulfur. This is a paradoxical situation; fresh additions of

sulfur are invited for completion of reactions, which may lead to improper balance in the treated stocks, often resulting in more sulfur than anticipated.

A simple reagent like lead sulfide alone can also do the same work as given by the following equation.

$$2RSH + S + PbS, Na(oH) \rightarrow PbS, (R_2S_2) + Na_2S + 2H_2O. \text{------- (2.9)}$$
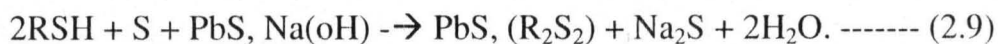
The reaction is carried out in presence of air or oxygen over a catalyst bed (lead sulfide) where, thorough contact of gasoline and sulfur takes place. When gasolines cantain naphthenic acids and phenols; sodium soaps shall be formed, resulting in a difficult situation i.e the soaps hinder the precipitation of lead sulfide. Exact amount of litharge for precipitation has to be calculated. Industrial dosage is about 0.02kg/bbI for straight run fractions and 0.5kg/bbI for cracked stocks.

At present this process is losing its place to other processes. Carbondioxide can also be removed simultaneously along with acid gases, thus; itself does not require any treatment.

### 2.5.3.2 Extraction processes

Physical extraction of sulfur compounds is practiced widely under different trade names. Atmospheric Distillation Unit (ADU) gases are relatively free from impurities compared to off gases from crackers. ADU gases and natural gas can be treated in a single stage itself. If high sulfur natural gas or wild gasolines are handled, it is preferred to first wash with caustic. Ethanolamines are profusely used for

washing purposes, because of the ease of regeneration. Ethanoamines react with acidic components as shown below:

$$(HOCH_2CH_2)NH_2 + H_2S \text{ -------> } (HOCH_2CH_2NH_3)_2S \text{ ------------- (2.10)}$$

$$(HOCH_2CH_2)NH_2 + CO_2 + H_2O \text{ ----> } (HOCH_2CH_2NH_3)_2 CO_3 \text{ ------ (2.11)}$$
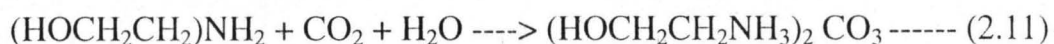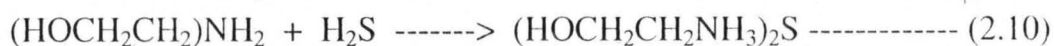
All forward reactions proceed below $40^0C$ where as backward reactions occur at about $105^0C$. 20 – 30% aqueous amine solutions are employed for this purpose. Fitzgerald et al(1969) presented the solubility data on $H_2S$ and $CO_2$ in amines. The equilibrium concentrations of $CO_2$ and $H_2S$ at loading conditions in MEA, DEA (Chyuan and Andrew, 1980) solutions are available in literature. The idea of concentrations (equilibrium) is pre-requisite for designing such absorbers. Extraction of $H_2S$ and mercaptans from naphtha cuts by using caustic soda solutions were dealt by Dunstan (1929) and the data is presented in Table 2.3

Table 2.4 Extraction of Hydrogen Sulphide and Macaptans from Naphtha using Caustic Soda Solution.

| Component | B.P. $^0C$ | % Removed | B.P of corresponding disulfide $^0C$ |
|---|---|---|---|
| $H_2S$ | | 100 | |
| Ethylmercaptan | 38.9 | 97.1 | 152.6 |
| n-propyl –do- | 67.8 | 88.8 | - |
| i-propyl-do- | 59.0 | 87.2 | 175.5 |
| n-butyl-do- | 98.2 | 63.2 | - |
| i-butyl-do- | 87.8 | 62.8 | 220 |
| i-amyl-do- | 117.8 | 33.0 | - |

### 2.5.3.3 Catalytic desulphurization

Of late, sweetening operations are carried out by catalysts. In such reactions whole molecule bearing sulfur is not removed, as seen in extraction or acid treatment, but only the sulfur atom is picked up. Thus material loss is negligible with possible recovery of sulfur.

The first catalytic process for removal of organic sulfur was introduced by (Carpenter and Evans , 1924) using sulfides of nickel. The success of this has led to many catalysts. Still search for better catalysts is going on. Iron oxide catalysts with 5 – 15% $Cr_2 O_3$ were used for hydrogenation and hydrolysis of carbonyl sulfide from gases (manufactured). Such catalysts operate at a temperature of $300 - 400^0C$ at 1 - 25 kg/cm$^2$ pressure.

Copper – chromia – Alumina Catalysts, Huff catalysts, (Copper Cr$_r$ – vanadium oxides) promote conversion of organic sulfur compounds to $H_2S$, which is retained in the form of metal sulfide, on catalyst. Holmes maxted (Maxted and Priestly, 1946) process employs molybdates of copper, iron, zinc and cobalt. Shell hydrodesulphurization techniques which is carried out in presence of hydrogen, uses sulfides of tungsten and nickel. But recycling is essential when hydrogen gas is a co-stream. Desulphurization as followed in Autofining process satisfactorily operates even without hydrogen recycle. Depending upon the nature of catalyst, 90 – 95% of sulfur can be removed. Catalytic desulphurization operation is shown in Fig 2.4 (Bhaskara, 1984).

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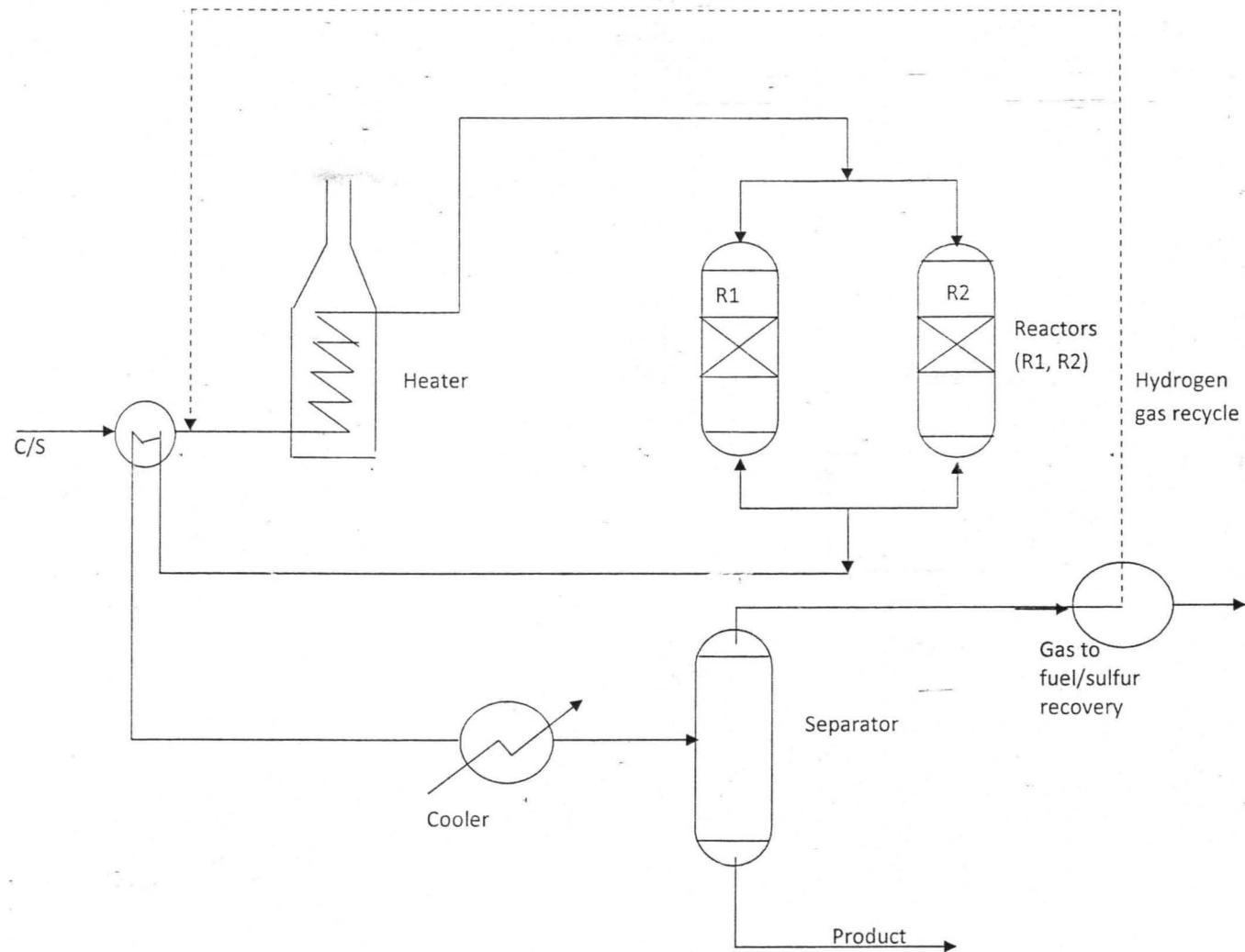
FIG. 2.4 Catalytic Desulfurisation

## 2.5.3.4  Sulfuric acid treatment process

In olden days sulfuric acid treatment was given for every fraction.  The treatment is quite simple although other disadvantages are quite in number.  In its essential the success of separation depends upon the strength of acid.  The outlines of the process are presented in Fig. 2.5. Acid and charge stock are proportioned and sent into an Orifice mixer (1). This mixer is advantageous due to the fact that it does not require any additional agitation system.  The reaction with sulfuric acid is exothermic; hence a care must be taken to see that the temperature does not exceed $40^0$C.  As a precautionary measure cold water sprays may be kept in reserve.  After the reaction is over the contents are sent into a settler (2) Where a settling time 5 to 6 hours is aptly given.  Gradually, the acid sludge separates out and concentrates at the bottom. Sulfur, unsaturated and metallic bodies are all attacked by the acid and all these find their way into sludge.  The hydrocarbon layer from the top of the settler is given a water wash in washer (3) to scrub of acid residues.  Sometime further doctoring is done by plumbite sulfur mixers. The doctoring solution and the hydrocarbom phase are thoroughly mixed in mixer (4) and the contents are again settled in a settler (5) Sludge separates out here, and the light phase is again water washed (6) The hydrocarbon phase is later neutralized with caustic in a contractor (7); and again washed with water and dried.

If doctoring is not required by plumbite technique, the treatment may be omitted.  But the caustic neutralization is a must, for acid treated stocks.  Some heavy

stocks may pose problems, due to emulsifying characteristics; in such cases, neutralization maybe given up; and clay (Bhaskara, 1990).

The action of sulfuric acid on mercaptan is shown below:

$$RSH + H_2SO_4 \text{-------------}> \quad RSHSO_3 + H_2O \text{------------------} (2.12)$$

$$RSH + RSHSO_3 \text{------------}> \quad (RS)_2SO_2 + SO_2 + H_2O \text{------------} (2.13)$$

$$RS)_2 SO_2 \text{---------------------}> \quad R_2S_2 + SO_2 \text{------------------------} (2.14)$$
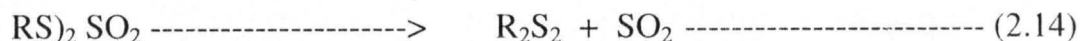
Sweetened gasolines are likely to be converted back to sour gasolines by decomposition of disulfides. Thiophenes are very slow to react and require fuming acid. Sulfoxides and sulfones are soluble in 75 – 93% acid. Carbondisulfide is immune to this treatment. It is found with fuming acid and at high temperatures any hydrocarbon can be reacted.

With increasing strength and temperature, acid sludge also in increases. Disposal of these sludges forms a major obstacle in generous adoption of this process. With modern technical advancements, material wastage is prevented; hence sulfuric acid treatment is replaced by other processes wherever it can be (Kalchersky and Stranger, 1942).

## 2.5.3.4.1 Sulfuric Acid Treatment Condition

With sulfuric removes resinous and alphaltic substances, unsaturated hydrocanbons, naphthanic acid parth nitrogen and sulfur containing compound. Paraffin and naphthane hydrocarbons are only slightly attached by 93% acid at room temperature, higher temperature and acid concentration cause attack, particularly upon isomers having several side chains. Benzene is only slightly attacked by 93%

44

Acid

C/S

Mixer 1

(2)

Settler sludge

Washer (3)

Water

Sulphur

(4)

(5)

Settler sludge

Plumbite solution

Washer (6)

Water

(7)

Product to dryer

Caustic neutralizer

Details of mixer

Orifice plate
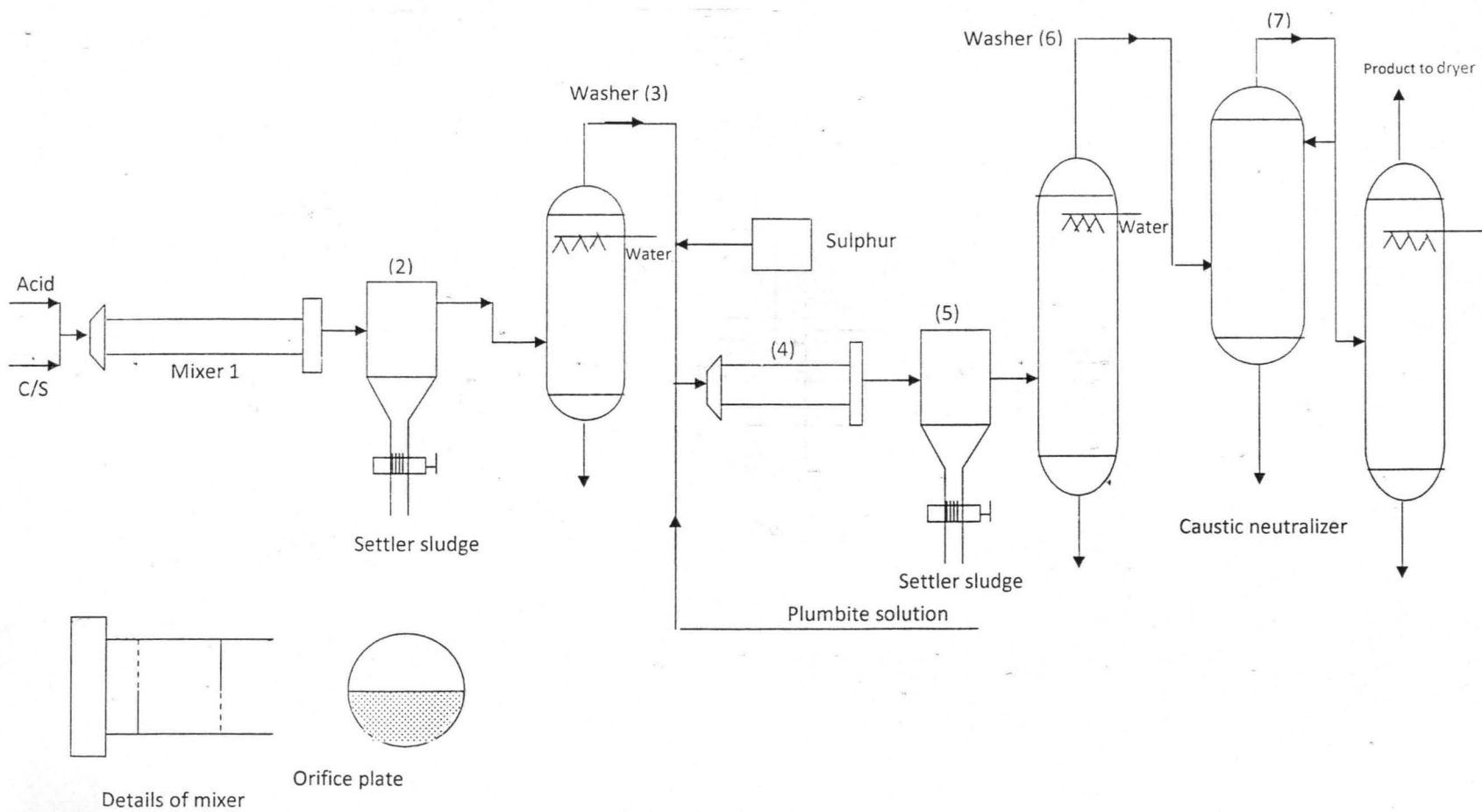
FIG. 2.5 Sulphuric Acid Treatment (with Doctor Sweetening)

45

acid but toluene and xylene are more readily attacked thus 93% and stronger that cause a smoky low temperature and acid concentration favour the formation of alky-acid sulfates, neutral esters and most sulfur components are sulfates dissolve to some extend in the oil. The rate of action of sulfuric acid on the various impurities appears to be some what as follows:

Nitrogen compound → Asphaltic substances → Oleifinic → Aromatics → Naphthanic acids.

A small amount of sulfuric acid may be entrained by the oil after treatment, the treatment result depends on the treatment temperature, duration of oil – acid contact, the concentration and amount of acid used, and how it is introduced.

**Treatment temperature**

Treatment temperature lowers possible temperature produces a better colour in the product and the acid far because solid and buttle owing to the transformation of the resins into asphaltenes and lift is difficult to drain off through the button connection of the apparation.

The temperature, acid concentration that are commonly used for various treating operation are as follows:

| | | |
|---|---|---|
| Straight run gasoline | - | 70 to 90$^0$F |
| Kerosene | - | 90 to 130$^0$F |
| Lubrication oil stocks | - | 110 to 180$^0$F |
| Cylinder stock | - | 130 to 170$^0$F and 150 – 180$^0$F |

If treating is conducted before dewaxing.

It has been found that cold treating methods have many advantages from a treating standpoint, but the refrigeration requirement and cost are enormous. Contacting may be applied (Britain, 1975).

**Contact time**

This time of oil acid contact is dependent on the intensity of mixing and condition of acid resident stock removal (Erikh, 1988).

Prolong contact of acid sludge and oil results in a poorer colour and less stability, but too short time may prevent complete utilization of the acid.

Straight run and cracked gasolines are completed with acid for less than minute in continuous – treating systems. This is found to be advantageous for cracker gasolines to minimize polymerisation and sulfonation of oil (John, 1959).

In chemical contactor for continuous systems, the time of contact is sometimes held to only a few seconds and setting time is eliminated almost by centrifugal means.

In conventional batch agitation, the time of contact is much longer. The following are for some common products (John, 1959).

| | | |
|---|---|---|
| Light distillate | - | 15 to 40min |
| Kerosene | - | 30 to 40min |
| Lubricating oil | - | 90min |

Time required to settle the sludge in an agitator ranges from a few minutes for gasoline to as 15 hours for very viscous stock.

## Acid concentration

Erikh, et. Al, 1988, have reported that the sulfuric acid used for treatment must have a concentration from 92 to 96 percent. It was also found that the activity of the acid lowers substantially when it concentration is below 90 percent. (Nelson, 1958) recommends 93 percent ($66^0$Be) acid concentration for several use. But for treating light distillates to colour only, a more dilute acid may be advantageous. For most other purposes, such as removing combine sulfur, improving the burning qualities of kerosene, and removing tar from lubricating oil, an acid concentration of 93 percent or stronger is recommended.

It was concluded that strong acid (93 to 103 percent) used and low temperatures ($25 - 50^0$F) removes sulfur from gasoline's and aromatic hydrocarbons from burning oils or transformer, but colour is generally poorer when using fuming acids (Honston, 1968).

Fuming acid causes the increase formation of sulphuric aids. The acid concentration drops as a result of one treatment.

Acid tars containing from $25 - 70$ percent of increased sulfuric acid (Erikh,1988).

If corrosive sulfur is low, an acid of acid on only 85 percent strength may be advantageous. Weak acid is also useful in removing nitrogen bases and for improving the colour without removing unsaturated compounds.

## Acid consumption

The consumption of sulphuric acid for treatment have been found to depend upon on the quality of the feedstock and the required degree of purification (Hobson, 1986). The colour of the oil improves when more acid is used, but too much acid have been found to result in poor colour and aloss of aromatics and unsaturated hydrocarbons (John, 1959).

(Nelson, 1958) have given the quality of acid that is commonly used as follows:

| | | |
|---|---|---|
| Natural gasoline | - | Usually none but occasionally 21b per bb1 |
| Straight run gasoline | - | Usually none but may require 51b per bbl for sulfur removal |
| Pressure distillate | - | Usually none but for high – sulfur oil and oils from naphthene – base crude oil even 81b per bb1 may be required. |
| Solvents | - | Usually 0 to 51b per bb1 if high-sulfur stock must be processed. |
| Kerosene | - | Usually 1 to 151b in as much as 751b per bb1. |
| Lubricating oils | - | Usually 0 to 601b per bb1 |

## Contacting pattern

Contacting pattern can either be batch or continuous, Batch process are usually done with air agitation to ensure proper contact but contacting time is very high and it may range from 30 to 40 min, continuous contacting equipment can be in various

form. Rotating disc contactors, packed extraction column, pulse extraction column, mixer settler decanter system minutes are required. Settling time too can be eliminated almost altogether by use of centrifugal means.

Other method include the use of sand material in contact with one oil and acid to create large superficial area for contact and when filtering the oil through this medium. Whenever possible, continuous treatment is used in preference to batch treatment, as it permit closer control, eliminates necessity of semi-skilled labour, distribute the power demand throughout the day, and permits economical application of heat or cooling if such is required.

The advantages of the principle of the counter current treatment were recognized long ago. It affords as complete utilization as possible of the acid, since it correspond to a sludge treatment in an infinite number of stages (Kalichasky and Strange, 1993).

## 2.6 Detection of Mercaptans, Hydrogen Sulphide, Elemental Sulphur – Doctor Test.

### 2.6.1 Scope

This standard specifies the "Doctor" test for the detection of the presence of Mercaptans, hydrogen sulphide and elemental sulphur in motor fuels, kerosenes and similar petroleum products.

### 2.6.2 Principle

A test portion is shaken with sodium plumbite solution and the mixture observed. From its appearance, the presence or absence of mercaptans, hydrogen

sulphide, or elemental sulphur may be deduced. Mercaptans may be confirmed by the addition of sulphur, shaking and observation of the appearance of the final mixture.

### 2.6.3 Procedure

Some of the steps to be followed are below.

**2.6.3.1 Preliminary test** Place 10ml of the sample and 5ml of the sodium plum bite in the stoppered cylinder and shake together vigorously for 15 seconds. Observe the appearance of the mixture and, after observation, continue the procedure as indicated in Table 2.5.

### 2.6.3.2 Hydrogen sulphide present

To remove $H_2S$, place 20ml of fresh sample and 1ml of the cadmium chloride solution into a stoppered separating funnel and vigorously for 15 seconds. Allow layers to settle then decant 10ml of the non-aqueous layer into a stoppered cylinder and carry out a further preliminary test (2.6.3.1). If this second test does not produce a black precipitate, continue as specified in 2.6.3.3. If the second test does produce a black precipitate, repeat the washing with a fresh portion of the cadmium chloride solution. Continue washing with fresh cadmium chloride until preliminary test (2.6.3.1) does not produce black precipitate. Continue as specified in 2.6.3.3

### 2.6.3.3 Final test

To the mixture obtained as specified in 2 6.3.1or 2.6.3.2 add a small quantity of the sulphur (not more than will just cover the interface between the sample and the sodium plumbite solution) shake the mixture for 15 seconds, and allow to settle for one minute.

Observe the contents of the cylinder. If a brown or black precipitate is formed on the addition of sulphur, Mercaptans are present.

**Table 2.5 Preliminary Test Procedure**

| Observation | Inference | Continue test as disabled in |
|---|---|---|
| Black precipitate forms immediately | Hydrogen sulphide present | 2.6.3.2 |
| During the shaking period the solution becomes opalescent and then darkens in colour | Mercaptans and elemental sulphur present | - |
| No change occurs or yellow colour is produced | - | 2.6.3.3 |

## 2.6.4 Expression of results.

a. If an opalescent colour is produced during shaking with the sodium ploumbite solution, and a brown or black precipitate is formed after adding sulphur, report the result of the test as 'Doctor positive Mercaptans present'.

b.    If, during the shaking, the solution becomes opalescent and then darkens in colour report the result as "Doctor positive Mercaptans and elemental sulphur present'

c.    If an immediate black precipitate is formed during shaking with the sodium plumbite solution, report the result as 'Doctor positive – hydrogen sulphide present'

d.    If, after removal of hydrogen sulphide, a brown or black precipitate is formed after adding sulphur, report the result of the test as 'Doctor positive – Mercaptans and hydrogen sulphide present'

e.    If no precipitate is formed after the addition of sulphur, report the result of the test as 'Doctor Negative – Mercaptans absent.

## 2.7 Determination of Mercaptan Sulphur

### 2.7.1 Scope

The determination of mercaptan sulfur in gasolines, kerosene and distillate fuels containing a mass fraction of from 0.0003% to 0.01% of mercaptan sulfur. Organic sulfur compounds such as sulfides, disulfides and thiophene do not interfere. Elemental sulfur in amounts of a mass fraction at less than 0.0005% does not interfere. Hydrogen sulfide will interfere, if not removed.

### 2.7.2 Principles

The hydrogen sulfide free sample is dissolved in an alcoholic sodium acetate titration solvent and titrated potentiometrically with silver nitrate standard alcoholic solution, using as an indicator the potential between a glass reference electrode and a

silver/silver sulfide indicating electrode. Under these conditions, the mercaptan sulfur is precipitated as silver merceptide and the end point of the titration is shown by a large change in cell potential.

Note: For the determination of Mercaptans of higher molecular mass such as kerosenes and distillate fuels, the acidic titration solvent is used to achieve more rapid equibrieum between successive additions of the titrant.

### 2.7.3 Procedure

### 2.7.3.1 Determination of density

If the test portion is to be measured out volumetrically, first measure the density of the sample directly at the temp at which the test potion is to be taken.

### 2.7.3.2 Removal of hydrogen sulfide

Test the sample qualitatively for hydrogen sulfide by shaking 5ml of the sample with 5ml of the acid cadmium sulfate solution. If no precipitate appears, proceed with the analysis of the sample.

If a yellow precipitate appears, remove the $H_2S$ in the following meaner.

1. Place quantity of the sample (three to four times that required for the analysis) in a separating funnel containing a volume of the acid $CdSO_4$ solution equal to one half that of the sample and shake vigorously.

2. Draw off and discard the aqueous phase containing the yellow precipitate. Repeat the extraction with another portion of the $CdSO_4$ solution. Again draw off the aqueous phase, and wash the sample with three 25ml to 30ml portions of water, drawing off the water after each washing.

3. Filter the washed sample through a qualitative filter paper. Test a small portion of the washed sample in a test tube with a few milliliters of the $CdSO_4$ solution.

4. If no further precipitate is formed, proceed as directed in analysis of sample.

5. If a precipitate appears, repeat the extraction with the $CdSO_4$ solution until all of the $H_2S$ has been removed.

### 2.7.3.3 Analysis of sample

a)    Measure with a pipe the, 20ml to 50ml of the original or treated sample into a 300ml tared titration beaker and determine the mass of the test portion. Add 100ml of titration solvent. Immediately place the beaker on the titration stand and adjust its position so that the electrodes of the cell system are about half – immersed. Fill the burette with 0.01 mol/litre alcoholic silver nitrate solution and place the burette in position in the titration assembly so that the tip extends approximately 25mm below the surface of the liquid in the beaker. Adjust the speed of the stirrer to give vigorous stirring with out spattering.

b)    Record the initial burette and cell potential readings. Add suitable small portions of 0.01mo/litre silver nitrate solution and, after waiting until a constant potential has been established, record the burette and meter readings. Consider the potential constant if it change less than 6mv per minute.

1.    When the potential change is small for each increament of silver nitrate solution, add volumes as large as 0.5ml.When the change of potential becomes greater than 6mv per 0.1ml. use 0.05ml increments of silver nitrate solution. Near the end

point of the titration, 5min or 10min may elapse before a constant potential is obtained. Nevertheless, it is important that the duration of the titration be as short as possible in order to avoid oxidation of the sulfur compounds by atmospheric oxygen. Once started, a titration shall never be interrupted and resumed later.

c)     Continue the titration until the meter reading has passed +350mv (see note below) and the change of cell potentials per 0.1ml of silver nitrate solution has become relatively constant.  Remove the titrated solution, rinse the electrodes well, first with alcohol and then with water, and wipe them with a dry tissue. Burnish the silver electrode lightly with abrasive cloth or paper.  Between successive determinations on the  same day, immerse the electrodes in 100ml of titration solvent containing approximately 0.5ml of 0.1mol/litre silver nitrate solution.

Note:  With certain instruments, the algebraic sign of the potentials may appear reversed.

## 2.7.4  Expression of results.

a)     Treatment of Data:  Plot the cumulative volumes of 0.01mol per litre silver nitrate solution added against the corresponding cell potentials.

b)      Select the end point at the most positive value of one sleepest portion of each "break" in the titration curve.  The shape of the titration curve may change with different instruments.

### 2.7.5  Calculation

Calculate the mercaptan  sulfur content of the sample as follows, mercaptan sulphur, weight percentage by mass, using the formula as:

$$\frac{V \times C \times 3.206}{M} \qquad\qquad\qquad (2.15)$$

where

V     =     the volume, in milliliters, of 0.01mol/litre silver nitrate solution required to reach the end point in the vicinity of + 300mv:

C     =     the exact concentration, in moles per litre, of the silver solution

m     =     the mass, in grams, of the test portion;

3.206 =     100 x the gram mole equivalent mass of sulfur (s) in mercaptan.


## 2.8. Sulphur Compounds in Crude Oil

Some of the sulphur compounds generally present in crude oil are hydrogen sulphide and mercaptans.  Both these are undersirable and processes are always incorporated in refineries to remove these compounds from finished products either by chemically converting them to other compounds, like in merox fixed bed process, or removing them by converting the mercaptans to $H_2S$ as is done in the Hydro desulphurisers. The sulphur is recovered from the hydrogen sulphtide thus formed in our sulphur recovery plant.

Mercaptans are the compounds of hydrocarbon and sulphur. They have the general formula R – SH where R stands for hydrocarbon redical and SH is the mercaptan portion of the molecule. Mercaptans have a foul odour and therefore have to be converted into odourless compounds or removed by reduction – presence of mercaptans in gasoline components reduces lead susceptibility of the component and the sulphur in the molecule combines with oxygen in the car engine forming corrosive sulphurous acid. A typical mercaptan can be represented as follows:

$$
\begin{array}{ccccccc}
H & H & H & H & H & H & \\
| & | & | & | & | & & \\
H - C - C - C - C - C - C - S - H & & & & & & \\
| & | & | & | & | & | & \\
H & H & H & H & H & H & \text{Mercaptain radical}
\end{array}
$$
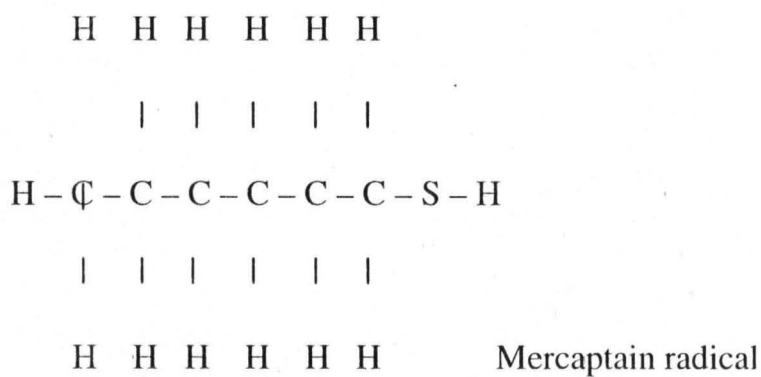
R    =    Organic radical

The process of converting mercaptains into odourless disulphides is called "sweetening".

Sulphur is present in the crude oil in a third form called thio-phenes. Thiosphene is represented as.

H – C -------- H – C

H – C -------- H – C

S

58
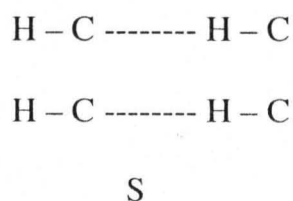
During the process of hydide sulphurising this compound is converted into hydrocarbon and $H_2S$.

Removal of sulfur compounds that cause damage is know as sweetening. Usually acidic sulfur can be removed by washing with any amines or caustic. The common type of sulphur compounds from petroleum are shown in Figure 2.6

## 2.9 Hydrodesulfurisation (HDS) Process

Hydrogen over a catalyst is capable of reacting with sulfur, nitrogen, halogens and oxygen, from the respective compounds available in the fractions. Sulfur, nitrogen and halogens escape as the respective hydrides, while oxygen escapes as water vapour. Metals found in the oil are generally absorbed on the catalyst surface, hence the product shall always contain less metals. However, increase in metal concentration on the surface of catalyst naturally rescinds the activity of catalyst.

Increase of boiling point of feed also brings alarmingly increasing difficulties to the process. Thiophenic compounds are major sulphur compounds in the high boiling fractions, and these being lethargic towards hydrogen render desulfurisation more difficult. Mercaptans do offer such difficulties but to less extent, hence may be placed in intermediate region. Nitrogen is quite adamant and requires very severe conditions.

Bauxite with impregnation of molybdenum is capable of removing 70 to 80% of metals (Kett, et al, 1975). Demetallisation (Demex) processes are being tried extensively. In this method the removal of metal concentrates is done by solvent

59
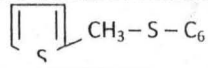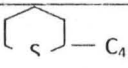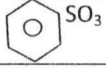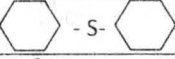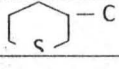
| Mercaptans | $C_nH_{n+1}SH$ | |
| C2H3SH→ | $C_2H_3SH$ | Ethyl mercapta |
| sulphones | $RSO_2$ | |
| | $C_7H_{15}SO_2$ | Heptyl sulphone |
| sulphides | $R_2S$ | |
| | $(CH_3)_2S$ | Dimethyl sulphide |
| Di sulphones | $R_2S_2$ | |
| | $CH_3S.S.CH_3$ | Dimethyl disulphide |
| sulfoxides | $\dfrac{R}{R}\!\!>SO$ | |
| | $\dfrac{CH_3}{CH_3}\!\!>SO$ | Dimethyl sulfoxide |
| Thiophenes | (ring, S) | |
| | (ring, S) $CH_3-S-C_6$ | Thiodeeyl thiophene |
| Thiophanes | $C_nH_{2n}S$ | |
| | (ring, S) $-C_4$ | Butyl thiocyclohexane |
| Sulphates | $(C_nH_{2n+1})SO_4R_2SO_4$ | |
| | (benzothiophene ring, S) | Thio benzols |
| sulphonates | (ring) $SO_3$  $R\,SO_3$ | |
| Carbonyl sulphide | $C\,O\,S$ | |
| | (ring) $-S-$ (ring) | Cyclohexyl sulphide |
| | (ring, S) $-C$ | Thio cyclo heptane |

FIG 2.6 Common Types of Sulphur Compounds from Petroleum

extraction resembling deasphalting operation by solvents. Manganese nodules (Clarance, et al, 1976) are found to be catalytically active in demetalation of topped crudes in presence of hydrogen. These nodules are cheaply available in marine and fresh water sediments. Manganese nodules deposited on Co-Mo on alumina base serve the best (Stephen, el al, 1976). Hung and Wei (Huns and Wei, 1980) studied demetalation of porphyrins using $CoO_3 - MoO_3$ on alumina. The report shows that 90% of nickel and vanadium could be eliminated.

In desulphurization of straight run hydrocarbons, catalyst such as bauxite, fuller's earth was once widely used.

Cobalt and molybdenum catalyst supported on bauxite or further earth was proven to be very effective. When use with hydrogen circulation and at a high pressure, catalysts actively can be maintained even when desulphurizing kerosene and straight run light dislillates. Desulphurization is a mild hydrogenation, so mild that aromatic are not hydrogenated to naphthenes. Sulphur is removed as hydrogen sulphide and the remaining hydrocarbon part of the molecule is hydrogenated.

In the process the feedstock is mixed with the platformer (or other source) and also with the hydrogen recycling gas recoverd from the desulphurised product. The mixture is heated in a furnace to a temperature between $300 - 380^0C$ and then pass though areactor, which is sharged pelleted catalyst, the pressure in the reactor being between $40 - 60kg/cm^2$.

The reactor effluent, consisting of desulphurised oil, hydrogen and hydrogen sulphide, is cooled and the product are separated in the high product separator. The

hydrogen – rich gas, from which hydrogen sulphide is removed, is recycled to the feed inlet and the liquid product passes to a stripping column, where dissolved hydrogen sulphide and light hydrocarbon are removed. Efficiency of desulphurization depends on the charge stock and the seventy of treatment, ranging from as low as 50 to 60 percent for mild operation to 80 to 99 percent and 95 to 98 percent is not common.

In general, increase in space velocity increase sulfur in products and hydrogen consumption. As reaction temperature increases hydrogen consumption too increases.

With Ni – Co catalysts, presulfurization with carbon disulphide or any sulphide is essential (Nelson, 19958). The fullest activity of these oxides occurs infact after interaction with sulphur and apart of catalyst is converted into sulphides.Simplified flow Diagram of the above process is shown in Figure 2.7

### 2.9.1 Chemistry of the process

Let us consider the most common reactions of the process; they are related to sulphur, nitrogen, metals and oxygen removal, to olefin saturation and to other chemical phenomena.

### 2.9.1.1 Sulphur removal

Sulphur in crude occurs in different forms like free sulphur, hydrogen sulphide, mercaptans and thiophene etc. These are frequently occurring compounds in almost all fractions of the crude though to a different degree. Heavier fractions contain sulfides, polysulfides, sulphonates and sulphates. However, refiners habitually remove

62
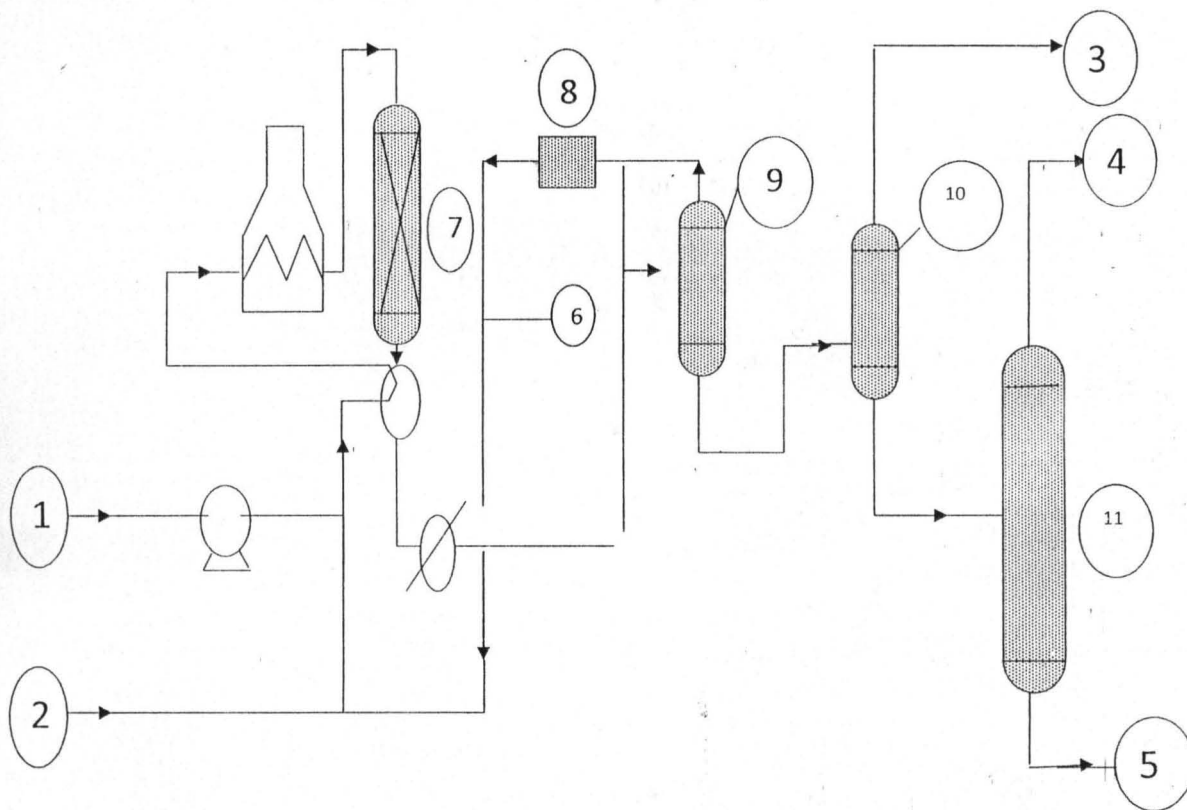
**FIG 2.7 Simplified Flow Diagram of the Kerosene HDS Unit (UNIBOM)**

| | | | |
|---|---|---|---|
| 1. | Charge stock (kerosene) | 7. | Reactor |
| 2. | Hydrogen make-up gas | 8. | Recycle compressor |
| 3. | Sour gas ($H_2S$) | 9. | Reactor products separator |
| 4. | Unstabilized naphtha | 10. | Low pressure separator |
| 5. | Hydro treated kerosene | 11. | Stripper |
| 6. | Recycle gas ($H_2$) | | |

more detrimental sulphur compounds and leave the less harmful ones into the products as seen in the case of sulphides converted to disulfides in gasolines

- (Mercaptan) $\quad$ C – C – C – C – SH + H$_2$ → C – C – C – C + H$_2$S

- (Sulfide) $\quad$ C – C – S – C – C + 2H$_2$ → 2 C – C + H$_2$S

- (Disulfide) $\quad$ C – C – S – S – C – C + 3H$_2$ → 2 C – C + 2H$_2$S

- (Cyclic sulfide) $\quad$ C —— C + 2H$_2$ → C – C – C – C (and C – C – C) + H$_2$S

- (Thiophene) $\quad$ C —— C + 4H$_2$ → C – C – C – C (and C – C – C) + H$_2$S
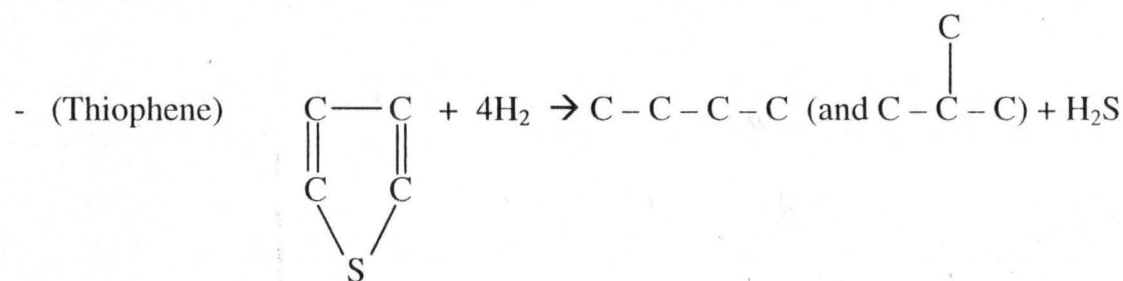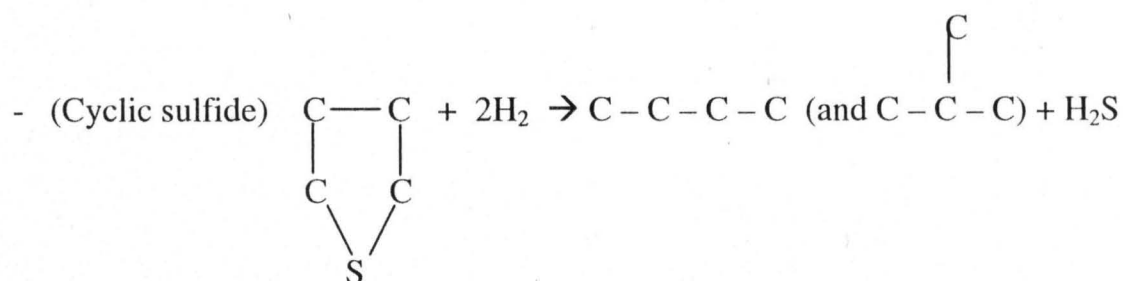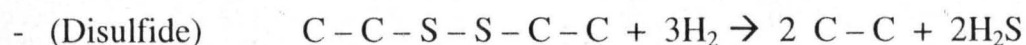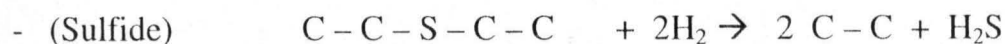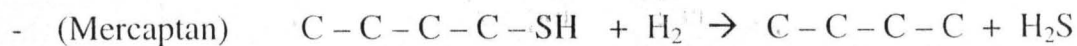
Fig 2.8: Structure of Sulfur Removal

## 2.9.1.2 Nitrogen removal

Nitrogen presence in free form is well known in natural gas only. Nitrogen exists in the form of pyrrole, indoles, pyridines, quinolines and amines, usually well below 2%. Nitrogen compounds exasperate problems in processing and stability of products. Catalyst deactivation or poisoning and gum formation are some of the

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offshoots of nitrogen. The most interesting compounds of nitrogen are porphyrins. These are obtained from living organisms and preserved in petroleum.

- (Phyridine)    [structure] $+ 5H_2 \rightarrow C-C-C-C$ (and $C-C-C$) $+ NH_3$

- (Quinoline)    [structure] $C + 4H_2 \rightarrow$ [structure] $C-C\,C\,C + NH_3$

- (Pyrrole)    [structure] $+ 4H_2 \rightarrow C-C-C-C$ (and $C-C-C$) $+ NH_3$
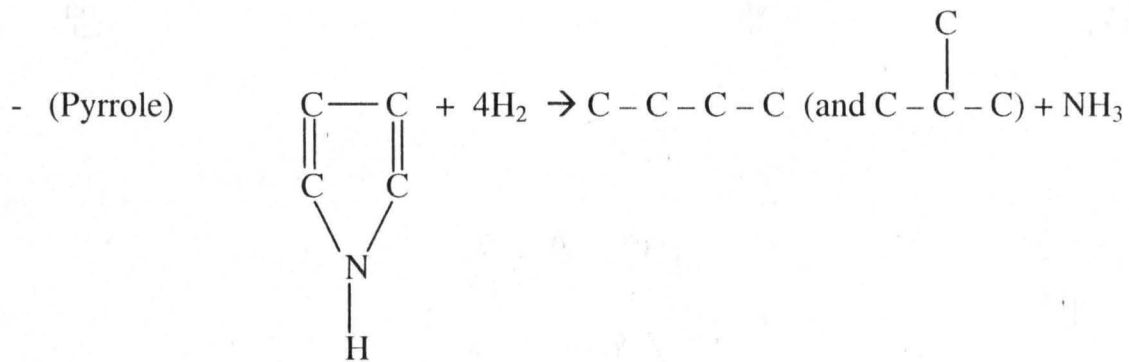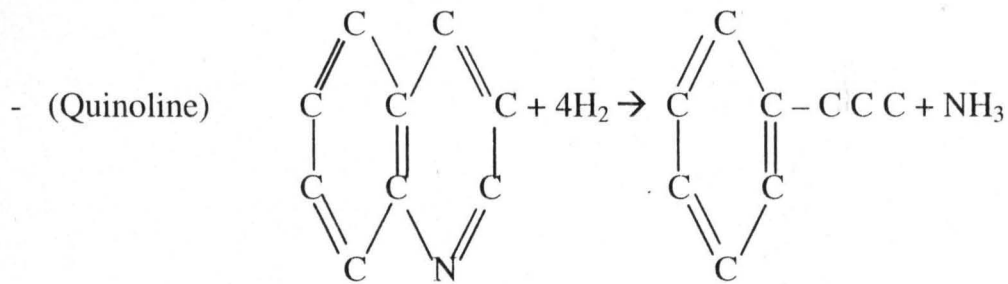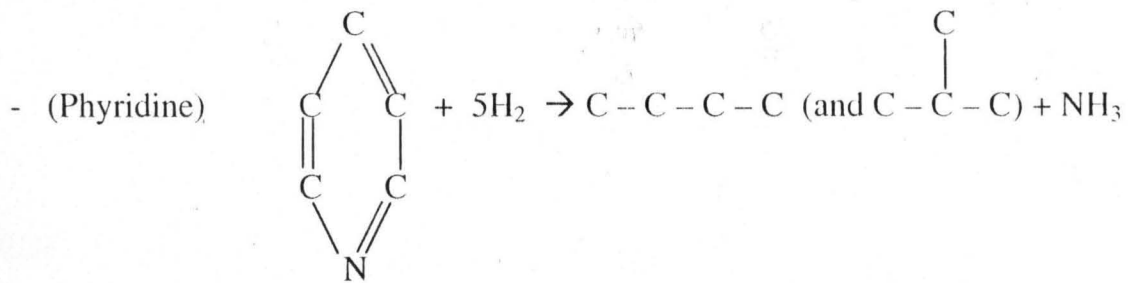
Fig. 2.9 Structure of Nitrogen Removal

## 2.9.1.3 Oxygen removal

Oxygen does not occur in free-state either in crudes or in fraction. Oxygen occurs as oxygenated compounds like phenols, cresols, naphthenic acids, sulphonates, sulphates and sulfoxides.

(Phenol)    [structure] $+ H_2 \longrightarrow$ [structure] $+ H_2O$
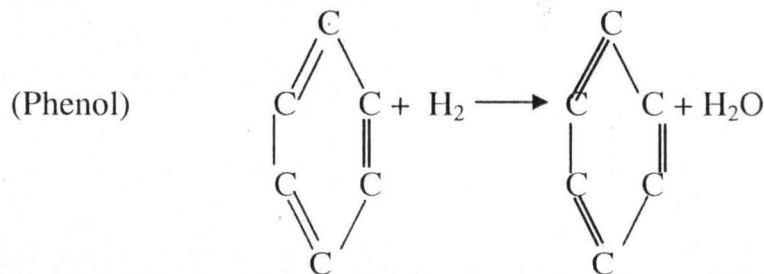
Fig. 2.10: Structure of Oxygen Removal

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## 2.9.1.4 Olefin saturation

Olefins are represented by the general formula $C_nH_{2n}$. They are easily attacked by sulfuric acid and some of them even polymerize. The boiling points of olefins are generally lower by few depress than the saturated compounds of the same carbon number. The absence of oil unsaturates to a large extent can be judged by the probable catalytic activity of the earth's crest in converting unsaturates to saturates and ring structures.

- (Linear olefin)  C-C=C-C-C-C+H$_2$ $\longrightarrow$ C-C-C-C-C-C (and isomers)

- (Cycle Olefin)
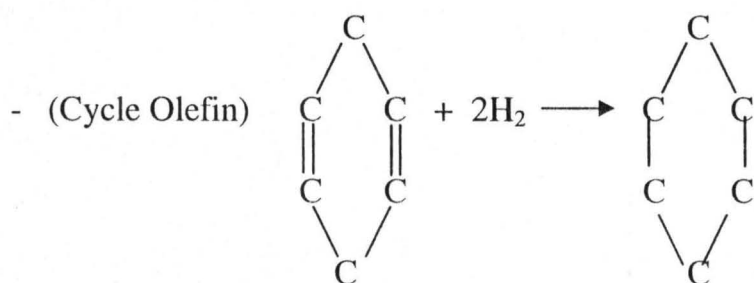


Fig. 2.11: Structure of Olefin Saturation.

## 2.9.1.5 Metal removal

The mechanism of the decomposition of organo – metallic compounds is complex; metals are retained on the catalyst by a combination of absorption and chemical reaction.

The catalyst has a certain tolerance, expressed as a fraction of the weight of the catalysts, for retaining metals. Metals break through will be observed at the reactor outlet once this tolerance level is exceeded.

### 2.9.1.6 Halides removals

Organic halides such as chlorides are decomposed in the reactor, and the inorganic acids and salts produced are dissolved by injecting water into the reactor effluent.

## 2.10 Properties and Uses of Tetraoxosulphate (VI) Acid

### 2.10.1 Physical properties of tetraoxosulphate(VI) acid

1. Pure tetraoxosulphate (VI) acid is dense and colourless and is the only liquid with density of 1.84gcm$^{-3}$.

2. It is very corrosive and causes serious burns when in contact with the skin

3. Concentrated tetraoxosulphate (VI) acid is very soluble in water and this evolves a great deal of heat in the process. Acid should be added to water and not water to acid because this may cause the water to boil and in that condition, the hot acid may spray from the container.

### 2.10.2 Chemical properties of tetraoxosulphate (VI) acid

*1.   As an oxidizing agent*

Hot concentrated tetraoxosulphate (VI) acid is a strong oxidizing agent. It oxidizes many elements both metals and non-metals to their oxides and is itself reduced to sulphur (IV) oxide.

$$Cu_{(s)} + H_2SO_{4(aq)} \text{------------>} CuSO_{4(aq)} + 2H_2O_{(L)} + 2SO_{2(g)}$$

$$Cu_{(s)} + H_2SO_{4(aq)} \text{------------>} CO_{2(g)} + 2H_2O_{(l)} + 2SO_{2(g)}$$
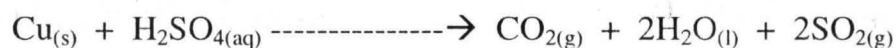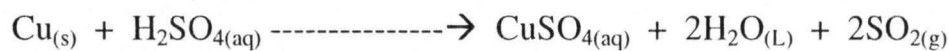
## 2.    *As a dehydrating agent*

Conc tetraoxosulphate (VI) acid is a good dehydrating agent. It removes water from many substances like sugar, ethanol and ethanedioc acid.

$$C_{12}H_{22}O_{11(s)} \xrightarrow[\text{Conc } H_2SO_4]{-11H_2O} 12\ C_{(s)}$$

$$\text{sugar} \qquad \text{charcoal}$$

$$\begin{array}{c} COOH_{(s)} \\ | \\ COOH \\ \text{ethanedioic} \\ \text{acid} \end{array} \xrightarrow[\text{Conc } H_2SO_4]{-11H_2O} CO_{2(g)} + CO_{(g)}$$

$$\text{sugar charcoal}$$

$$\begin{array}{c} CH_2\text{-}H \\ | \\ CH_2OH \end{array} \xrightarrow[\text{Conc } H_2SO_4]{-H_2O} C_2H_4(g)$$

$$\text{ethene}$$
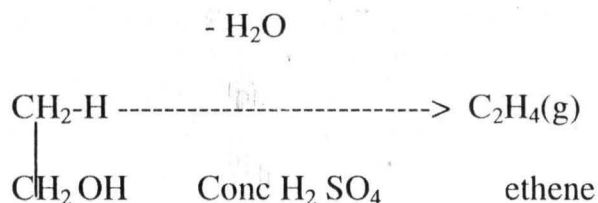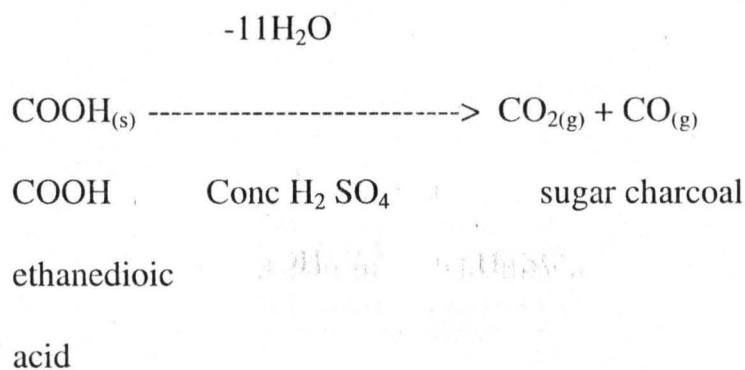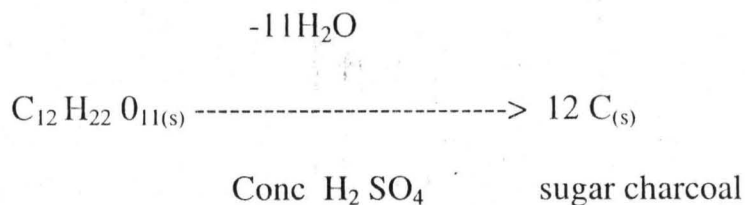
## 3.    *As a drying agent*

Conc tetraoxosulphate (VI) acid is hydroscopic. It is used to dry many gases which are not oxidized by the tetraoxosulphate (VI) acid. It is used to dry all the common gases with the exeption of the hydrogen halides and the alkaline gas ammonia.

## 4.    *As a typical strong dibasic acid*
Dilute tetraoxosulphate (VI) acid is strong and dibasic.

a)    It turns blue litmus red.

b)    It reacts with alkalis and bases to form salts and water.

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c)      It reacts with more electropositive metals to liberate hydrogen.

d)      It reacts with trioxo carbonate (IV) to liberate carbon (IV) oxide.

## 2.10.3 Uses of concentrated tetraoxosulphate (VI) acid

1)      It is used in removing impurities from crude oil (sulphur compounds).

2)      It is used in the manufacture of paints and pigments.

3)      It is used as an electrolyte in car batteries and accumulators.

4)      In the manufacture of fertilizer (e.g. $NH_4 SO_4$).

5)      In the production of tetraoxosulphate (VI) salts.

6)      It is used in making cellulose film, natural and artificial fabrics, as well as plastics.

7)      It is used to clean or pickle metals before electroplating.

8)      It is used to manufacture rayon (artificial silk), detergents and car batteries.

## 2.11. Sulphur and its Compounds

Sulphur: Sulphur is the second member of group (VI) in the periodic table of elements. Unlike the first member – oxygen which is a gas, sulphur is a solid.

It is a yellow, non-metallic, naturally occurring element, found mainly in the upper surface of the earth in sicily and deep in the earth in the U.S.A. It has a relatively low melting point of 387k ($114^0C$) and is practically insoluble in water. This would suggest that sulphur is a covalent element.

It is found in the combined state as sulphides such as iron pyrites ($FeS_2$), copper pyrites ($CuS_2$), lead sulphide (PbS) (also called galena), Zinc sulphide (ZnS) (also called Zinc blende) and mercury. Sulphur is also found in combined state as the

tetraoxosulphate (VI) salts of calcium, magnesium and barium, e.g. gypsum ($CaSo_4.2H_2O$) and Epsom salt ($MgSO_4.7H_2O$). Sulphur also occurs as hydrogen sulphide in petroleum, coal gas and natural gas.

Small amount of sulphur is also present in plants and in bodies of animals including man. Sulphur is also present in some protein. Each molecule of sulphur is made up of eight sulphur atoms arranged in a crown-shaped ring covalently bonded to each other.

Sulphur is found in most of the crudes in variable amounts. Generally sulphur compounds are present in more quantities in higher molecular weight stocks. Usually the sulphur content does not exceed 5%, however rare exemptions area: venezula (5.25%), California (USA 5.21%), Qaiyarah (Iraq 7%) etc crudes.

Sulphur in crude occurs in different forms like free sulphur, hydrogen sulphide, mercaptans and thiophenes etc. These are occurring compounds in almost all fraction contain sulphides, polysulfides, sulphenates and sulphates.

Sulphur occupies prominent position in refining due to its ominous problems of corrosion and odour. Pollution problems and following cost of waste treatment is punitive for all refiners with high sulfur stocks. However, refiners habitually remove more detremental sulfur compounds and leave the less harmful ones into the products, as seen in the case of sulfides converted to disulfides in gasolines.

Sulphur in gasoline inevitably depresses the effect of lead and demands more amount of additive. Further, sulfur containing residiums when cracked leaves cross linked structures, resembling the phenomenon of valcanization of rubber and offer

perennial problems in desulfurization. Its presence in different fractions complicates the refining and treating methods. Yet another problem is, it desists the effects of additives. When crude contains more than 0.5% S, it is denoted as high sulphur crude. A terse distinction, at this juncture between sour crudes and sulphur crudes is desirable. Free hydrogen sulphide is available in some crudes, which naturally fosters corrosion. Such crudes are classified as sour crudes; other sulphur bearing compounds are not taken into this account. The crudes containing sulphur compounds other than hydrogen sulphide and exceeding 0.5% are denoted as high sulfur crudes (Bhaskara, 1984).

In addition to corrosiveness and pollution, sulphur compounds are extremely harmful to the susceptibility of gasolines to tetra ethyl lead (TEL) (Nelson, 1958). More TEL is required if sulfur components are present in gasolines. The effect of over coming sulphur compounds is done by adding more lead. The effect of sulfur on lead can be predicted by the relation given as:

$$L = \frac{a_o - a}{a_o} \times 100 \quad \text{-----------------> 2.16}$$

Where $a_o$ = TEL present in gasoline with sulphur compounds

$a$ = TEL present in gasoline, free of sulphur compounds

$L$ = % TEL excess required to boost the octane number of sour gasoline to the same extent as sweet gasoline.

Sulphur is also termed as non corrosive sulphur, provided the sulphur exists in alkyl disulfide form only. Most of the sulfur in crude is concentrated in heavier fractions, lighter fractions require relatively less cumbersome treatment techniques. Total sulphur is estimated by bomb method or lamp method and mercaptan sulfur as silvermercaptide (Bhaskara, 1984,1990)

### 2.11.1 Physical properties of sulphur

i.      Sulphur has a melting point of $115^0$C and boiling point of $444^0$C.

ii.     Sulphur is soluble in organic solvents such as benzene and toluene. It is also soluble in carbon (IV) sulphide ($CS_2$) but insoluble in water.

iii.    Sulphur is a bad conductor of heat and electricity.

iv.     It is brittle.

### 2.11.2 Chemical properties of sulphur

i.      Reaction with air or oxygen: Sulphur burns in air or oxygen with a blue flame to produce sulphur (IV) oxide gas which is acidic to litmus.

$$S_{(s)} + O_{2(g)} \text{--------------------> } SO_{2(g)}$$

ii.     With metals: Sulphur combines directly without heating with metals to form sulphides and some of these reactions are very vigorous. Reactive metals like sodium and potassuim. With metals like iron and copper produce iron (ii) sulphide and copper (i) sulphide when heated.

$$Fe_{(s)} + S_{(s)} \text{ --------------------------> } FeS_{(s)}$$

$$Cu_{(s)} + S_{(s)} \text{ --------------------------> } Cu_2S_{(s)}$$

sulphide which vapourizes readily, forming poisonous and highly flammable fumes.

$$C_{(s)} + 2S_{(s)} \text{ -----------------------------> } CS_{2(l)}$$

iv. Reaction with oxidizing agents: Sulphur is readily oxidized on warming with concentrated tetraoxosulphate (VI) acid to form sulphur (IV) oxide. If warmed with trioxonitrate (V) acid using bromine as catalyst, sulphur is oxidized to form tetraozosulphate (VI) acid.

$$S_{(s)} + H_2SO_{4(aq)} \text{ ------------------------> } 2H_2O + 3SO_{2(g)}$$

$$S_{(s)} + HNO_{3(aq)} \text{ --------------------------> } H_2SO_{4(aq)} + 6NO_{2(g)} + 2H_2O_{(s)}$$

### 2.11.3 Uses of sulphur

1. Sulphur is used in the manufacture of tetraoxosulphate (Vi) acid.

2. Sulphur is used in the manufacture of bleading agent used in the pulp and paper industry. It is used as sulphide in the manufacture of matches, fireworks and gun powder.

3. It is used for the manufacture of drugs. Many modern drugs. Contain sulphur such as m & B which prevents pneumonia, antibiotics e.g. sulphathiazole and sulphurointment for curing skin diseases.

4. Sulphur acts both as an insecticide and as a fungicide.

5. In the production of important chemicals such as carbon (IV) sulphide ($CS_2$) and calcium hydrogen trioxo sulphate (IV) $Ca(HSO_3)_2$.

6. For the vulcanization of rubber – a process which converts the soft pliable rubber into the hard, tough substance from which motor tyres and similar products are made.

# CHAPTER THREE

## 3.0 EXPERIMENTAL WORK

This chapter outlines the materials, apparatus and experimental methods used in carrying out both the determination and purification of total sulfur content of the raw and refined kerosene using different concentrations of tetraoxosulphate (VI) acid at various contacting times.

### 3.1 Method and Scope

The untreated sample of kerosene was collected from Kaduna refinery and Petrochemical Company, Ltd. The sulphur in Oil Analyzer was used to confirm the amount of total sulphur content in the untreated kerosene before carrying out the purification and determination of the sulphur content using different concentrations of tetraoxosulphate (VI) acid with contacting times.

Due to small amount of treated kerosene produced from different concentrations and times, only the following were determined: smoke point, flash point, colour of treated sample (using Lovibon Tintometer) and specific gravity.

### 3.2 Materials

This list of materials used in carrying out the whole project is given in Table **3.1**

**Table 3.1: List of materials used.**

| S/N | Materials | Source |
|-----|-----------|--------|
| 1 | Raw Kerosene | KRPC Kaduna Nigeria |
| 2 | Concentrated tetraoxosulphate (VI) acid (96%) | Fisher Scientific U. kingdom |
| 3 | Silver nitrate | Burley in Wharfedale England |
| 4 | Sodium plumbite | Burley in Wharfedale England |
| 5 | Sodium hydroxide Solid | Scientific supplies Ltd London |
| 6 | Sulphur | KRPC Kaduna, Nigeria |
| 7 | Distilled water | Fed. Ploy. Tech., Bida |
| 8 | Cadmium sulphate | Fisher Scientific U. kingdom |
| 9. | Potassium ioxide | Fisher Scientific U. kingdom |
| 10 | Sodium Sulphide ($Na_2S$) | Burley in Wharfedale England |

## 3.3. Apparatus/Equipment

This list of apparatus used in carrying out the whole project is given in Table 3.2

### Table 3.2:  List Apparatus/Equipment Used

| S/N | Apparatus | Manufacturers |
|---|---|---|
| 1 | Sulphur in oil analyzer | Horiba, japan |
| 2 | Stop clock | W.G. Pyeand Co. Ltd |
| 3 | Pipette, Burette | Technics, England |
| 4 | Beakers, conical flask and volumetric | Tamsin; Holland |
| 5 | Flask | Moller & Co. Gemany |
| 6 | Weighing balance | Gallen Kamp, Horrison |
| 7 | Measuring cylinder | Scientific Eqpt. Minna |
| 8 | Stoppered cylinder | Nig |
| 9 | Seperating funnal | Tamsin, Holland |
| 10 | Cell for liquid | Horiba, Spain |
| 11 | Meter | Moller & Co. Germany |
| 12 | Titration stand | Technics, England |
| 13 | Abrasive cloth or paper | Technics, England |
| 14 | Electric stirrer | Dickey England |
| 15 | Cell window sampling | Horiba, Japan |
| 16 | Lovinbond tintometer | Ishihara, Japan |
| 17 | Pensky - Martens Closed Cup tester | Natural   Standard   Institute, Washington |
| 18 | Smoke Point Lamp | New Cavendish, London |

## 3.4    Method for the  Removal of  Total Sulfur from Raw Kerosene

400ml of the raw kerosene was put into a 2 litre beaker and 100ml of 75 percent concentrated tetraoxosulphate (VI) acid was added to it and stirred for 10 minutes, the stirring was electrically done.   The content was transferred into a separating funnel and two layers were formed.   The dark coloured sulphonated fraction was separated as extract from the upper layer fraction as raffinate.

The upper layer fraction was subsequently washed with 35ml aliquot concentrated tetraoxosulphate (VI) acid and two layers separated.   The traces of concentrated tetraoxosulphate (VI) acid remaining with the upper layer after separating it from the sulphonated layer was then neutralized with 15 grammes of sodium hydroxide (NaOH) which was then dissolved in 50ml of distilled water and kept for 20 minutes.  The solution with 250ml of distilled water was shaked, settled and separated until litmus test indicated neutral. This gave final treated kerosene.

The procedure repeated for various concentrations of (80, 85, 90 and 95). The whole procedure was ten repeated for 20, 30, 40 and 50 minutes of stirring.

The treated kerosene samples at various concentrations and times were collected in bottles for final analysis to determine total sulphur content using Sulphur in oil Analyser.Simplified flow diagram of the above treatment is shown in Figure 3.1

## 3.5.    Determination of Total Sulphur in Oil

The method used here is automatic and the experiment was carried out with the aid of an automatic machine called sulphur in oil analyzer (Noriba, Japan).  This was

Acid

(2)    Mixer    (4)
       (3)
                        Distilled water (8)
                                   (7)

Settler sludge

Settler sludge

Caustic    Sludge
neutralizer

Settler sludge
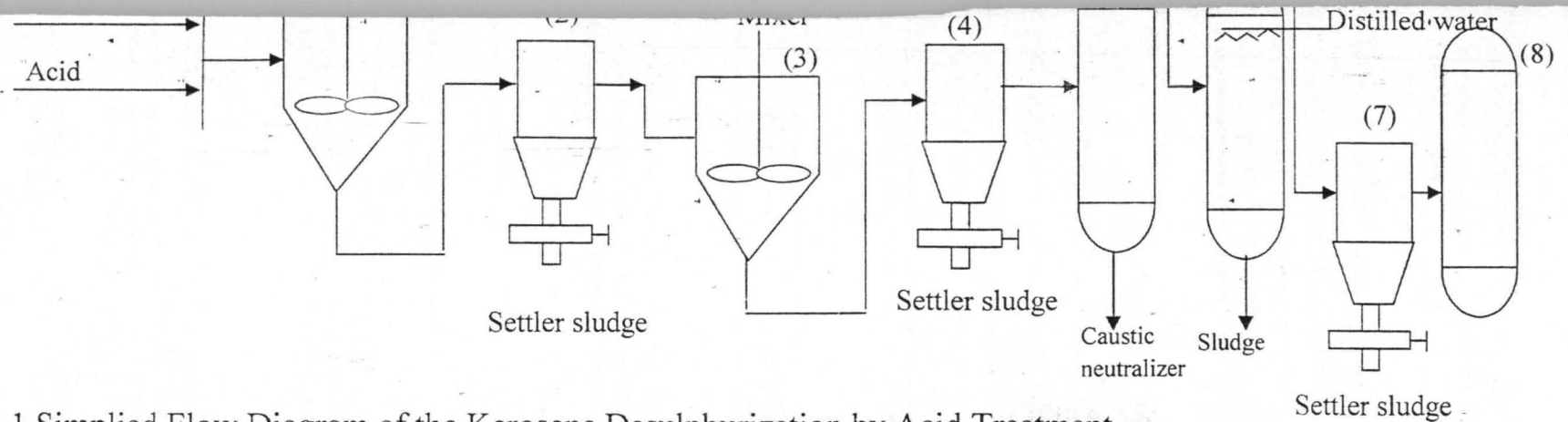
FIG. 3.1 Simplied Flow Diagram of the Kerosene Desulphurization by Acid Treatment

1.    Mixer for raw kerosene + concentrated tetraoxosulphate (VI) acid.

2.    Saperating funnel for saparating raffinate and extract

3.    Mixer for aquot acid (fresh acid) + raffinate from (2)

4.    Saparating funnel to obtain raffinate remaining with fresh acid (aquot acid)

5.    Caustic neutralizer for raffinate from (4) + caustic soda

6.    Washer for washing raffinate from (5)

7.    Saperating funnel for saparating raffinate from extract to obtain treated kerosene

8.    Storage tank for treated kerosene

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done by placing enough sample to be analysed in a small beaker of a capacity 5ml, three quarter full (at least). The sample was then placed in between the x-ray analyzer and the screen within the apparatus. The lid I was then covered and the instrument switch on. The apparatus used weight percent total sulphur present in the oil and the resulted was shown on the screen. The equipment did the measurement three times and the average result was given within 100 seconds of measurement. The result was then printed automatically.

## 3.6 Characteristics of Treated Kerosene

This section deals with the determination of the properties of the refined kerosene.

### 3.6.1 Colour determination by the lovinbond tintometer

This method was the comparison of colour of sample with institute of petroleum (IP) standard colour glasses. The IP standard colour glasses were used only for determining the colour of refined kerosene in a 457mm cell. The colour standards are mounted in racks of up to nine (9) slides each, arranged so that the colours may be moved into the field of view as required. The value of the standard or combination of standards which gives the best match is recorded as the colour of the sample.

#### 3.6.1.1 Procedure

Small quantity of sample was poured into a clean glass cell and the cell was placed inside the Lovibond tintometer at a position where light reflected from a white background passes through the cell containing the sample.

The ray of light was switched on in the instrument and the colour of the sample was viewed. The illumination of the light was viewed in a white background and the colour of the sample was compared with IP standard colours. The results of the observation were recorded depending on which of the standard colour best match as sample colour.

### 3.6.2 Determination of specific gravity

Kerosene has a specific gravity or relative density of 0.80 - .86 at $20^0$C. Specific gravity depends on temp and it decreases when samples are heated.

Generally, kerosene is a high hydrocarbon with specific gravity well below 1.0 and therefore lighter than water. Any water in storage tank will therefore always sink to the bottom where draw for its removal should be located.

### 3.6.2.1. Procedure

The specific gravity bottle was thoroughly washed, cleaned and dried in a hot air oven at $150^0$C and allowed to cool in a desicator. The weight of the bottle was taken using the analytical balance. A clean specific gravity bottle 5ml was filled with sample and the weight recorded. This was poured out, the bottle cleaned, thoroughly and the same volume of water was put into the bottle and the weight taken.

This procedure was applied to each of the treated kerosene.

$$\text{Specific gravity} = \frac{\textit{Weight of sample}}{\textit{Weight of equal volume of water}} \quad\text{..........................} 3.1$$

### 3.6.3 Determination of smoke point

This method describes a procedure of evaluating kerosene in respect of its ability to burn without producing smoke. The sample was burnt in a standard

temperature in which flame height could be varied against a background of a graduated millimeter scale. The smoke point was measured by rising the wick until a smoky flame was produced and then lowering to the point where the smoky tail just disappears. The flame height, measure to the nearest millimeter, was the smoke point of the sample.

### 3.6.3.1. Procedure

Twenty millilitres of the treated sample was introduced into clean, dry oil container at room temperature. The wick tube in the candle was placed and screw home. The candle was inserted into the lamp (the wick was carefully pulled through the tube without twisting). The candle was then lighted and the wick adjusted to that the flame was approximately 10 millimeter high and allowed to burn for five minutes. The smoke point was determined by rising the wick until a smoky flame was produced and then lowered until the smoky tail disappeared. The height of the flame at this point was read in millimeters from the scale. And finally, the oil container from the lamp was then removed and ready for other samples.

### 3.6.4  Determination of flash point

This test method covers the determination of the flash point of petroleum products in the temperature range from 40 to $360^0$C by a manual Pensky – Martens closed cup apparatus. The sample was placed in the cup of the tester and, with the lid closed, heated at a slow constant rate. An ignition source was directed into the cup at regular intervals, until a flash point was detected. That is the lowest temperature at

which application of the ignition source causes the vapour above the specimen to ignite.

### 3.6.4.1. Procedure

Seventy five milliliters of sample was required for each test. The test cup was filled with the test specimen to the filling mark inside of the cup. The temperature of the test cup and test specimen was $30^{o}For$ $18^{0}C$ below the expected flash point. The test cover was placed on the test cup and placed in the apparatus of the assemble. The temperature measure device was inserted into the holder.

The test flame was lighted and adjusted to a diameter of 3.2 to 4.8mm, the heat was then applied in such a rate that the temperature, as indicated by the temperature measuring device, increases 5 to $6^{0}C$ per minutes until a bluish light flash was noticed indicating a flash point on the first application and the temperature at that time was recorded. The test then discontinued and repeated with a fresh test specimen. Before the commencement of the second test, the apparatus must be cooled down to a safe handling temperature, of around $30^{0}C$. The test cover and the test cup were then cleaned for reuse.

# CHAPTER FOUR

## 4.0    RESULTS AND DISCUSSION

This chapter is deals with the results obtained from the experiments carried out and detailed discussion of these results.

## 4.1    Tables for Results

The results are presented in tabular and graphical form under the two different experimental tests carried out.

1)    Total sulfur content in oil

2)    The resulting properties of the refined kerosene

3)    The calculated percentage removal of sulphur content of kerosene

The results of total content of raw kerosene sample shows that the average total sulphur of raw kerosene is equal to 0.3208 weight percent.

### Table 4.1    Total Sulphur content for 10 minutes Stirring

| Percentage Concentrations | First Reading Values | Second Reading values | Third Reading Values | Average Reading Values |
|---|---|---|---|---|
| 95 | 0.1285 | 0.1255 | 0.1251 | 0.1264 |
| 90 | 0.1559 | 0.1576 | 0.1521 | 0.1552 |
| 85 | 0.2079 | 0.2107 | 0.2109 | 0.2098 |
| 80 | 0.2353 | 0.2413 | 0.2434 | 0.2400 |
| 75 | 0.3082 | 0.3129 | 0.3096 | 0.3102 |

## Table 4.2 Total Sulphur Content for 20 Minutes Stirring

| Percentage Concentrations | First Reading Values | Second Reading values | Third Reading Values | Average Reading Values(wt%) |
|---|---|---|---|---|
| 95 | 0.0620 | 0.0536 | 0.0560 | 0.0572 |
| 90 | 0.0704 | 0.0692 | 0.0736 | 0.0711 |
| 85 | 0.1025 | 0.1086 | 0.1083 | 0.1065 |
| 80 | 0.2359 | 0.2336 | 0.2343 | 0.2346 |
| 75 | 0.2659 | 0.2670 | 0.2726 | 0.2685 |

## Table 4.3 Total Sulphur Content for 30 Minutes Stirring

| Percentage Concentrations | First Reading Values | Second Reading values | Third Reading Values | Average Reading Values(wt %) |
|---|---|---|---|---|
| 75 | 0.0471 | 0.0474 | 0.0494 | 0.0480 |
| 90 | 0.0587 | 0.568 | 0.0571 | 0.0575 |
| 85 | 0.0997 | 0.0988 | 0.0925 | 0.0971 |
| 80 | 0.1593 | 0.01622 | 0.1582 | 0.1599 |
| 75 | 0.1451 | 0.1411 | 0.1461 | 0.1441 |

## Table 4.4 Total Sulphur Content for 40 Minutes Stirring

| Percentage Concentrations | First Reading Values | Second Reading values | Third Reading Values | Average Reading Values ( wt %) |
|---|---|---|---|---|
| 95 | 0.0476 | 0.0443 | 0.0479 | 0.0466 |
| 90 | 0.0597 | 0.0659 | 0.0586 | 0.0614 |
| 85 | 0.0853 | 0.0849 | 0.0907 | 0.0870 |
| 80 | 0.2593 | 0.2596 | 0.2547 | 0.2579 |
| 75 | 0.1820 | 0.1897 | 0.1966 | 0.1915 |

## Table 4.5 Total Sulphur Content for 50 Minutes Stirring

| Percentage Concentrations | First Reading Values | Second Reading values | Third Reading Values | Average Reading Values (wt %) |
|---|---|---|---|---|
| 95 | 0.0451 | 0.0456 | 0.0448 | 0.0452 |
| 90 | 0.0540 | 0.0600 | 0.0578 | 0.0573 |
| 85 | 0.0925 | 0.0918 | 0.0936 | 0.0926 |
| 80 | 0.2418 | 0.2428 | 0.2519 | 0.2455 |
| 75 | 0.2714 | 0.2798 | 0.2738 | 0.2750 |

## Table 4.6 Summary of Total Sulphur Content at Various Time and Concs

| Percentage Concentration | 10 minutes | 20 minutes | 30 minutes | 40 minutes | 50 minutes |
|---|---|---|---|---|---|
| 95 | 0.1246 | 0.0572 | 0.0480 | 0.0466 | 0.0452 |
| 90 | 0.1552 | 0.0711 | 0.0575 | 0.0614 | 0.0573 |
| 85 | 0.2098 | 0.1065 | 0.0971 | 0.0870 | 0.0926 |
| 80 | 0.2400 | 0.2346 | 0.1599 | 0.2579 | 0.2455 |
| 75 | 0.3102 | 0.2685 | 0.1441 | 0.1915 | 0.2750 |

For ease of analysis, the results in Table 4.6 are shown in Fig. 4.1

## Percentage Total Sulphur Content Removed

The percentage total sulphur content removed could be obtained or calculated below

as:    Raw kerosene value        =        0.3208 weight percent

For 75% value        =        0.3102wt%

% total sulphur content removal = $\dfrac{0.3208 - 0.3102}{0.3208} *100$        =        3.304wt%

wt% total sulphur content removal at 75% in 10 minutes = 3.304wt%

The procedure remains the same for the remaining percentage concentrations at

various interval of times as could be seen on the Table 4.7.

**Table 4.7 Results of the Percentage Total Sulphur Removal at Various**

**Concentrations (%) and Times (minutes)**

| Percentage Concentration | 10 minutes | 20 minutes | 30 minutes | 40 minutes | 50 minutes |
|---|---|---|---|---|---|
| 95 | 60.598 | 82.170 | 85.037 | 85.474 | 85.910 |
| 90 | 51.621 | 77.837 | 82.076 | 80.860 | 82.138 |
| 85 | 34.601 | 66.802 | 69.732 | 72.880 | 71.35 |
| 80 | 24.187 | 26.870 | 50.156 | 19.607 | 23.473 |
| 75 | 3.304 | 16.303 | 55.081 | 40.305 | 14.277 |

For better analysis of the results, Table 4.7 is presented as a graph in Fig. 4.2.

**Table 4.8 Results for Colour Determination at various concentrations (%) and Times (Minutes)**

| Sample | IP Standard Glass | Colour |
|---|---|---|
| Raw Kerosene | 2.5 | Prime White |
| 95/50 min | 0.5 | Water White |
| 95/30 min | 0.25 | " |
| 95/10 min | 0.25-0.5 | " |
| 90/50 min | 0.25 | Water white |
| 90/30 min | 0.25 | ,, |
| 90/10 min | 1.25 | Super fine white |
| 85/50 min | 0.5 | Water white |
| 85/30 min | 0.25 | ,, |
| 85/10 min | 0.25 | ,, |
| 80/50 min | 0.5 | Water white |
| 80/30 min | 0.25 | " |
| 80/10 min | 1.25 | Super fine white |
| 75/50 min | 0.5 | Water white |
| 75/30 min | 0.25 | " |
| 75/10 min | 0.25 | " |

## Table 4.9 Specific Gravity of Treated Kerosene

| Acid conc.% | 50 minutes | 30 minutes | 10 munites |
|---|---|---|---|
| 95 | 0.8255 | 0.7851 | 0.8532 |
| 90 | 0.8489 | 0.8383 | 0.8532 |
| 85 | 0.8383 | 0.8489 | 0.8319 |
| 80 | 0.8383 | 0.8404 | 0.8362 |
| 75 | 0.8553 | 0.8553 | 0.8191 |

Raw kerosene = 0.8617

## Table 4.10 Smoke Point of Treated Kerosene in milliliter

| Percentage Concentration | 10 minutes | 20 minutes | 30 minutes | 40 minutes | 50 minutes |
|---|---|---|---|---|---|
| 95 | 16.0 | 18.20 | 20.40 | 22.70 | 25.00 |
| 90 | 13.80 | 15.80 | 17.80 | 19.80 | 21.90 |
| 85 | 12.00 | 13.70 | 15.40 | 17.20 | 19.00 |
| 80 | 10.80 | 12.10 | 13.30 | 14.60 | 15.90 |
| 75 | 10.00 | 10.75 | 11.50 | 12.22 | 13.00 |

Raw kerosene = 9.00mm

## Table 4.11 Flash point of Treated Kerosene in Degree Fahrenheit.

| Percentage Concentration | 10 minutes | 20 minutes | 30 minutes | 40 minutes | 50 minutes |
|---|---|---|---|---|---|
| 95 | 129.20 | 129.64 | 130.08 | 130.52 | 131.00 |
| 90 | 126.50 | 125.95 | 127.45 | 127.91 | 128.40 |
| 85 | 123.80 | 124.24 | 124.70 | 125.14 | 125.60 |
| 80 | 120.20 | 120.64 | 121.10 | 121.54 | 122.00 |
| 75 | 116.60 | 117.04 | 117.50 | 117.94 | 118.40 |

Raw Kerosene = $45^{0}C \longrightarrow 113^{0}F$

$^{0}F = 1.8(^{0}C) + 32.$

## 4.2 Discussion of Results

This section deals with detailed discussion of the results.

### 4.2.1 Effect of acid concentration on total sulphur content of the kerosene

The results in Table 4.7 are expected because at the time the highest sulphur removal occurs, acid with higher concentration reacts with more sulphur than those with lesser concentration. Therefore the highest sulphur removal increases with concentration of acid. The Table also shows that acid concentration below 90 percent at 10 minutes did not give much sulphur removal. Similarly, the acid concentration below 85 percent at 20 and 50 minutes also gives little sulphur removal. The effects may be due to amount of water used during acid preparation i.e the lower the acid concentration, the higher the amount of diluents.

However, it can't be noticed from the result that the highest sulphur removal for 80 percent was less than 75 percent. Also in addition to acid concentration, no appreciable amount of sulphur compounds removed occurs below 90 percent at 10 minutes, 80 percent at 30 minutes and below 75 percent at 50 minutes. This is expected because literature has mentioned that below 93 percent, for the mixture of acid and kerosene, reactions are reversible leading to poor removal of sulphur compounds. Besides below 93% acid strength, the acid may have slight reaction on the sulphur on the sulphur compounds (Nelson, 1954). This indicates that the result is well correlated because it agrees with the literature findings

### 4.2.2 Effect of time on total sulphur removal from kerosene

From Table 4.7 the acid concentration of 75 percent at different times showed that the highest percentage removal of total sulphur from kerosene occurred at 30 minutes. The same result was also obtained for 80 percent. However, for acid concentration for 85 and 90 percent, the highest percentage removal occurred at 40 and 50 minutes respectively and finally for 95 percent acid concentration, the highest removal of sulphur occurred at 50 minutes.

The results also show that the time at which the maximum sulphur removal occurs increases with concentration. This is also expected because the contact time between the sulphur compounds and the reacting sulphuric acid increases with concentration of the acid, therefore acid with higher concentration will give the maximum sulphur removal in a shorter time. The results obtained above are within acceptable standard limits of 3 to 40 minutes for kerosene treatment (John, 1959).

Total sulphur being solube in 75 – 93% acid reaction (Erich, 1988). However, it can be noticed from the results that the highest sulphur removal for 80 percent is less than that of 75 percent. This may be due to human error while carrying out the laboratory analysis.

### 4.2.3 Effect of acid concentration used on colour

From Table 4.8, colour was improved as a result of acid treatment as the time for treatment was increased from 10 to 50 minutes. This is expected because the greater the amount of sulphur compound removed the brighter t he colour of the treated sample. Hence the colour serves as an indication of the thoroughness of the treatment process.

In commercial applications, it is important for kerosene to be an extra – white colour (water – white on the Saybolt scale) but this property has no special practical importance form the quality point of view. The colour of kerosene may change considerably during its storage and transport. Laboratory tests were performed on kerosene to estimate the tendency of this product to change colour. It was discovered that the charge in colour was principally caused by the presence, even though only in traces, of nitrogenous and phenolic bases.

Basically, colour of treated samples obtained was found to improve from prime white to water white for most samples. However, it could be noticed that for sample 80/10 minutes and 90/10 minutes, the colour improvement was from superfine white to water white. The discrepancy may be due to improper contacting of the kerosene with acid inside the beaker. Nevertheless, the overall results are within the acceptable

limits of the standard specification for kerosene which is prime white to water white on the Saybolt chrome (John, 1959).

### 4.2.4  Effect of acid concentration used on specific gravity

The specific gravity of untreated and treated kerosene are shown in Table 4.9. All the results showed that the specific gravity of the treated sample was less than that of the untreated sample. This confirmed that compounds of sulphur have actually been removed. However, samples treated with acid concentration of 95 percent at 50 minutes gave the best result in conformity with acceptable literature value (Enterprises, 2006).

### 4.2.5  Effect of acid concentration used on smoke point

The smoke point of untreated and treated kerosene samples are shown in Table 4.10. All the results obtained showed that the smoke that the smoke point values of treated samples were higher than that of untreated sample, which confirmed that sulphur compounds have actually been removed. It is considered that kerosene is good when its smoke point is above 25mm. When it is below 18mm, it is considered as a low quality product. The values obtained for acid concentration of 95 and 90 percent at 30 to 50 minutes and 40 to 50 minutes and finally, for acid concentration of 85 percent at 50 minutes are in accordance with KRPC test certification. The sample treated with acid concentration of 95 percent at 40 to 50 minutes gave the best results (Enterprise, 2006).

### 4.2.6 Effect of acid concentration used on flash point

The flash point of untreated and treated kerosene samples are shown in Table 4.11. All the results obtained showed that the flash point values of treated samples are more than that of untreated sample. This confirmed that compounds of sulphur have actually been removed. All the results are in accordance to the specification of test certification of KRPC with minutes. And maximum of 131 degree Fahrenheit at 95 percent concentration in 50 minutes (Enterprise, 2006).

# CHAPTER FIVE

## 5.0   CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommadations ca be drawn from this work.

## 5.1   Conclusions

The kerosene desulphurization was carried out using different concentrations of tetraoxosulphate (VI) acid and times. The highest removal of sulphur was achieved within the contact time of 30 to 40 minutes (John, 1959).

The results confirmed that sulphur compounds are slightly soluble in acid concentration of less than 93 percents (Kalichersky and Stranger, 1933). But at high acid concentration, they are soluble and hence can be removed by tetraxosulphate (VI) acid of 93 percents and higher.

The colour of the treated samples was found to improve from prime white to water white for most samples, except samples 90/10 minutes and 80/10 minutes which were super fine white (Britain, 1975).

For specific gravity, the treated samples showed the best results with tetraoxosulphate (VI) acid of 95 percent at 50 minutes treatment (Enterprise, 2006)

Smoke point showed best results with acid concentration of 95 percent at 40 to 50 minutes (Enterprise, 2006).

Finally, for Flash point, the best result showed at acid concentration of 95 percent in 50 minutes (Enterprise, 2006).

## 5.2    Recommendations

From the investigations carried out the following recommendations are made, which if properly implemented will help to improve the effectiveness and standardization of the treated kerosene quality.

1.    For health problems such as impaired eye sight associated with the use of kerosene, treated kerosene should be used to avoid causing eye irritation.

2.    This project work is recommended for industrial use only where cost is not the overriding factor. However, the overall cost of production could be reduced by (a) recovery of tetraoxosulphate (VI) acid used. This can be achieved from the sludge by mixing with water and filtering out the water and bleaching with activated carbon or charcoal. The acid could then be concentrated back and recycle if so desired. (b) selling the recovered acid from (a) as a by product for wet cell battery.

3.    Determination of mercaptan contents and percentage removal should be carried out using potentiometric titration method.

4.    Characteristics of treated kerosene like distillation recovered at 200 degree centigrade, copper corrosion (3 hours at 50 degree centigrade) and char value should be determined.

5.    Other methods for deodorizing kerosene like caustic treatment, catalytic treatment, hydrogenation and oxidative sweetening method should be used for further work.

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# APPENDICES

## A. OPERATING CONDITIONS FOR DESULPHURIZATION OF KEROSENE

| | |
|---|---|
| Contact time: | 10 – 50 minutes |
| Acid concentration: | 75 – 95 minutes |
| Acid consumption: | 4:1 |
| Contact pattern: | Batch process |

## B    FORMULAR FOR ACID PREPARATION

 Vol of original liquid required + X = % strength of original liquid

$$100+5$$

Where X is the volume of the diluents (Idehen, 1990)

Example:

For a liquid of 85% solution strength to be prepared from a 96% strength original liquid.

$$\frac{85 + X}{100} = \frac{96}{100}$$

$$100(85 + X) = 96 \times 100$$

$$85 + X = 96$$

$$X = 96 – 85 = 11cm^3 \text{ Diluent.}$$

## C.    THE PROFILE MASS OF TOTAL SULPHUR CONTENT WITH DIFFERENT CONCENTRATED TERAOXOSULPHATE (VI) ACID IS SHOWN IN FIGURE.

4.1

D.    THE PROFILE FOR PERCENTAGE OF TOTAL SULPHUR REMOVAL WITH DIFFERENT CONCENTRATED TETRAOXOSULPHATE (VI) ACID IS SHOWN IN FIG. 4.2

E.    RANGES FOR COLOUR DETECTION

Water white = 0.2 – 1.0

Superfine white = 1.25 – 2.0

Prime white = 2.25 – 3.0

Standard white = 3.5 – 4.0

F.    Specific Gravity = $\dfrac{\text{weight of sample}}{\text{weight of equal volume of water}}$

Raw kerosene = 4.05g

Water = 4.70g

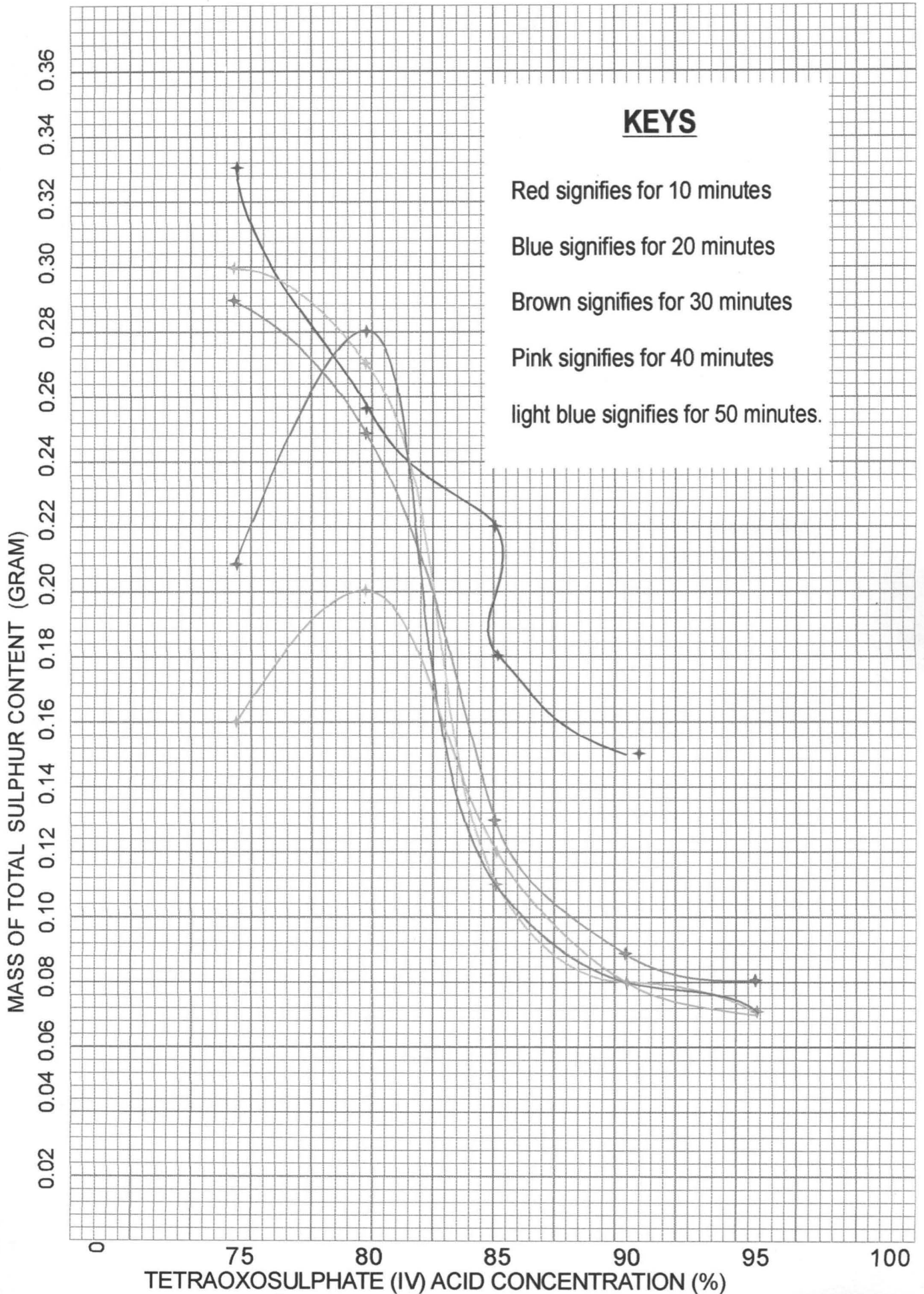Therefore specific gravity of raw kerosene = $\dfrac{4.05}{4.70}$ = 0.8617

Fig. 4.1 The Profile of Mass of Total Sulphur Contents With Different Concentrated Tetraoxosulphate (VI) Acid
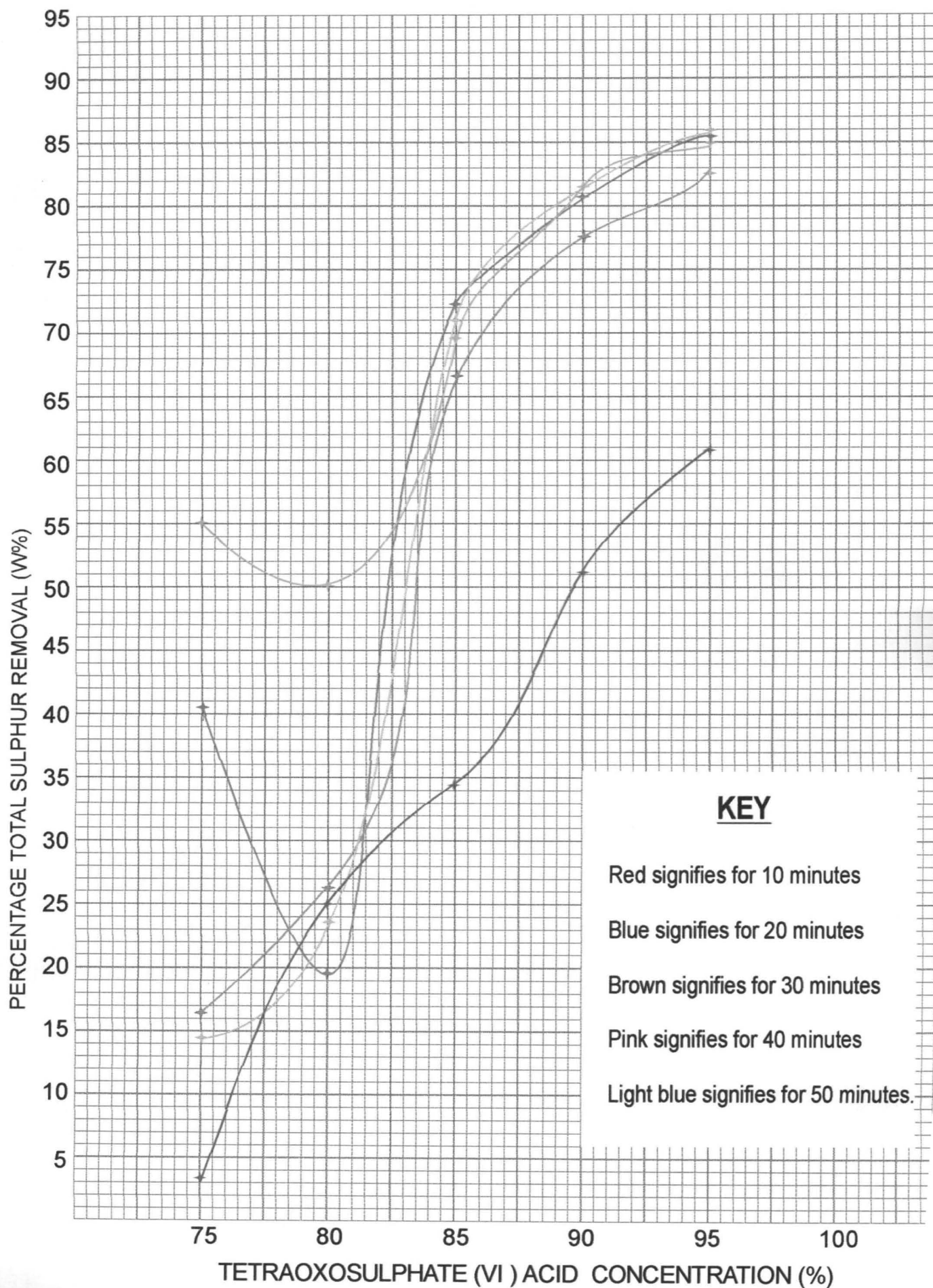
Fig. 4.2 The Profile of Percentage in Total Sulphur Removal with Different Concentrated Tetraoxosulphate (VI) Acid.

KEY

Red signifies for 10 minutes

Blue signifies for 20 minutes

Brown signifies for 30 minutes

Pink signifies for 40 minutes

Light blue signifies for 50 minutes.