DESULPHURIZATION OF HEAVY CRUDE OIL USING SOLVENT EXTRACTION METHOD

BY

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2005/21781EH

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A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA NIGERA.

IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF BACHELOR OF ENGINEERING (B. ENG) DEGREE IN CHEMICAL ENGINEERING

NOVEMBER 2010.

DECLARATION

I OKOPI EMMANUEL SOLOMON declared that this project report entitled "desulphurization of heavy crude oil using extraction method" is carried out by me under the supervision of Engr. A. D. Mohammed No part of this project was presented for another degree or diploma elsewhere at any institution to the best of my knowledge.

OKOPI EMMANUEL SOLOMON		23/11/10
Name of student	**Signature**	**Date**

CERTIFICATION

This project report entitled Desulphurization of heavy crude oil using solvent extraction method by Okopi Emmanuel Solomon (2005/21781EH) meets the requirements for the award of the bachelor of Engineering (B. Eng.) degree in Chemical Engineering. Federal University of Technology, Minna.

24th/11/2010.

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Name and Signature

Date

DEDICATION

This project work is dedicated to God Almighty, my loving parents and my beloved late sister Grace Abahi Okopi.

ACKNOWLEDGEMENT

I will first of all give my thanks to God Almighty, for his infinite mercy and blessings bestowed upon me. My warm appreciation goes to my parents Mr. and Mrs. Solomon Owoicho Okopi for their love and care showered on me. Engr. Solomon Ocheola Okopi, what could I have done without your love and support? You are like a diamond in the midst of Gold, you are my idol.

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Mr. Ali Ahmed Mohamed, this acknowledgement will not be complete without mentioning you name, you are a brother from another mother, thanks for your love and support.

To all academic and non-academic staff of the department of chemical engineering, thank#s for impacting this great knowledge on me. To all my lovely brothers and sisters, thanks for been there for me. To all my course mates, it's nice working with you fellas, I will miss you all.

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My loving and caring neighbors who show love and care on me in so many ways, you guys are really God sent.

Finally, to the beginner, the sustainer, the provider and the overseer of everything in life, the Lord Almighty, I will worship you forever.

ABSTRACT

Generally, it is well known that sulphur compounds are undesirable in refining process as it can cause several corrosion in pipeline, and refining equipment which also cause some environmental pollution. High sulphur content crude oil is treated by mixing methanol as a solvent with a sulphur containing crude oil for a predetermind period of time allowing the mixture to separate so as to form a sulphur – rich solvent contain liquid phase, and a crude oil phase of lowered sulphur content. at the end of this process the sulphur containing compound in the crude oil is reduced by several percentage, depending on the following ratios 1:1, 2:1, 3:1, without a significant loss of crude oil volume.

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Chapter One

1.0 INTRODUCTION

Heavy crude oil is any type of oil which does not flow easily. It is referred to a "heavy" because it's density or specific gravity is higher than that of light crude oil. Heavy crude oil has been defined as any kind of liquid petroleum with an API gravity less than 20^6, meaning that it's specific gravity is greater than 0.933 (Dusseault, 2001).

However, such crude contain sulphur, typically in the form of organic sulphur compound. The sulphur content and the API gravity are two properties which have a great influence on the value of crude oil. The sulphur content is expressed as a percentage of sulphur by weight and varies from less than 01 % to greater than 5 % depending on the type and source of crude oils. Sulphur compounds exist in various forms and can be classified into four main groups: mecaptans sulphides,disulphides, and thiophenes. It is well known that the sulphur compounds are undesirable in refining process as they tend to deactivate some catalyst used in crude oil processing (Abdullah, 2004).

Sulphur in crude oil exist in two forms: the first is termed as "active sulphur" which can react with metal directly and the second is "inactive sulphur" which can not directly react with metals. Active sulphur includes elemental sulphide, carbon disulphide thiophene (TH), and so on. It is fund that in fluid catalytic cracking (FCC) gasoline, more than 90 % sulphur exists in the form of thiophenes and it's derivative; whicl in diesel, thiophenic sulphur accounted for 80 % of the total sulphur, and benzothiophere (BT) and dibenzothiophene (DBT) accounted for more than 70 % of this thiophenic category. As a result, sulphur of thiophenes removal is the main desulphurization for the study.

However, a lot of processes have been in used over the years to reduce the sulphur content of the fuels. The most widely used process is the convectional catalytic hydrodesul phurization (HDS) even though efforts have also been made in utilizing other process like oxidative desulphurization and biodesulphirization. Mean while the major problems encountered with the use of this HDS involve huge investment requirement and its inability to remove refractory organosulpur compounds that are statically hindered in higher boiling range fuels like diesel fuel. Even in applying HDS to the lower boiling range fuel like gasoline feed stock to achieve low sulphur levels will saturate a significant portion of olefins in the gasoline thereby substantially lowering the octane number.

In addition, the current requirement of sulphur level in the transformation fuels has shifted the attention of crude oil refiners from the convectional HDS to other process. In recent years, industry has sought to develop less expensive desulphurization alternatives in hydroteating one of such alternatives that have been successful in meeting this requirement is the oxidative/extraction method of desulphurization which uses organic or inorganic peroxides as oxidants.

Previous study have shown that, contacting a petroleum fuels to an oxidant converts the organosulphur nitrogen compounds in the fuels into sulphones. (or sulphoxides) and organic nitric oxides, respectively. These polar organic oxides can be removed from the fuels by solvent extraction and or adsorption. More so, oxidative desulphurization can easily oxidize and remove thiophenic sulphur compounds which cannot be readily treated by HDS due to the stereo hindrance effect around the sulphur atom in the molecule for example, it has been reported that the activity of thiophenic compounds in responding of HDS treatment follows the sequence below: DBT (D.benzothiophene) >4-MDBT (4 – methyl dibenzothiophene) > 4, 6 DMDBT (4,6

– dimethl dibenzothiophene). In contrast, it has been reported that the activity of thiophenic compounds in responding to oxidative treatment is just the opposite, namely: 4,6 – DMDBT > 4 MDBT > DBT. These study suggest that oxidative desulphurization can be effective in removing the most difficult residual sulphurs from hydrotreated oil to yield ultra – low sulphur products.

1.1 Aim of the Research

The aim of this research is to reduce sulphur content in heavy crude oil.

1.2 Objectives of the Research

The objectives of this research areas as follows;

i. To collect samples of heavy crude oil which will be analyze to know the sulphur composition.
ii. To apply the suitable solvent i.e methanol, in different ratio of solvent to crude oil at room temperature.
iii. To seperate the solvent from the crude oil sample and analyze the crude oil sample to make sure there is reduction in sulphur composition.

1.3 Scope of Research

This research work covers the desulphurization of heavy crude oil by the use of methanol as solvent and the analysis of desulphurised crude oil by the use of sulphur in oil analyzer.

1.4 Problem Statement

It is well known that the sulphur compounds are undesirable in refining process as they tend to deactivate some catalysts used in crude oil processing. Sulphur compounds can cause several corrosion problems in pipeline, pumping and refining equipment, as well as the premature failure of combustion engines and poisoning of the catalytic converters that are used in automotive engines. Today, the strongest motivation for the reduction of sulphur in fuels is due to environmental regulation which is imposing stringent limits for sulphur levels in transportation fuels. Sulphur responsible for the emission of sulphur oxides (SOx) resulting from the combustion of fuels used in transportation. High sulphur content is also responsible for the particulate emissions from trucks and buses. It also preludes the used of advanced after treatment system which cannot work with such sulphur content;

1.5 Justification of the Research

Hydrotreating techniques of desulphurization which is mostly practice by refiners is generally cost intension and ineffective, possibly some sulphur containing compounds are not completely substituted by hydrogen. The completion of the this research will serve as a measure for desulphurization of crude oil that minimizes polution and equipment corrosion due to sulphur content in crude oil.

Chapter Two

2.0 LITERATURE REVIEW

2.1 Crude Oil

Crude oil is the term for "unprocessed" oil, the substance that comes out of the ground. It is also known as petroleum. Crude oil is a fossil fuel meaning that it was made naturally from decaying plants and animals living in ancient seas millions of years ago most places you can find crude oil were once sea bed. Crude oil vary in colour from clear to tar-black, and in viscousity, from water to almost solid. Crude oil are such a useful starting point for so many different substances because they contain hydrogen s. hydrocarbons are molecules that contain hydrogen and carbon and in various lengths and structures from straight chains to branching chains to rings (www.oilprice.org, 2009).

2.1.1 Composition of Crude Oil

Crude oil is not a uniform material, its composition can vary not only with the location and age of the oil field but also with the depth of the individual well. Two adjacent walls may produce oils with different characteristics. On the molecular basis, crude oil is a complex mixture of hydrocarbons with small amounts of organic compounds containing sulphur, oxygen and nitrogen as well as some metallic compounds. The hydrocarbon content may be as high as 97 % lighter paraffinic crude oils as low as 50 wt% in heavy crude oil (James, 1999).

2.1.2 Chemical Composition of Crude Oil

Generally, crude oil comprises of hydrocarbon component non-hydrocarbon components, and organometalic compounds and inorganic salts. However, this general classification is inadequate in determining crude oil's behaviours during repining operations. And understanding of the chemical composition of any crude oil can lead to an understanding of the chemical aspect of processing it (Sami, 2000).

2.1.2.1 *Hydrocarbon components*

The major constituents of most crude oils are hydrocarbon compounds: all the classes of hydrocarbon are present in the crude mixture except alkenes and alkyner whose presence is not certain. This may indicate that crude oils originated under a reducing atmosphere (Sami 2000).

Crude oils are classified based on their hydrocarbon components as paraffins, naphthenes, and aromatics (Sami, 2000).

Paraffins are saturated hydrocarbons with straight or branched chains, but no any rang structure. The part of parafins in crude oil varies with the type of crude but within and one oil the proportion of paraffinic by drocarbons usually decreases with increasing molecular weight of it's fractions. More so, hydrocarbons can be in forms of normal parafins which are branched – chain parafins (Sami, 2000).

Napthenes are cycloparaffin hydrocarbon. The content of naaphthenes in crude oil varies up to 60 % of the total hydrocarbons they are represented in all fractions in which the constituent molecules contain more than five carbon atmos. The principle structural vibration of naphteness is the number of rings in the molecules. The mono – and dicyclic nappthenes are generally the major types of cyclopraffins in the lower boiling fractions with boiling point or molecular weight increased by the presence of alkyl chains (James, 1999).

Aromatic hydrocarbons are common to all crude oils these is a general increase in the proportion of aromatic hydrocarbons with increasing molecular weight. All hydrocarbon compounds that have aromatic rings with the same molecule are classified as aromatic compounds (James, 1999).

The presence of unsaturated hydrocarbons like olefins has been under dispute for many years. Nevertheless, there is evidence that few crude oils contain olefins up to 3 wt% (James, 1999).

2.1.2.2 *Non-Hydrocarbon components*

Crude oil contains organic non-hydrocarbon components, mainly sulphur, nitrogen and oxygen – containing compounds. These constituents appear through out the entire boiling range of the crude oil but tend to concentrate mainly in the heavier fractions and in the non-volatile residues. Traces of metallic compounds are also found in all cruds. The presence of these impurities is harmful and may cause problems to certain catalytic processes. Fuel having high sulphur and nitrogen levels cause pollution problems in addition to the corrosive nature of their oxidation products these non-hydrocarbons components may also impart some characteristics in the finished products such as discoloration, lack of stability on storage, or a reduction in the effectiveness of organic lead antiknock additives (James, 1999).

2.1.2.3 *Properties of crude oil*

The properties of crude oil differ according to the origin and the ratio of the different components in the mixture. Lighter crudes generally yield more valuable light and middle distillates and are sold at higher prices. Crudes containing a high percent impurities, such as sulphur compounds, are less desirable than low sulphur crudes because of their corrosive ability and the extra treating cost (Sami, 1994).

The physical and chemical properties of crude oils and the yields, and the properties of the products prepared from them vary considerably and are dependant on the concentration of the various types of hydrocarbons and minor constituents present. Crude oil exhibit a wide range of physical properties and several relationships can be made between various physical properties. Whereas the properties such as viscosity, density, boiling point and colour of petroleum may vary widely (James, 1999).

***Density and specific gravity*:** Crude oil and their products are characterized both by their absolute density, generally called density which is measured in g/cm^3 or kg/m^3 and their specific gravity (relative density). The latter is a dimensionless quantity equal to the ratio of the mass of petroleum or its product to that of pure water at 4 ^0C taken in the same volume as the petroleum or its product (Rasina, *et al.,* 1988). The density and specific gravity of crude oils are two properties that have found wide use in the industry for preliminary assessment of the character of the crude oils (James, 1999).

Viscosity: Viscosity is the force in dynes required to move a plane of 1 cm^2 area at a distance of 1cm from another plane of 1 cm^2 area through a distance of 1 cm in 1 s. In the centimeter gram second (cgs) system, the unit of viscosity is the poise or centipoises (0.01 p) (James, 1999).

The other common terms are kinematic viscosity, dynamic viscosity and fluidity. The kinematic viscosity is the dynamic viscosity divided by the specific gravity, and the unit is stock (cm^3/s) reciprocal of viscosity (James, 1999).

Volatility: The volatility of a liquid or liquid gas can be defined as it's tendency to vaporized, that is to change from the liquid to the vapour or gaseous state. Because one of the three essentials for combustion in a flame is that the fluid is in gaseous state volatility is a primary characteristic of liquid fuels. The vapourise tendencies of petroleum and it's products are the basis for the general characterization of liquid petroleum fuels (James, 1999).

Flash points: The vapours of all combustible substances when mixed with air from explosive mixtures that ignite, if a foreign source of flame is present depending on the concentration of the vapour of a combustible liquid or gases. The air, lower and upper explosive are distinguished (Rasina *et al.*, 1988). The lower limit corresponds to the minimum concentration of fuel vapour in the mixture with air at which it flashes when a flame is brought up to it. The upper explosive limit corresponds to the maximum concentration of fuel vapour in the mixture with air above which no flash occurs because of the lack of oxygen. The narrower the explosive limits, the safer is a given fuel, and the broader they are, the more explosive is the fuel (Rasina *et al.*, 1988).

Pour, cloud and freezing points: Crude oil and its products do not have a definite temperature transition from one state of aggregation to another. When the temperature drops, part of the components of this complicated mixture gradually become more viscous and less fluid, while the dissolved solid hydrocarbons can separate in form of precipitate or crystals. This process has a very adverse effect on handling and transportation operations and on the use of petroleum product at low temperatures. Therefore, unlike the melting point of crude oil and its products which have limited usefulness, solidification has received attention in petroleum chemistry (Rasina *et al.*, 1988).

Specific heat capacity: Specific heat is the quality of heat required to raise a unit mass of material through one degree of temperature. Specific heats material are extremely important engineering quantities in refinery practice because they are used in all calculations on heating and cooling petroleum products. The specific data for most purpose may be summarized by the general equation.

$$c = \frac{1}{d(0.388 + 0.00045t)} \qquad ------(2.1)$$

Where C is the specific heat at t °F of oil whose specific gravity 60/60 °F is d, this, specific heat increases with temperature and decreases with specific gravity (James, 1999).

Thermal conductivity: The thermal conductivity characterizes the process of heat propagation in a stationary substance due to motion of the molecules, that is to heat transfer, the thermal conductivity k of the hydrocarbon oils (in cgs units) is given by

$$k = \frac{0.28}{d(1 - 0.0054)x10^{-3}} \qquad ------------(2.2)$$

Where d is the specific gravity (James, 1999).

2.2 Sulphur – Containing Compounds

Sulphur compounds are among the most important heteroatom constituent of crude oils, generally, the higher of the crude oil, the higher the sulphur content (James, 1999).

The main part of the sulphur-containing compounds of crude oils has a high molecular mass and a high boiling point. This is why from 70 to 90 % of all the sulphur-containing compounds are concentrated in the fuel oil and tar (Rasina *et al.,* 1988).

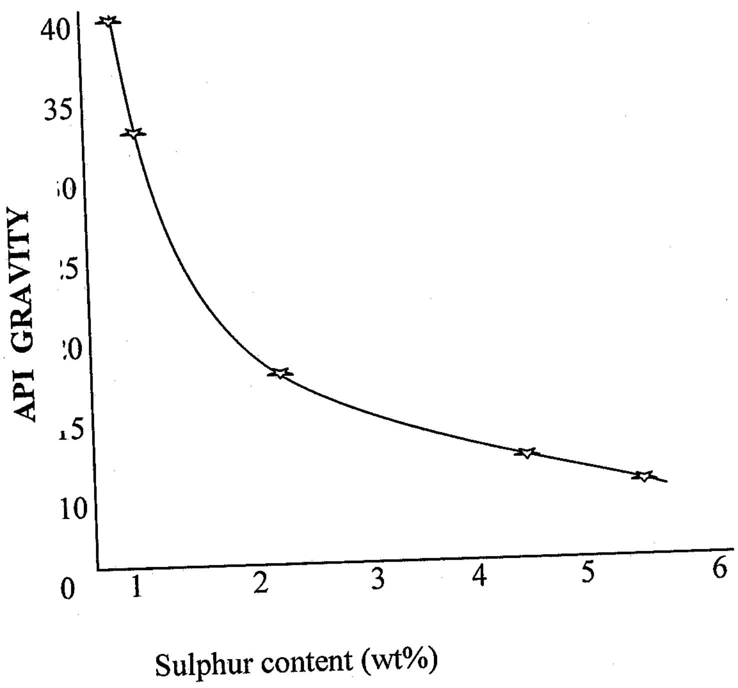
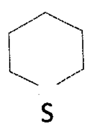
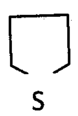
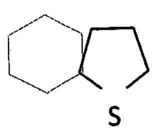
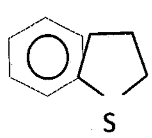
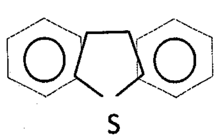
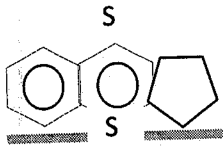


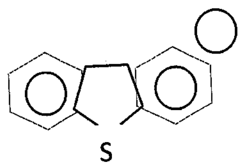
Fig2.1: Relationship between API Gravity and sulphur content.

The general relationship of sulphur content to API gravity the chemical structure of the sulphur – containing compounds of crude oils are quite diverse as shown in Fig. 2.1 (James, 1999 and Rasina *et al.,* 1988). The higher the API gravity of a petroleum or it's fractions, the lower the sulphur content present and vice versa, the statement can be observed in the plot shown in Fig 2.1 above.

Sulphur – containing compounds vary from the simple thiols (R – SH) to the simple sulphides (R – S – R) and the polycyclic sulphides, such as compound with two condensed rings (James, 1999), various thiophenes have also been found from a variety of crude oils. Benzothiophene and it's derivative are usually present in the higher boiling fractions (James, 1999).

Table 2.1: Nomenclature and Type of Sulphur – Containing Compounds.

Sulphur compounds	Nomenclature
R S H	Thiols (mercaptans)
RSA^{I}	Sulphides
	Cyclic sulphur
$RSSR^{I}$	Disulphides
	Thiophanes
	Thiophenes
	Thiocycloalka
	Benzothiophenes
	Dibenzothiophenes
	Naphthothiophenes



Nhthobenzothiophenes

Source: (Mohamed *et al.*,2006)

2.2.1 Effects of Sulphur in Crude Oil

Sulphur – containing compounds in fuels continue to be a major source of environmental pollution. During combustion they are converted to sulphur oxides, which in turn, give rise to sulphur oxy-acids and also contributes to particulate emissions (Grossman *et al.*, 1999). The presence of sulphur compounds in finished petroleum products often produces harmful or toxic effects for example, in gasoline, they are believed to promote the corrosion of engine parts, when especially under winter conditions, when containing sulphur dioxide from the combustion may accumulate in the crank case. In addition, Mercaptans in hydrocarbon solution causes the corrosion of copper and brass in the presence of air and also affect lead susceptibility and colour stability. Free sulphur is also corrosive, as are sulphides, disulphides and thiophenes which are detrimental to octane number response to tetraethyl lead. The mercaptons are very harmful to commercial products because they cause corrosion, especially to non-ferrous metals, promote gum formation when cracking gasoline, and impart an abominable small to petroleum products (Rasina *et al.,* 1988). In diesel fuels, sulphur compounds increases wear and contribute to the formation of engine deposit. Although, high sulphur content can sometimes be tolerated in industrial fuel oils, the situation for lubricating oils is that a high content of sulphur compounds seems to lower resistance to oxidation and increases the deposition of solids (James, 1999).

2.3 Desulphurization Processes

Crude oil desulphurization is the process that removes sulphur and it's compound from various streams during the refining process. Desulphurization process include catalytic hydro-treating and other chemical or physical process such as adsorption (Anonymous, 2006).

According to Martmie *et al.*,(2005), it is said to be the removal of sulphur compounds and particularly chemically-combined sulphur, such as organosulphur compounds, from feed streams to be highly desirable to meet environmental concerns and to prevent potential catalyst deactivation as well as equipment corrosion.

Several processes have been proposed in the past to deal with the problem of removing these compounds from fuels. The most prevalent and common industrial processes and only large scale desulphurization process used to treat liquid fuels in refineries, is that of treating the fuels under high temperature and high pressures with hydrogen in the presence of catalyst. This process is called the conventional catalytic hydrodesulphurization (HDS) and it has receive extensive attention since its original invention in Germany before the second world war (Gore *et al.*, 2008).

Presently, oil desulphurization technology can be broadly divided to two categories, hydrodesulphurization (HDS) and non – HDS (NHDS). One can get hydrogen sulphide when hydrogen adsorbed on catalyst at high temperature and high pressure reacts with sulphur. HDS is a kind of more matured technology, but there are several shortcomings such as a one – time investment, high running costs and needing a lot of hydrogen, all these increase the cost of oil significantly. Non – HDS technology does not use hydrogen source and is in line with the requirements of deep desulphurization, so researchers are now focusing on non – HDS technology consuming techniques and it includes Biodesulphurization, oxidative desulphurization, physical separation and recently ultrasound – assisted oxidative desulphurization (Gaofei *et al.*, 2009).

2.3.1 Hydrodesulphurization (HDS)

Conventional hydrodesulphurization (HDS) with MO-Ni or are widely w – based catalyst used to reduce sulphur content mercaptans, thioethers, and desulphides for example, can be removed using this process. HDS is a process in which a petroleum fraction is heated, mixed with hydrogen, and fed to a reactor packed with a particular catalyst temperatures in the reactor typically range from 600 to 700 ^{0}F. At these temperatures, some of the feed may vapourise depending on the boiling range of the feed and the pressure in the unit.

For heavier feeds, it is common for the majority of the feed to be liquid. Reaction pressure ranges from as low as 500 Psig (34.03 atm) to as high 2500 Psig (170.1 atm) depending on the difficulty of removing sulphur. HDS involves catalytic treatment of fuel with hydrogen to convert the various sulphur compounds to hydrogen sulphide (Mohammed *et al.*, 2006).

2.3.2 Non – Hydrodesulphurization

The non-hydrogen consuming desulphurization studies can be categorized in four techniques; Biodesulphurization, oxidative/extraction, insertion using homogeneous catalyst and physical separation (Mohammed *et al.*, 2006).

2.3.2.1 *Biodesulphurization*

The Biodesulphurization approach has progressed significantly and it has a potential to be implemented on a larger scale. The basis of this approach is to convert the sulphur organic compounds to corresponding sulphoxides or sulphones bio – catalytically. (Mohammed *et al.*, 2006).

Biodesulphurization has been around for years, but has yet to enter a detailed engineering design phase because of the limitation posed by the slow biodegradation process (Mohammed *et al.*, 2006). Typically, organosulphur oxides compounds, such as dibenzothiophene and it's alkylated homologues are oxidized with genetically engineered micros and sulphur is removed as water soluble sulphate salt (Anonymous, 2006).

2.3.2.2 *Oxidative Desulphurization (ODS)*

ODS is a kind of technology using oxidants oxidizing organic sulphur to strong polarity matters, and the reaction products can be separated by absorption or extraction. ODS is operated at atmospheric pressure and the temperature is below 100^0c, so it has mild reaction conditions no needs of hydrogen pressure reactor and special operating technology. ODS can remove nitrogen at the same time, and has high sensitivity, so that the sulphur compounds which are very difficult to remove in HDS can be easily removed by oxidation. So ODS is a promising desulphurization technology as it has low production cost (Gaofei *et al.*, 2009).

ODS is one of the desulphurization approaches that have been successful in the desulphurization of crude oil products. It has been given much interest as an alternative technology for deep desulphurization. The ODS is basically a two – stage process; oxidation, followed by liquid extraction. This was first introduced by Guth and Diaz in 1974 and Guth et al.

in 1975 using nitrogen dioxides as an oxidant followed by extraction with methanol to remove both sulphur and nitrogen compounds from petroleum with stocks (Mohammed *et al.*, 2006).

Solvent extraction technique only has been used in the petroleum industry to remove sulphur and nitrogen compounds from high oil without any pre-treatment of the petroleum feed stocks. The solvent can be recovered and reused through a distillation process. Generally, employing only solvent extraction of petroleum products to remove sulphur creates an associated loss of useful hydrocarbons, in addition to poor sulphur removal which is probably due to the small difference in the polarity between sulphur compounds and other aromatic hydrocarbons (Mohammed *et al.*, 2006).

2.4 Types of Solvents Used

The extraction efficiency depends on the solvent's polarity, which have to be sufficient to remove sulphur compounds. Hildebrand solubility parameter Delta for some solvents liquids with a delta higher than about 22 have been successfully used to extract compounds (Mohammed *et al.*,2006). Examples of polar solvents include those with high values of the Hildebrand solubility parameter deltas as shown below in the table.

Table 2.2: Hildebrand Solubility Table

Solvent	Hildebrand values (delta)
Acetone	19.7
Butyl cellosolve	20.2
Carbon disulphide pyridine	21.7
n – propanol	24.9
n – buthyl alcohol	28.7
Methanol	29.7
Propylence glycol	30.7
Ethylene glycol	34.7

Source: (Mohammed *et al.*, 2006).

Chapter Three

3.0 METHODOLOGY

3.1 Oxidizing The Crude Oil

3.1.1 Materials used for Oxidixing

- One (1) litre of Russian urals crude oil obtained from Kaduna refinery and petrochemical company (KRPC). From the assay of the crude oil, the content of sulphur is 1.12 wt%

3.1.2 Apparatus Used

- Magnetic heater and stirrer with temperature regulator
- Thermometer
- Beakers, measuring cylinder, conical flasks,
- Lagging materials.

3.1.3 Experimental Procedure

A magnetic stirring bar was placed inside a 500 ml conical flask which contains 50 ml of the crude oil, the magnetic stirrer and heater, supplied the heat at a regulated temperature and stirred appropriately so as to enable the sample to oxidise. The set up is shown in Fig. 3.1a,

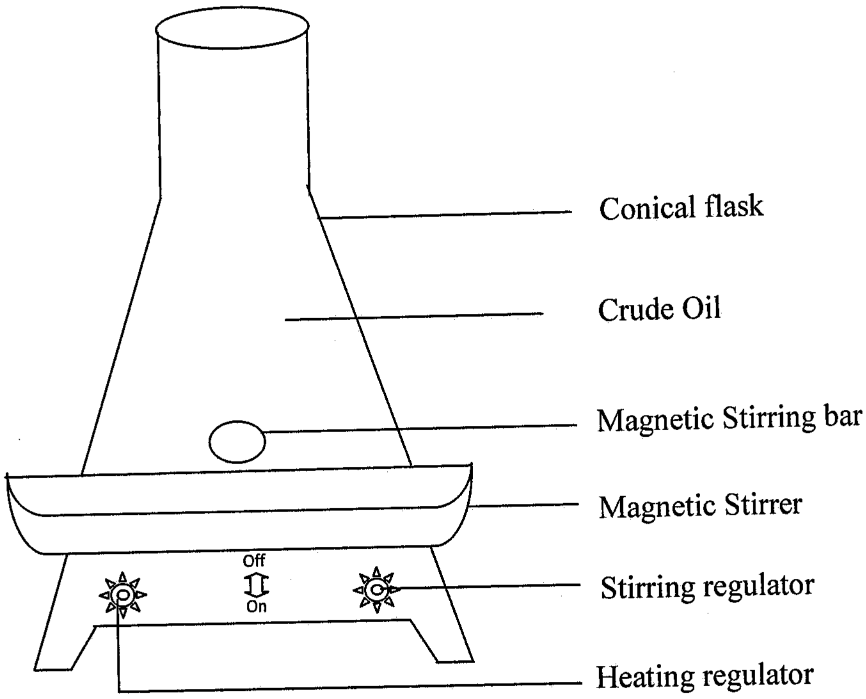


Fig. 3.1 (a): Experimental set up for oxidation process

3.2 EXTRACTION OF SULPHUR

3.2.1 Materials for Extraction

- Two and half (2.5) litres of extraction solvent (methanol)

- Ten (10) litres of water in a laboratory bucket

3.2.2 Experimental Apparatus

- separating funnel.

- Sample bottles,

- Retort stand,

- Beakers, measuring cylinder, conical flasks,

3.2.3 Experimental Procedure

The oxidized crude oil sample was mixed with methanol as the extraction solvent at a crude oil to solvent ratios which are 1:1, 1:2, 1:3 and allow to seperate for 2 hours to ensure complete phase separation so as to form the oil rich phase and the solvent rich phase which is been drain as the raffinate. See set up in Fig. 3.1b

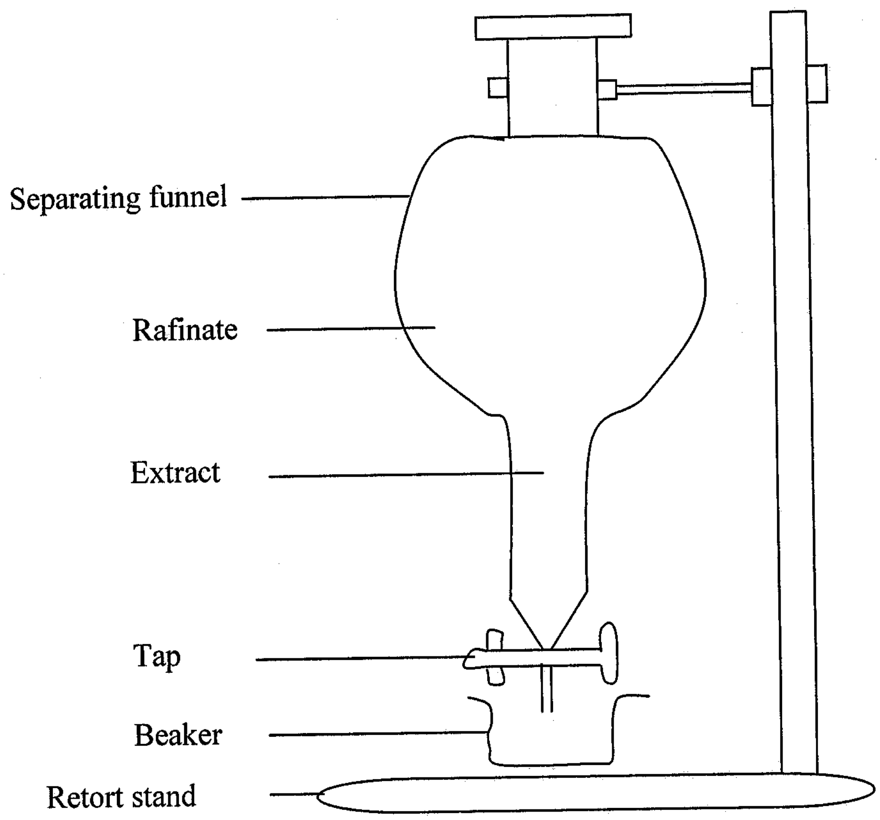


Fig 3.1 (b) Experimental set up for extraction process

3.3 Procedure for Sulphur Content Determination

The sulphur content was determined with the help of a sulphur-in-oil analyzer which employs energy dispersive X – ray florescence spectroscopy technique. The analyzer is equipped with X – ray source, sample holder, disposable sample cells, inner and outer frame of the cell are transparent plastic films.

The sample cell was filled with the sample above a minimum depth, this was done by filling the sample cup to at least three quarter of the sample cell (10 ml capacity) and covered with X- ray transparent plastic film window. The power switch located at the rear of the analyzer was switched on to display the "READY" memon the screen and light up the X – ray lamp within seconds. The analyzer was then set using the soft keys on the panel to give three different readings at 30 seconds intervals.

The average of these three readings (in weight %) was taken as the sulphur content of the sample.

Chapter Four

4.0 RESULTS AND DISCUSSIONS

In chapter four and five, each of the desulphurized crude oil and it's fraction will be denoted by the ratio of the actual amount of the extraction solvent requirement during extraction for example, "1:2" represents a desulphurized sample obtained using twice the stoichiometric amount of the extraction solvent.

4.1 Experimental Results

Table 4.1: Result of Material Balance

Sample	Volume (ml)	Volume (ml)	Volume (ml)
Unreactected crude	50	50	50
Solvent (methanol)	50	100	150
Crude after desulphurization	53	48.6	445
Rafinate	46.3	100.9	155
Loss	0.7	0.5	0.5

4.1.2 Analysis of Crude Oil

The sulphur contents, of the crude oil sample was measured using sulphur – oil analyzer and was presented from table 4.2 to table 4.4, below.

Table 4.2: Result of Crude Oil to Solvent desulfurization in Ratio 1:1

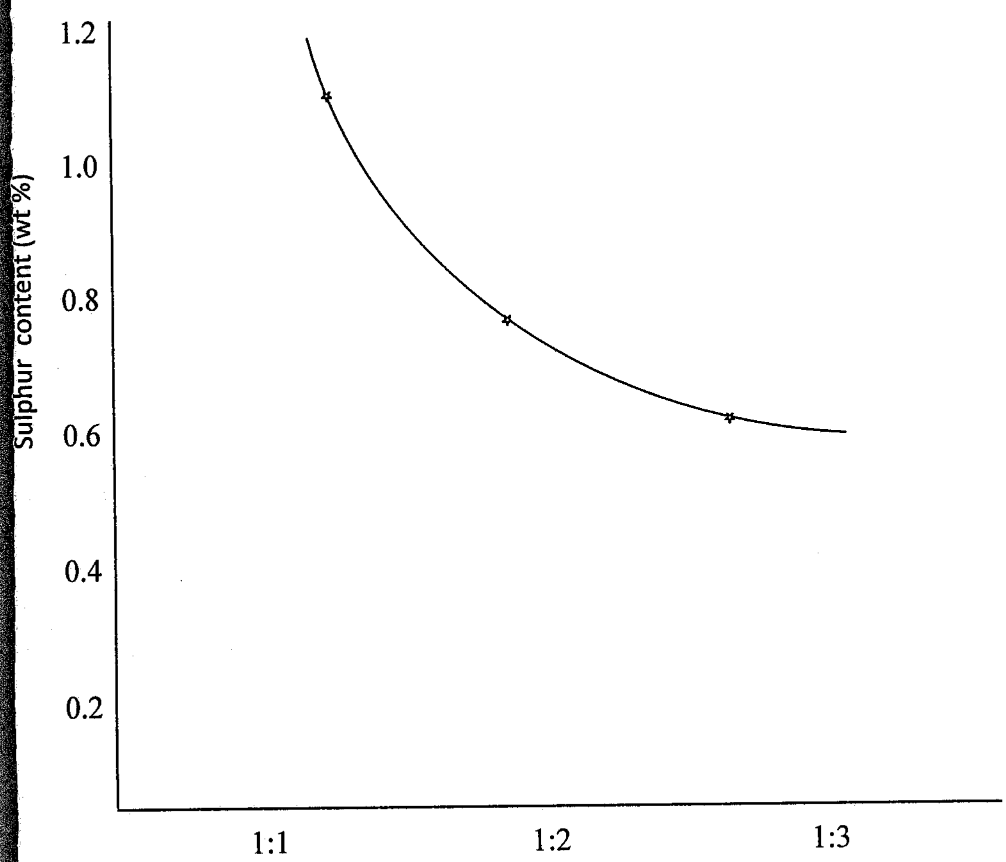
Sample	Raw (wt %)	Sulphur reduction (wt%)
Crude	1.1293	1.0027

Table 4.3: Result of Crude Oil to Solvent desulfurization in Ratio 1:2

Sample	Raw (wt %)	Sulphur reduction (wt%)
`Crude	1.1293	0.9032

Table 4.4: Result of Crude Oil to Solvent desulfurization in Ratio 1:3

Sample	Raw (wt %)	Sulphur reduction (wt%)
Crude	1.1293	0.7078



Ratio of oxidized crude oil

Fig 4.1: Reduction of Sulphur Content of Treated Crude

The figure above shows the trend of the reduction in sulphure content. It can be seen from the figure that an increase in the amount of the solvent leads to corresponding increase in sulphur content removal.

4.2 Discussion of Result

From table 4.2 to 4.3 generated above, the crude oil sulphur content ranges from 1.1293 to 0.7078 wt % where the lowest value of sulphur reduction was obtain from table 4.2, and the highest value of the reduction was obtain from table 4.4. This implies that, as the amount of solvent (methanol) increased, the more the sulphur containing compounds are reduced into more polar compound that can easily be removed by extraction.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

In refining process sulphur compounds are undesirable as they tend to deactivate some catalysts used in crude oil processing. Sulphur causes several corrosion problems in pipeline, pumping and refining equipment, as well as the premature failure of combustion engines. Reducing the sulphur content in a crude oil will not only remediate the problems faced during refining process,but will also save the environment from some kind of pollution that could cause a life treating diseases. This research can therefore be concluded that;

The sulphur content of the raw crude oil at ratio 1:1, 1:2, and 1:3, reduces in the following order respectively, 1,0027, 0.9032, 0.7078 wt %. This implies that, at ratio 1:1, there is 11.2 % reduction, at 1:2 there is 20.02 % reduction and finally, at 1:3, there is 37.32 % reduction. This signifies that, the more the solvent used, the more amount of sulphur that will reduced.

5.2 RECOMMENDATION

1. Equipments for smooth running of every stage of the analysis should be made available in chemical engineering laboratory.

2. Further research should be carried out to determine the effect of time in oxidizing the crude oil sample.

3. Crude oil refining companies should practice oxidative/extractive method of desulphurization so as to enable more quality product at low cost of operation.

4. There is a need to carry out further research on this work so as to determine the economic analysis of this method of desulphurization.

5. Also further research should be carried out to design the plant that will effectively utilizes this technology.

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APPENDIX A

Reading's from sulphur in oil analyzer

Crude oil Raw sample

Table of Value for Crude Oil Raw Sample

1^{st} reading (wt %)	2^{nd} reading (wt %)	3^{rd} reading (wt %)
1.1293	1.1294	1.1293

$$\therefore \quad sulphur\ content\ in\ raw\ sample = \frac{1.1293 + 1.1294 + 1.1293}{3}$$

$$= 1.1293\,wt\ \%$$

Desulphurized Crude Oil

Table of value at 1: 1

1^{st} reading (wt %)	2^{nd} reading (wt %)	3^{rd} reading (wt %)
1.0028	1.0027	1.0027

$$\therefore \quad at\ 1:1, sulphur\ content = \frac{1.0028 + 1.0027 + 1.0027}{3}$$

$$= 1.0027\,wt\%$$

Table of value at 1:2

1^{st} reading (wt %)	2^{nd} reading (wt %)	3^{rd} reading (wt %)
0.9032	0.9033	0.9032

$$\therefore \quad at\ 1:2, sulphur\ content = \frac{0.9032 + 0.9033 + 0.9032}{3}$$

$$= \quad 0.9032\, wt\,\%$$

Table of value at 1:3

1^{st} reading (wt %)	2^{nd} reading (wt %)	3^{rd} reading (wt %)
0.7077	0.7078	0.7078

$$\therefore \quad at\,1:3\, sulphur\ content\ = \frac{0.7077 + 0.7078 + 0.7078}{3}$$

$$\therefore \quad at\ 1:3\, sulphur\ content = 0.7078$$