

PHYSICOCHEMICAL CHARACTERIZATION OF CRUDE OIL,  
FROM DIFFERENT FIELDS IN AKWA IBOM, NIGERIA.

BY

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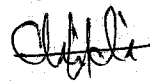
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## DECLARATION

I, OKORO CHIDI HENRY, declare that this project work is solely the result of my work and to the best of my knowledge has never been submitted anywhere for any degree award. All the literature cited have been duly acknowledged in the reference.

OKORO CHIDI HENRY

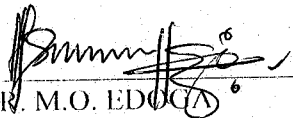
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## CERTIFICATION

This project work titled PHYSICOCHEMICAL CHARACTERIZATION OF CRUDE OIL FROM VARIOUS FIELD IN AKWA IBOM, NIGERIA, by OKORO CHIDI HENRY meets the regulation governing the award of the degree of Bachelor of Engineering (Chemical Engineering) of the Federal University of Technology, Minna and is approved for its contribution to knowledge and literary presentation.



DR. M.O. EDOGA  
PROJECT SUPERVISOR AND  
HEAD OF DEPARTMENT

28-11-07

DATE

EXTERNAL EXAMINER

DATE

## DEDICATION

This project is dedicated to the giver and sustainer of life, Almighty God Jehovah, who has kept me in his love down to this moment of my life in The Federal University of Technology, Minna.

## ACKNOWLEDGEMENT

Much gratitude to my Head of Department and dependable supervisor - Dr. M.O. Edoga, for taking me through this drill during the entire course of my project work. Mrs. Olugbenga G.A., your kind assistance is not unnoticed. The entire lecturers and staff of The Chemical Engineering Department, I appreciate your academic guidance so far.

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To my innumerable friends – you were friends in deed. And to my fellow finalist (2006/2007 session), the interchange of encouragement saw us through our long course of study.

## ABSTRACT

This project was carried out to characterize two crude oil samples from different oil fields in Akwa Ibom, Nigeria. The test method adopted for the analysis was based on the American Society for Testing and Materials (ASTM).

From the analysis carried out on the crude oil samples A and B, it was clearly observed that no two crude oil samples have the same physicochemical properties. The American Petroleum Institute (API) gravity of the Ukpenekang (A) and Enang (B) crude oil samples, confirm that the samples are of the light crude oil grade with their respective values as 32.14 and 31.07 °API. The two samples are sweet crude oils since the value of their sulfur content is lower than 0.5 weight percent. Both oil samples are naphthenic base crude since their characterization factors 11.04 and 10.92 respectively.

## TABLE OF CONTENTS

CONTENTS	PAGE
Title Page	i
Declaration	ii
Certification	iii
Dedication	iv
Acknowledgement	v
Abstract	vi
Table of contents	vii
List of figures	viii
List of table	ix
<b>CHAPTER ONE</b>	
1.0 INTRODUCTION	1
1.1 Background	1
1.2 Aim and Objectives	3
1.3 Approach	3
1.4 Justification	3
<b>CHAPTER TWO</b>	
2.0 LITERATURE REVIEW	4
2.1 Crude Oil	4
2.2 History of Petroleum	4
2.2.1 Petroleum in Nigeria	4
2.3 Characteristics of Petroleum	5
2.4 Composition of Crude Oil and Refined Products	5
2.5 Classification of Crude Oils	8
2.5.1 Based on characterization factor (K)	8
2.5.2 Based on sulphur content	9
2.5.3 Based on API gravity	9
2.6 Characterization of Crude Oils and Heavies	9
2.6.1 Characterization tools	10
2.6.2 Fractionation methods	13
2.6.3 Boiling point separation	13
2.7 Physicochemical Properties	14
2.7.1 Specific gravity and API gravity.	14
2.7.2 Viscosity	15
2.7.3 Reid vapor pressure	15
2.7.4 Pour point	15
2.7.5 Basic sediment and water (BSW)	16
<b>CHAPTER THREE</b>	
3.0 METHODOLOGY	
3.1 Materials and Equipment Used	17
3.2 Procurement of Crude Oil Samples	18
3.3 Experimental Procedure	18
3.3.1 Determination of specific gravity and API gravity.	18
3.3.2 Determination of kinematic viscosity	18
3.3.3 Determination of Reid vapor pressure	19
3.3.4 Determination of pour point	19
3.3.5 Determination of the basic sediment and water	20
3.3.6 Determination of ash content	20
3.3.7 Determination of carbon residue	21
3.3.8 Determination of sulphur content	22
3.3.9 Determination of the total acid number	22
3.3.10 Determination of salt content	23
3.3.11 Determination of the metals in crude	23
<b>CHAPTER FOUR</b>	
4.0 RESULTS AND DISCUSSION	24
4.1 Results	24

2	Discussion of results	25
<b>CHAPTER FIVE</b>		
0	CONCLUSIONS AND RECOMMENDATIONS	28
1	Conclusions	28
2	Recommendations	29
<b>REFERENCE</b>		
<b>APPENDIX</b>		
		30
		32



**LIST OF FIGURES**

**FIGURES**

2.1 Schematic Diagram of SARA Separation

**PAGE**

12

**LIST OF TABLES**

**TABLE**

3.1 Materials and Equipment

4.1 Physicochemical results of the Qua - Iboe Light Samples.

**PAGE**

17

24

# CHAPTER ONE

## INTRODUCTION

This project work entails defining the physicochemical properties of some selected crude oil samples from Nigeria (i.e. Qua-Iboe light, Ukenekang(A) and Enang (B)).

Crude oil also known as "petroleum" is derived from Latin and means "rock oil". It is mainly used to identify two closely related compounds- natural gas (methane, CH<sub>4</sub>) and oil. Both substances seep to the surface through cracks in the earth. As for oil, it exists in the liquid or solid phase. They are usually drilled from what are called oil wells (onshore, offshore or under water wells) that issues from below the ground.

It can be defined as a flammable, yellow-black organic mixture of gaseous, liquid and solid hydrocarbons that occurs naturally beneath the earth's surface. Being a mixture of basically Hydrogen and Carbon, crude oil can be separated by fractional distillation into its various fractions. These fractions can further serve as raw materials or fuels in other process industries.

### 1.1 Background

There have been many attempts in the past to classify crude oil into its various types based on different factors some of which are explained below:

**GEOGRAPHICAL SOURCE:** this method of classifying crude oil is often used by the petroleum industry in characterizing it according to their source, example, Qua- Iboe (Akwa Ibom) crude, Alaska North slope crude, e.t.c. This however, is generally not a very useful classification type due to the fact that various geographical areas have their unique properties.

**OIL SPILL RESPONSE PERSONNEL:** this is based on the unique properties of crude oil which varies in consistency from a light volatile fluid to a semi-solid. It seeks information about general

toxicity, physical state, and its reaction to weathering. The classification scheme as provided by (The U.S. Environmental Protection Agency) is shown below:

**CLASS A: LIGHT VOLATILE OILS.** These oils are highly fluid, often clear, spread rapidly on solid or water surfaces, have a strong odor, a high evaporation rate, and are usually flammable. They penetrate porous surfaces such as dirt and sand and may be persistent in such a matrix. They do not tend to adhere to surfaces, flushing with water generally removes them. Class A oils may be highly toxic to humans, fish and other living organisms. Most refined products and many of the highest quality light crude can be included in this class.

**CLASS B: NON STICKY OILS.** These oils have a waxy or oil feel. Class B oils are less toxic and adhere more firmly to surfaces than class A oil, although they can be removed from surfaces by vigorous flushing. As temperature rises, their tendency to penetrate porous substances increases and they can be persistent. Evaporation of volatiles may lead to a class C or D residue. Medium to heavy paraffin-based oils fall into this class.

**CLASS C: HEAVY STICKY OILS.** Class C oils are characteristically viscous or sticky and brown or black. Flushing with water will not readily remove this material from surfaces, but the oil does not readily penetrate porous surfaces. The density of class C oils may be near that of water and they often sink. Weathering or evaporation of volatiles may produce solid or tarry class D oils. Toxicity is low, but wild life can be drowned when contaminated. This class includes fuel oils and medium to heavy crude.

**CLASS D: NON FLUID OILS.** Class D oils are relatively non toxic, do not penetrate porous substances, and are usually black or dark brown in color. When heated, class D oils may melt and coat surfaces making clean up very difficult. Residual oils, heavy crude oils, some high paraffin oils, and some weathered oils fall into this class.

## **1.2 Aim and Objectives**

The aim of this study is to determine the physicochemical properties of the crude oil samples from different oil fields.

## **1.3 Approach**

In achieving the stated aim, the procedures adopted are as follows:

1. Procurement of the crude oil samples
2. Analysis of the crude oil samples
3. Characterization of the samples.

## **1.4 Justification**

The project is justified due to the fact that knowing the worth of a crude oil sample begins with having good crude assay. This is achieved by the analysis of the physicochemical properties of crude samples which provides the basis for economic valuation (whether crude is sweet or sour; light, medium or heavy e.t.c.); engineering design and refinery processing.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Crude Oil

The biogenic theory, an opinion that has prevailed among most scientists since the 1870's "holds that biological debris buried in sediments decays into oil and natural gas in the long of course time and that the petroleum then becomes concentrated in the pore space of sedimentary rocks in the uppermost layers of the earth's crust." (Awake, 2003). This process then produces petroleum, whose main components are hydrocarbons.

#### 2.2 History of Petroleum

The use of oil from petroleum for artificial lighting was oil's spring board to fame. As early as the 15th century, oil from surface wells was used in lamps in Baku, present capital of Azerbaijan. In 1650, shallow oil reservoirs were dug in Romania, where oil in the form of kerosene, was used for lighting. By the mid- 19<sup>th</sup> century, Romania and others in Eastern Europe already had a prosperous oil industry.

In the United States, it was mainly the search for a high-quality illuminant in the 1800's that led to the decision of drilling for oil to produce enough kerosene for market supply. A 22m deep well to the first crude oil near Titusville, Pennsylvania, U.S.A. was successfully drilled by Edwin L. Drake in 1859. This marked the beginning of the oil era. (Awake, 2003)

##### 2.2.1 Petroleum in Nigeria

In 1958, petroleum was discovered in Ogoni land (south-east Nigeria). There is also petroleum in the homelands of other coastal peoples, such as the Ijaw. Petroleum rapidly became Nigeria's main export earner. There are over a hundred oil wells in Ogoni land, mainly operated by Shell jointly with the Nigerian government. Between 1976 and 1991 there were about 3000 oil spills mostly due to poorly constructed and poorly maintained pipelines. Some were caused

by local people as sabotage or in an attempt to access the petroleum. Many gas flares burn continuously. The environmental impact of all this have been disastrous, with water supplies and soils contaminated, and the fall of acid rain. This has made farming and fishing very difficult for the Ogoni people, who are forced instead to by food for survival. (Microsoft Encarta, 2005)

### **2.3 Characteristics of Petroleum**

All petroleum consists principally of hydrocarbons, although a few sulphur and oxygen-containing compounds are usually present. Petroleum contains gaseous, liquid and solid elements. The consistency of petroleum varies from liquid as thin as petrol to liquid so thick that it will barely pour. Small quantities of gaseous compounds are usually dissolved in the liquid: when larger quantities of these compounds are present, the petroleum deposit is associated with a deposit of natural gas.

Three broad classes of crude petroleum exist: the paraffin types, the asphalt types and the mixed-base types. The paraffin types are composed of molecules in which the number of hydrogen atoms is always two more than twice the number carbon atoms (i.e.  $C_nH_{2n+2}$ ). The characteristic molecules in the asphalt types are naphthenes, composed of twice as many hydrogen atoms as carbon atoms (i.e.  $C_nH_{2n}$ ). In the mixed-base group are both paraffin hydrocarbons and naphthenes. (Microsoft Encarta, 2005)

### **2.4 Composition of Crude Oil and Refined Products**

Crude oils can vary greatly in composition, viscosity, density, and flammability. They can be found in a continuum ranging from highly flammable, light liquids (similar to gas condensate), to highly viscous and heavy tar-like materials. Organic compounds range from methane to extremely heavy hydrocarbon molecules with up to 80 carbon atoms. The chemical composition of crude varies between regions and even within the same geologic formation. No

two batches of crude oil are chemically identical. Crude oil is categorized based on the molecular weight distribution of their constituents, and distinctions are made between light, medium, and heavy crude oil.

Crude oil is composed of varying fractions of different boiling point ranges of hydrocarbon mixtures. The most flammable components are in the light ends through medium naphtha fractions, which together form a mixture somewhat similar in properties to gasoline. The heavy naphtha through residual fractions, reflect properties typically perceived as those associated with oils.

The aromatic components of the crude oil, found primarily within medium to heavy naphtha fractions and gas oil fractions, include benzene, a known human carcinogen. Other aromatic compounds include toluene, ethyl benzene, and xylene. These aromatic compounds have relatively high solubility in water, compared with other hydrocarbons.

Crude oils also contain varying amounts of non-hydrocarbon sulfur, nitrogen, oxygen and trace metals. Sulfur is present as hydrogen sulfide ( $H_2S$ ), as thiols, mercaptans, sulfides, benzothiophenes, polysulfide, or as elemental sulfur. As a rule, the proportion, stability and complexity of sulfur compounds are greater in heavier crude oil fractions.  $H_2S$  is a primary contributor to corrosion in refinery process units and combustion of sulfur containing petroleum products can produce undesirable byproducts such as sulfuric acid and sulfur dioxide. Total sulfur contents of crude oils spans a range of  $<0.1\%$  -  $5.0\%$  by elemental analysis. In general, as API gravity decreases, sulfur content increases. For example, light US crude (Rodessa, Louisiana) has an API gravity of 42.8 and a sulfur content of 0.28%, while extremely heavy crude from Venezuela has an API gravity of 9.5 and contains 5.25% sulfur (Dickey, 1981; IARC, 1989). Crude oils high in sulfur are designated "sour crude oils", and those low in sulfur

are "sweet crude oils". Sulfur is removed during refining by catalytic hydro treating or by caustic wash (sweetening) processes. Nitrogen types include anilines, pyridines, quinolines, pyrrols, carbazoles, benzonitrils and amides. Nitrogen is found in lighter fractions as basic compounds and in heavier fractions as non-basic compounds. Total nitrogen varies from <0.01% -1.0% by elemental analysis. Oxygen compounds are generally phenols, ketones and carboxylic acids. Metals found in crude oil include nickel, iron, vanadium, and arsenic in small quantities. These are removed during refining to avoid poisoning of catalysts, and when burning heavy fuel oils, to minimize deposits of vanadium oxide, and nickel oxide in furnace boxes, ducts and tubes. Inorganic salts such as magnesium chloride or calcium chloride are suspended as minute crystals in crude oil or dissolved in entrained water (brine). These salts are removed or neutralized prior to processing to prevent catalyst poisoning, equipment corrosion and fouling.

Crude oils are complex mixtures of a vast number of compounds:

- every single crude source gives a highly individual mixture which cannot be matched exactly by any other crude oil;
- the traditional products which the petroleum industry provides by refining crude oils are themselves, however, complex mixtures used either to generate power (gasoline, kerosene, diesel fuels) or heat (gas oil, fuel oil) or for specialty purposes (lubricants, road asphalts) and more recently as base stocks for chemicals (naphtha for ethylene manufacture). The petroleum industry therefore has a host of semi-empirical measurements. However, tests have generally sufficed to ensure that the quality of each petroleum product sold to the user is such as to give satisfactory service.



## 2.5 Classification of Crude Oils

### 2.5.1 Based on characterization factor (K)

As already mentioned, crude oils consist mainly of paraffin, cycloparaffin (naphthenic hydrocarbons) or aromatics. The molecular size of the constituent varies: some oils may be particularly rich in hydrocarbons of low molecular weight; others have a high percentage of large molecules. Crude oils are classified by the group of hydrocarbons which typifies the crude. This does not mean however, that the other hydrocarbons are not represented in the crude. In light fractions, aromatics may predominate, while the normal paraffin is concentrated in the high-boiling range, e.g. Syria crude Borneo. This crude which gives easily crystallizable paraffin wax is predominantly aromatic in the light fractions. Apart from hydrocarbons which can be grouped in one of the main classes, paraffin, naphthenes (cycloparaffin) and aromatics, crude oils may also contain mixed type hydrocarbons e.g. naphthenes with paraffin side chains or aromatic nuclei with side chains which may not be classified easily in the above groups. A rigid classification of crude in paraffin, naphthenic or mixed type is therefore not possible.

The different crude bases have the following value ranges of the characterization factor (k) developed by Watson:

BASE	k
Paraffin	12-13
Mixed	11.5-12
Naphthenic	10.5-11.5
Aromatic	9.5-10.5

From;

$$k = \frac{T^{1/3}}{S.G_{60/60^{\circ}F}}$$

Where;

$$S.G_{60/60^{\circ}F} = \text{Specific gravity at } 60^{\circ}F$$

$$T = \text{Average molar boiling point in } ^{\circ}R = T^{\circ}F + 460$$

### 2.5.2 Based on sulphur content

Crude oil may be classified as sour or sweet crude depending on the sulphur content of such crude. The term 'sour' is used for crude oil with sulphur content greater than 0.5wt%, while 'sweet' is for that lower or equal to 0.5wt%.

### 2.5.3 Based on API gravity

API gravity is an indication of the gasoline potential of crude oil;  ${}^{\circ}\text{API} = \frac{141.5}{\text{S.G}_{60/60^{\circ}\text{F}}} - 131.5$ .

The higher the API gravity (the lower the specific gravity), the more valuable is the crude.

A crude with a high API gravity (Platts, 2003), and high % hydrogen usually contains a higher concentration of naphtha, which can be processed readily to make gasoline and is considered a light crude. Crude oils with high % carbon and low % hydrogen are usually rich in aromatics and tend to contain more residual material (e.g. asphalts) and heteroatom (e.g. sulfur, nitrogen, oxygen-containing hydrocarbon analogs).

The "heavy crude oils" require more steps in processing, and are more costly to refine.

## 2.6 Characterization of Crude Oils and Heavies

- Characterization of crude oil and heavies is necessary to be able to understand and predict their behavior.
- During production, transportation and processing various problems such as solids deposition, clogging and coking occur due to presence of heavy components in oil.
- Characterization can be based on single carbon number or on compound class.
- A compound class characterization common in industry is **SARA** (Saturate, Aromatic, Resin and Asphaltene) characterization.

- Asphaltene- highly polar high molecular weight solids, the fraction of oil insoluble in low molecular weight aliphatic hydrocarbons. Highly condensed aromatic ring system with high N, S, O and metal content.
- Soluble part of oil is termed as maltenes. Consists of Saturate, Aromatic and Resin fractions separated by column chromatography.
- Saturates- Consists of saturated hydrocarbons with straight or branched chains without ring structure (paraffins) or with one or more rings attached (cycloparaffins). Contain little or no N, S, O and metals.
- Aromatics- Hydrocarbons containing one or more aromatic ring.
- Resins- Also known as poplars. Second heaviest fraction in crude oils.
- Characterization of the individual SARA fractions can help in providing a map of the crude oil and its behavior.
- Crude oils from different sources will have different SARA distributions and different properties.
- High asphaltene content in crude oils has been linked to deposition problems during production and coke formation during processing. Highly paraffin oils are prone to wax formation and deposition.
- Detailed characterization of the heavier components like asphaltenes and resins from crude oils and residue can help in providing better models for prediction of properties.

### **2.6.1 Characterization tools**

- SARA characterization methods employ adsorption chromatography for fractionation step.

- In column chromatography the adsorbent is contained in a tube, the sample is introduced at one end of the adsorbent bed and induced to flow through the bed by means of a suitable solvent.
- As the sample moves through the bed the various components are held (adsorbed) to a greater or lesser extent depending on the chemical nature of the component.
- Choice of a suitable adsorbent and solvents is thus important.
- SARA methods differ in the type of adsorbent and solvent elution scheme used.
- In most methods asphaltenes are first isolated as a separate fraction. This is because their highly polar nature would cause them to be irreversibly adsorbed on the adsorbent.
- Preparative (prep.) scale SARA separation methods have been developed so that the fractions obtained can be further characterized using different techniques.
- Two different methodologies have been developed for this separation
  - Prep. Scale Low Pressure Liquid Column chromatography (Wet chemistry method)
  - Prep. Scale High Pressure Liquid Column Chromatography (HPLC)
- The asphaltenes were first isolated from the samples and chromatographic separation of the deasphalted oil (Maltenes) followed. Sample may need to be distilled or topped to remove volatile fraction.
- n-heptane is used as the solvent for precipitation of the asphaltenes from the crude oil or residue sample. A 40:1 ratio of n-heptane to sample is used. It is important to remember that asphaltenes are a solubility class. Initial sample weight of up to 35 grams.
- Precipitated asphaltenes are separated by vacuum filtration, dried in an oven and weighed.

- Maltenes are isolated from the filtrate by rotary evaporation and subsequently fractionated into Saturates, Aromatics and Resins. (Kaushik Gandhi,)

The SARA separation is illustrated below:

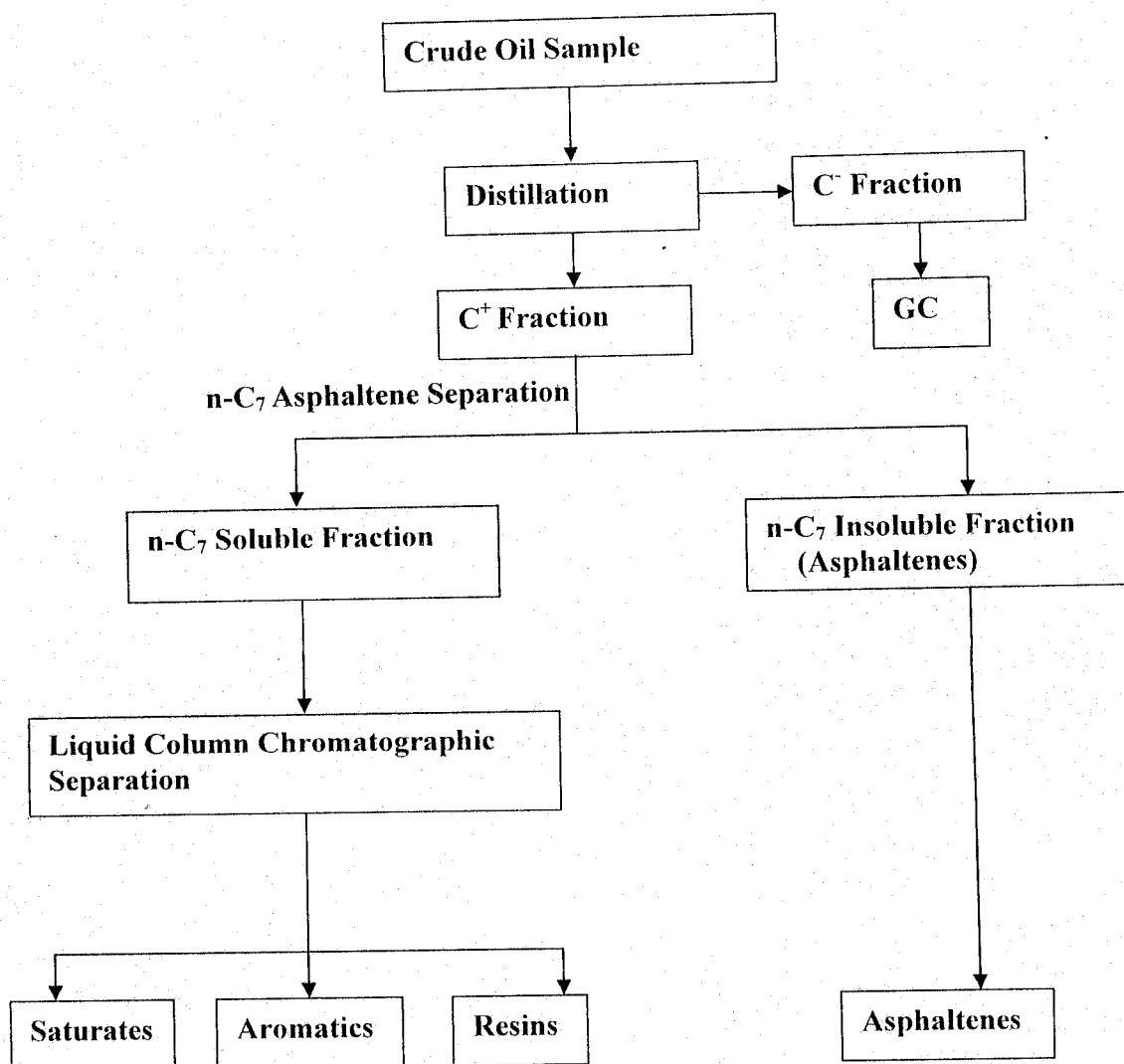


Fig. 2.1 Schematic Diagram of SARA Separation

### **2.6.2 Fractionation methods**

To study and characterize these structures, a preliminary step of matrices simplification is recommended. The objective is to isolate sub fractions of common characteristics, thereafter more easily analyzable by various chromatographic, spectroscopic or other techniques. Different fractionation methods can be considered. Separation as a function of the boiling point can be achieved by distillation. Separations by selective adsorption onto varied supports or through chemical derivations can be also proposed. Finally, the tolerance to solvents may be used to define solubility classes like for asphaltene molecules (separation by polarity).

### **2.6.3 Boiling point separation**

Results show a direct relationship between the boiling point and certain properties such as viscosity or density. However, boiling points are not directly proportional to the average molecular weight, but depend on the chemical structure of the compounds present in the fractions. It has been shown that polar compounds able to form aggregates are less volatile than the non-polar species of a similar given molecular weight. This can explain why poly condensed aromatic compounds enriched in heteroatom (resins and asphaltenes) are mainly concentrated in high boiling point fractions. Several normalized methods of distillation are proposed: preparative scale and simulated distillations (DS).

The True Boiling Point method (TBP, ASTM D2892) is a preparative distillation used to obtain distillation cuts from initial point to 400°C with 5°C cuts up to 170°C and 10°C cuts from 170°C to 400°C. Pot still distillation (ASTM D5236) is often used to obtain vacuum distillation cuts (400-550°C) with steps of 50°C. To control the quality of products or for routine analyses, simulated distillation (DS) is well adapted and can replace conventional distillation methods. Time can be saved and smaller sample volumes are required (few ml in simulated distillation versus 200 to 500 ml in preparative distillation). This technique is used at the analytical scale and

normalized methods have been developed (ASTM D2887, D6352). The selectivity being higher, this technique can cover a wider temperature range than that of vacuum preparative distillations (Durand and Petroff, 1984). Simulated distillation is based on the hydrocarbons aptitude to be eluted according to their boiling point from a non-polar chromatographic column under specific conditions. Retention time (RT) of the species is converted into boiling point temperature by using a calibration curve, established from normal paraffin retention times. The normalized cumulative corrected sample areas of each consecutive recorded time interval are used to calculate the boiling range distribution. The boiling point temperature at each reported percent of increment is calculated from the RT calibration. A profile of cumulated percentages in function of the boiling point is obtained. When applied to 550°C- distillation cuts, the conventional simulated distillation is generally used (ASTM D2887) (Feeney and Huber, 1984; Feillens et al., 1984). For the analysis of higher boiling point fractions (550°C+), high temperature (430°C) gas chromatography allows to extend the carbon distribution up to 100 (nC100 - 700°C) (ASTM D6352, Neer and Deo, 1995; Durand et al., 1998; Bacaud et al., 1998; Reddy et al., 1998). However, this technique has to face several limitations such as:

- the oven temperature below 430°C to avoid compound degradation;
- preliminary de-asphaltening required;
- extrapolation of calibration curve impossible due to modification of elution conditions.

## **2.7 Physicochemical Properties**

### **2.7.1 Specific gravity and API gravity**

Specific gravity is the ratio of the mass of a given volume of liquid at a specific temperature to the mass of an equal volume of pure water at the same or different temperature (specified).

$$\text{S.G} = \frac{\text{Mass of given volume of substance}}{\text{Mass of equal volume of pure water.}}$$

The standard reference temperature is 60°F.

API gravity is a special function of specific gravity, represented by:

$$^{\circ}\text{API} = \frac{141.1}{\text{S.G}_{60/60^{\circ}\text{F}}} - 131.1$$

### 2.7.2 Viscosity

Viscosity (kinematics) is the resistance to flow of a fluid under gravity. It is the product of the measured flow time and the calibration constant of the viscometer. This is given as:

$$\nu = C \times t$$

Where;

$\nu$  = kinematic viscosity

C = calibration constant of the viscometer

t = flow time.

Unit = centi-stoke (cSt)

### 2.7.3 Reid vapor pressure

Reid vapor pressure is an absolute pressure at 37.8°C (100°F) of petroleum products and crude oils with initial boiling point above 0°C (32°F). It is an important physical property of crude oil beneficial to crude producers and refiners for general handling and initial refinery treatment. It is in kilopascals (kPa) or pounds-force per square inch (psi).

### 2.7.4 Pour point

Pour point of petroleum is the lowest temperature at which movement of the test specimen is observed when cooled. It is important in industry as it indicates the lowest



temperature at which crude oil would be stored or handled without congealing in storage tanks or flow lines. It is measured in °C or °F.

### 2.7.5 Basic sediment and water (BSW)

Basic sediment and water is a measure of water and other sediments (impurity) in a crude specimen. It is given as:

$$\text{BSW} = \frac{\text{volume of separated fraction}}{\text{Total volume of original sample}} \times 100$$

## CHAPTER THREE

### METHODOLOGY

#### 3.1 Materials and Equipment Used

The table below shows the materials and equipment used for the analysis:

**Table 3.1:** Materials and Equipment

Equipment	Materials
Density meter	Syringe, Ultra pure water, samples A and B
Viscometer	Stop watch, Beaker, samples A and B
Reid Semi Automat.	Water, samples and A and B
Pour Point tester (automatic)	Beaker, samples A and B
Centrifuge Machine (Manual)	Stop watch, samples A and B
Electric Muffle furnace Gas burner	Evaporating dish, samples A and B
Skidmore Apparatus Gas burner	Porcelain Crucible, samples A and B
Sulphur Analyzer	Beaker, samples A and B
Weighing balance	Samples A and B, Beakers, Burette, Glass electrode, Reagents (KOH, Toluene)
Salt analyzer	Reagents(Xylene, Mixed alcohol) Cylinder, Pipettes, samples A and B
Atomic absorption spectrometer	Sample A and B

### **3.2 Procurement of Crude Oil Samples**

The crude oil samples A and B (Ukpenekang and Enang respectively) were procured from different oil sources in Akwa Ibom state, Nigeria.

### **3.3 Experimental Procedure**

#### **3.3.1 Determination of specific gravity and API gravity. (ASTM D 1298)**

The DMA machine was switched on and allowed to initiate. The machine calibration was carried out by inputting water density variation (i.e. real density value - observed value) into the system.

About 3ml (representative of the bulk) of the crude oil sample was fed into the measuring cell (1.5ml) of the machine, with the aid of the syringe and the overflow received in a drain.

The processed result was read and recorded from the output display of the machine.

#### **3.3.2 Determination of kinematic viscosity. (ASTM D445)**

The bath was maintained at constant temperature (85°C). A clean dry calibrated viscometer having a range covering the estimated viscosity was selected. The viscometer was set in the bath so that the capillary assumed a vertical position. The viscometer was allowed to reach the bath temperature and the oil sample was poured in to the filling mark. The oil sample was allowed to flow through capillary with the liquid column unbroken until it reaches just below the lower filling mark. The flow was arrested at that point by closing the timing tube with a cork.

More samples were added to the filling tube to bring the oil surface to just below the filling mark. The sample was allowed to reach the bath temperature and any air bubbles to rise to the surface (about 30min). The stop watch was started simultaneously with the sample meniscus

at the upper mark, and stopped with the meniscus at the lower mark of the capillary by removing the stop cork from the timing tube.

The flow time ( $t$ ) of the sample and the calibrated capillary constant ( $c$ ) is then used to obtain the viscosity ( $v$ ). (i.e.  $v = c \times t$ ).

### **3.3.3 Determination of Reid vapor pressure. (ASTM D 323)**

The main switch of the Reid vapor pressure apparatus was powered on. The stirrer which aids temperature uniformity of the bath was also switched on. The heater was then switched on to elevate the bath temperature to working temperature of 37.8°C. This was regulated by the thermostat over the working period. The sample chamber was chilled (between 0-1°C) same with crude sample.

The air/vapor chamber was immersed in the bath for about 10min to attain the working temperature. It was then removed and coupled with the chilled sample chamber with sample filled to its brim, and then coupled back into the bath by means of the coupling hose (this was done within 10sec) This setup was agitated for about 5min to pressure out the volatile matter from the sample chamber to be read by sensors and displayed on the output.

The value on the output was read and recorded after about 30min (for consistency)

### **3.3.4 Determination of pour point. (ASTM D 97)**

The oil sample was poured into the test jar to the level mark (about 30ml). The test jar was closed tightly with the cover carrying the light-pour thermometer, with its bulb immersed so that the beginning of the capillary was 3mm below the surface of the oil. A ring gasket around

the test jar and disk at the bottom of the jacket, prevented direct contact between them, when the test jar was inserted inside the jacket. (The jacket is in the cooling bath)

The machine was set to test for pour of the sample at every 3°C decline in temperature. The temperature at which the oil just ceased to flow when tilted on cooling was displayed at the output.

### 3.3.5 Determination of the basic sediment and water. (ASTM D 4006)

The sample was gently shaken to homogeneity and poured into a centrifuge tube. It was then placed into the centrifuge jacket. The above step was repeated for the second jacket to create balance in the centrifuge machine.

The hand wheel was rotated to about 5000rpm for about 5min and the machine was allowed to come to rest on its own. This is to allow for proper sedimentation and settling. The basic sediment and water BSW, was then obtained.

$$\%BSW = \frac{\text{volume of separated fraction (x)}}{\text{Total volume of original sample}} \times 100$$

### 3.3.6 Determination of ash content. (ASTM D 482-00)

The evaporating dish was heated to temperature range of 700-800°C for about 10min and allowed to cool to room temperature in a container. It was then weighed to the nearest 0.1mg.

The oil sample was gently shaken for homogeneity for about 10min and weighed into the evaporating dish. This was carefully heated with a burner until the content was ignited by the flame. The temperature was maintained such that the sample continues to burn at a uniform and moderate rate, leaving only a carbonaceous residue when the burning ceased.

The residue was heated in the muffle furnace at about 775°C until all carbonaceous material disappeared. The dish was cooled to room temperature and weighed to the nearest 0.1mg.

$$\text{Ash, wt \%} = \frac{w}{W} \times 100$$

Where:

w = wt. of ash

W = wt. of sample.

### 3.3.7 Determination of carbon residue. (ASTM D 189-01)

The oil sample (about 10g) was weighed into a porcelain crucible containing two glass beads (about 2.5mm in diameter). The crucible was placed in the centre of the Skidmore crucible. The bottom of the larger iron crucible was covered with a 10mm layer of sand and set in the smaller Skidmore crucible in the centre of the larger crucible. Covers was applied to both the Skidmore and the iron crucible, with the later fitting loosely to allow free exit to the vapors as formed.

The Nichrome wire triangle was placed on the stand and the insulator on it. The sheet-iron crucible was centered in the insulator with its bottom resting on top of the triangle. The hole was covered with the sheet-iron hood for the heat to be uniformly distributed.

Heat with a high, strong flame from the burner was applied so that the pre-ignition period is about 10min. The burner was filled when smoke appeared above the chimney so that the gas flame plays on the sides of the crucible for the purpose of igniting the vapors. The burner was removed and adjusted from time to time in such a way that oil vapors burn above the chimneys but not above the wire bridge. The heat was maintained as at the beginning, for 7min when the vapors ceased to burn so as to make the bottom and lower part of the sheet-iron crucible cherry red. The total period of heating is about 30min.

The burner was removed and the apparatus allowed to cool until no smoke appeared, and then, the cover of the Skidmore crucible. The porcelain crucible was removed and allowed to cool and then weighed.

$$\text{Carbon residue} = \frac{A \times 100}{W}$$

Where:

A = wt. of carbon residue

W = wt. of sample.

### **3.3.8 Determination of sulphur content. (ASTM D 1266)**

The sulphur analyzer was powered on and allowed to initiate for about 30min. The instrument was calibrated by introducing known sulphur standards. The sample was introduced into the sample cell and covered with a seal. The cell and its content were then slotted into the sample pot of the sulphur analyzer with the sealed side facing downwards. The Sulphur content of the sample was analyzed after about 5min and the result displayed on the output.

### **3.3.9 Determination of the total acid number. (ASTM D 664)**

A weighted oil sample was introduced into the beaker. Alcoholic KOH solution (0.1mol/Kmol) was used to fill the burette, and then about 125ml of the titration solvent with 0.5 ml of the indicator was added to dissolve the sample. The cleaned electrode was then partially immersed into the solution of the beaker placed on the titration stand. The solution was agitated all through without spattering by the stirrer as the burette content was titrated into the beaker until end point was attained (about 15min). The pH reading of the sample was displayed on the meter.

### **3.3.10 Determination of salt content. (ASTM D 3230-99)**

To the dry, 100ml graduated, glass-stoppered cylinder, 15ml of Xylene was added and 10ml of oil sample (homogenized) was poured into it using the pipette. The pipette was rinsed free of oil with Xylene to bring the cylinder mixture to about 50ml. The cylinder was stoppered and vigorously shaken for about 60s. It was then diluted to 100ml with mixed alcohol solvent and shaken vigorously (about 30s). The solution was poured into the beaker after 5min.

The electrode was placed into the solution in the beaker with the upper edge of the electrode plate just below the surface of the solution. The indicated electrode voltage was adjusted to a series of values and their corresponding readings obtained. The meter displayed the salt concentration corresponding to the net current reading of the sample.

### **3.3.11 Determination of the Metals in crude. (ASTM D 5863)**

The atomic absorption spectrometer (AAS) was powered on and allowed to initiate. The test sample was diluted with diluents and introduced into the cell of the machine. The electrical detector as opposed to the photographic plate helps to determine the distribution of ion in the sample and the concentration of metals is computed and displayed on the output of the machine.



## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1 Results

**Table 4.1: Physicochemical results of the Qua - Iboe Light Samples.**

S/N	PARAMETERS	NAMES OF TESTED CRUDE OIL SAMPLES		UNIT	TEST METHOD
		Qua Iboe light <i>UKPENKANG A</i>	Qua Iboe light <i>ENANG B</i>		
1.	Specific Gravity	0.8647	0.8704		ASTM D 1298
2.	API	32.14	31.07	<sup>o</sup> API @ 60 <sup>o</sup> F	ASTM D 1298
3.	Viscosity	2.88	5.7	cSt @ 85 <sup>o</sup> C	ASTM D 445
4.	Reid Vapour Pressure	0.97	0.85	psi	ASTM D 323
5.	Pour Point	17.0	23.0	<sup>o</sup> C	ASTM D 97
6.	BSW	0.74	0.90	Vol %	ASTM D 4006
7.	Total Acid Number	4.13	3.5	Mg KOH/g	ASTM D 664
8.	Carbon Residue	6.05	1.5	Wt %	ASTM D 189-01
9.	Ash Content	0.21	0.35	Wt %	ASTM D 482-00
10.	Salt Content	15	12	Ibs/1000bbl	ASTM D 3230-99
11.	Heavy Metals			ppm	ASTM D 5863
	I. Vanadium	0.005	0.001		
	II. Nickel	8.66	1.05		
	III. Copper	0.002	0.001		
	IV. Lead	0.001	0.00		
12.	K- Factor	11.04	10.92		
13.	Molecular Weight	159	152	gmol	
14.	Boiling Point	410	399	<sup>o</sup> F	
15.	Sulphur Content	0.03	0.04	Wt %	ASTM D 1266

## 4.2 Discussion of results

From the table of results, it is observed that both Qua-Iboe light Ukpenekang (sample A) and Enang (sample B) have low specific gravity (0.8647 and 0.8704 respectively); and high API gravity. This is an indicator of better quality and price. This implies that they are of the light crude grade and of higher demand, since it yields more of the light fractions (e.g. petrol). However, in the course of spillage, they remain above water, since they are less dense.

The viscosity of sample A from the result obtained at 85°C is 2.88cSt as against 5.70cSt of sample B. This indicates that sample A will pose less resistance to flow than sample B in the course of transporting the crude in flow lines. Being of relatively less viscosity, the samples will spread rapidly on solid or water surfaces and will penetrate porous surfaces such as sand. An increase in temperature of the samples will lead to a decrease in their viscosities. This implies a high evaporation rate.

The Reid vapour pressure of sample A and B are 0.97 and 0.85PSI respectively. Being light crude samples with high evaporation rate, the low vapour pressure results indicate loss of some volatile matter during sample storage. Since vapour pressure is an important physical property of volatile liquids which can be used as an indirect measure of evaporation rate, care must be taken by crude producers and refiners in the general handling and initial refinery treatment of such crude.

The observed pour point for sample A is 17°C while that of sample B is 23°C. This implies that sample B will cease to flow on cooling before sample A. Since the pour point of a petroleum specimen is an index of the lowest temperature of its utility, care must be taken when constructing flow lines for such crude in colder climatic regions. Also, provision should be made

for pre-heating in storage tanks sited in regions where climatic temperature goes below the pour points of the samples.

From the basic sediment and water (BSW), the percentage volume of oil from sample A is 99.26 while its impurity is 0.74. For sample B, its percentage volume is 99.1 while its impurity is 0.9. Comparing the results indicates that the source well is still rich in oil reserve. However, little will be expended in the pre-treatment of these samples, since the API standard for basic sediment and water should not exceed 0.5% for the crude oil to be marketable.

The acid number of the samples from the results is observed to be high. This could facilitate corrosion in metal parts of equipment in production and refinery units, thereby leading to high maintenance cost. The acid number could also be used as a guide in the quality control of lubricating oil industry. It can also be used as a measure of lubricant degradation in service.

The residue formed by evaporation and thermal degradation of the oil samples are 6.05 wt. % for sample A and 1.5 wt. % for sample B. This residue is not composed entirely of carbon but is a coke that can be further changed by carbon pyrolysis. The carbon residue of burner fuel serves as a rough approximation of the tendency of the fuel to form deposits in vaporizing burners.

From the ash content experiment conducted, sample A is 0.21 wt. % while sample B is 0.35 wt. %. The knowledge of the amount of ash-forming material present in the samples provides information as to whether or not the product is suitable for use in a given application. The ash can result from oil or water-soluble metallic compounds or from extraneous solids such as dirt and rust.

The approximate chloride content of the crude oil samples is determined to be 15 and 12 lbs/1000bbl for sample A and B respectively. This could result in higher corrosion rate in refining units and has detrimental effects on catalyst used in these units if not pretreated.

The metals in the crude samples (Vanadium, copper, lead) are observed to be in trace quantity in relation to nickel content which is 8.66 and 1.05 ppm for sample A and B respectively. This could vary with respect to oil source, and its presence affects catalyst activity.

The sulphur content of sample A is 0.03 wt% while that of sample B is 0.04 wt%. The crude samples are of low sulphur content and are termed sweet crude, since its sulphur content is less than 0.5 wt%.

From a chart correlating API gravity with other crude properties, the characterization (k) factor, molecular weights and boiling points of the samples were obtained. The k-factor for sample A and B are 11.04 and 10.92 respectively. These falls within the range 10.5-11.5, an indication that the oil samples are predominantly Naphthenic hydrocarbons.

## CHAPTER FIVE

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

This project on the preliminary physicochemical characterization of Qua-Iboe light crude oils from different oil fields in Akwa Ibom Nigeria has satisfied its scope. The procedure adopted for the analyses is that of the American Society for Testing and Materials (ASTM).

Having seen from the table of results that no parameter of the different sample have the same physicochemical characteristics under the same test condition; it can rightly be concluded that crude oil samples from different well or field sources have different physical and chemical properties. Also, the American Petroleum Institute (API) gravity obtained for both samples confirms them to be of the light crude grade, with sample A and B having the values 32.14 and 31.07°API respectively. From the analysis conducted, it can likewise be concluded that the samples are sweet crude oil; since they both have sulphur content values less than 0.5%.

## 5.2 Recommendations

In accordance with the objective of this project work, I would recommend that the department in collaboration with the management of the Federal University of Technology Minna, should make adequate plans to opening a related department i.e. Petroleum Engineering in the institution. This, I believe will enhance the quality and productivity of our great citadel of learning. However, previous, present and future work on petroleum should have a special library where they are preserved for reference purposes. Likewise, the department could have a sample bank, where crude oil samples from various wells and fields in Nigeria and abroad could be clearly labeled and adequately stored for academic and research purposes. This would help in making available detailed and comparative crude oil assays.

I am also of the opinion that the Chemical engineering department of this institution should embark on organizing more seminar, workshop and excursions, where students will be active participants, in the course of their undergraduate program. This would better orientate the students in their field of study and keep them informed on latest developments.

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## APPENDIX (CALCULATIONS)

### 1. Specific Gravity and API Gravity

(a) For sample A:

Specific gravity S.G = 0.8647

$$\text{API gravity} = \frac{141.5}{\text{S.G}_{60^{\circ}\text{F}/60^{\circ}\text{F}}} - 131.5$$

$$\begin{aligned} \text{°API} &= \frac{141.5}{0.8647} - 131.5 \\ &= 32.14 \end{aligned}$$

(b) For sample B:

Specific gravity S.G = 0.8704

$$\text{API gravity} = \frac{141.5}{\text{S.G}_{60^{\circ}\text{F}/60^{\circ}\text{F}}} - 131.5$$

$$\begin{aligned} \text{°API} &= \frac{141.5}{0.8704} - 131.5 \\ &= 31.07 \end{aligned}$$

### 2. Viscosity

(a) For sample A @ 85°C:

$$v = C \times t$$

Calibrated capillary constant C = 0.2617cSt/s

Flow time t = 11.0s

$$v = 0.2617 \times 11$$

$$= 2.88\text{cSt}$$

(b) For sample B @ 85°C:

$$C = 0.2617\text{cSt/s}$$

$$t = 21.78\text{s}$$

$$v = 0.2617 \times 21.78$$

$$= 5.70\text{cSt}$$

### 3. Basic Sediment and Water BSW

(a) For sample A:

$$\text{BSW} = \frac{\text{volume of separated fraction (x)}}{\text{Total volume of original sample (10ml)}} \times 100$$

$$x = 0.074\text{ml}$$

$$\text{BSW} = \frac{0.074}{10} \times 100 = 0.74\text{vol\%}$$

(b) For sample B:

$$x = 0.09\text{ml}$$

$$\text{BSW} = \frac{0.09}{10} \times 100 = 0.9\text{vol}\%$$

#### 4. Carbon Residue

(a) For sample A:

W = weight of sample

x = weight of crucible = 40.500g

x + W = 50.824g

W = 50.824 - 40.5 = 10.324g

A = weight of carbon residue

x + A = 41.125g

A = 41.125 - 40.5 = 0.625g

% carbon residue =  $\frac{A}{W} \times 100$

$$\frac{0.625 \times 100}{10.324} = 6.05\text{wt}\%$$

(b) For sample B:

W = weight of sample

x = weight of crucible = 40.498g

x + W = 50.731g

W = 50.731 - 40.499 = 10.233g

A = weight of carbon residue

x + A = 40.651g

A = 40.651 - 40.498 = 0.153g

% carbon residue =  $\frac{A}{W} \times 100$

$$\frac{0.153 \times 100}{10.233} = 1.5\text{wt}\%$$

#### 5. Ash Content

(a) For sample A:

W = weight of sample

x = weight of crucible = 40.550g

x + W = 50.700g

W = 50.700 - 40.550 = 10.150g

w = weight of ash

x + w = 40.571g

w = 40.571 - 40.550 = 0.021g

% ash content =  $\frac{w}{W} \times 100$

$$\begin{aligned} &= \frac{0.021}{10.150} \times 100 \\ &= 0.21\text{wt}\% \end{aligned}$$

(b) For sample B:

W = weight of sample

x = weight of crucible = 40.551g

x + W = 50.699g

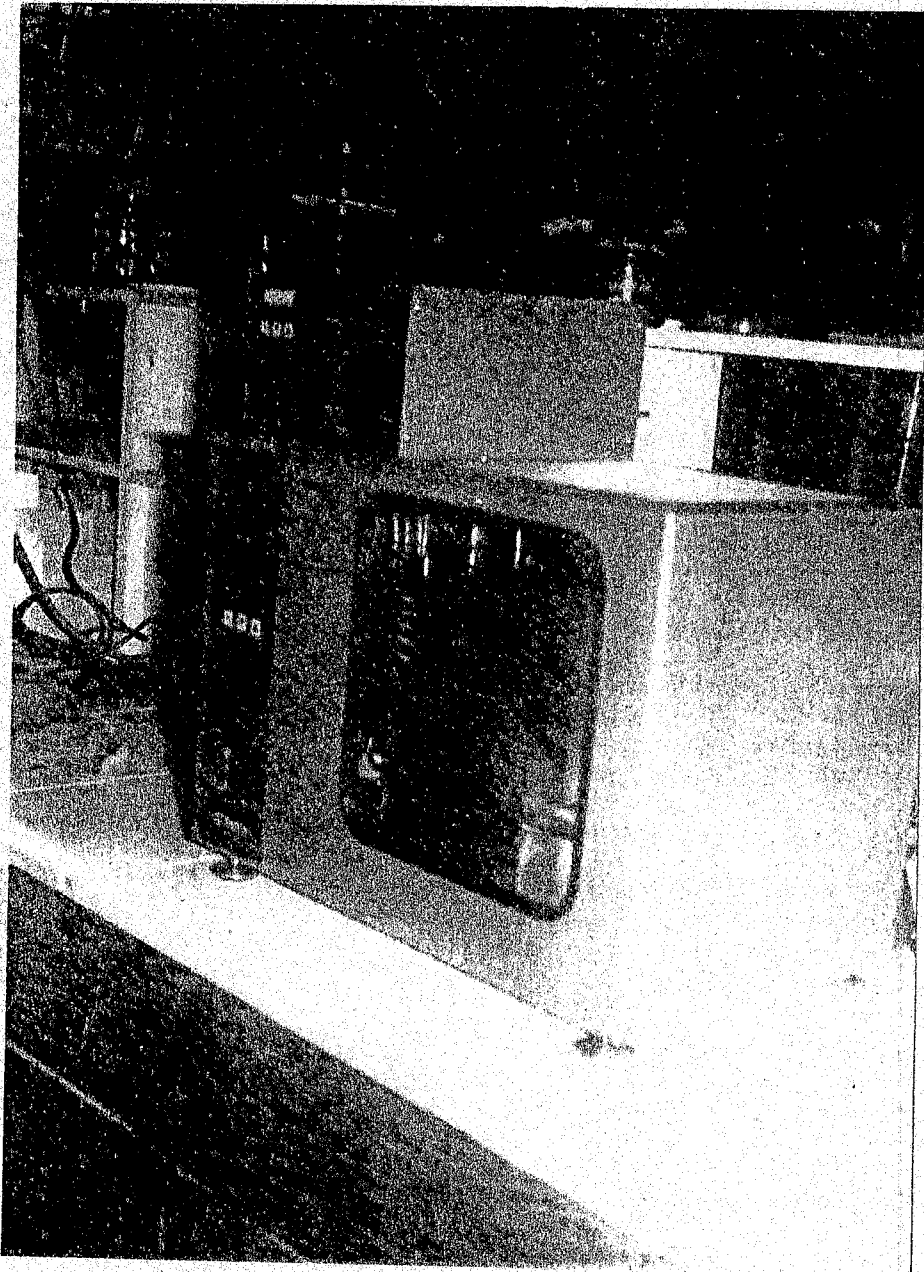
W = 50.699 - 40.551 = 10.148g

w = weight of ash

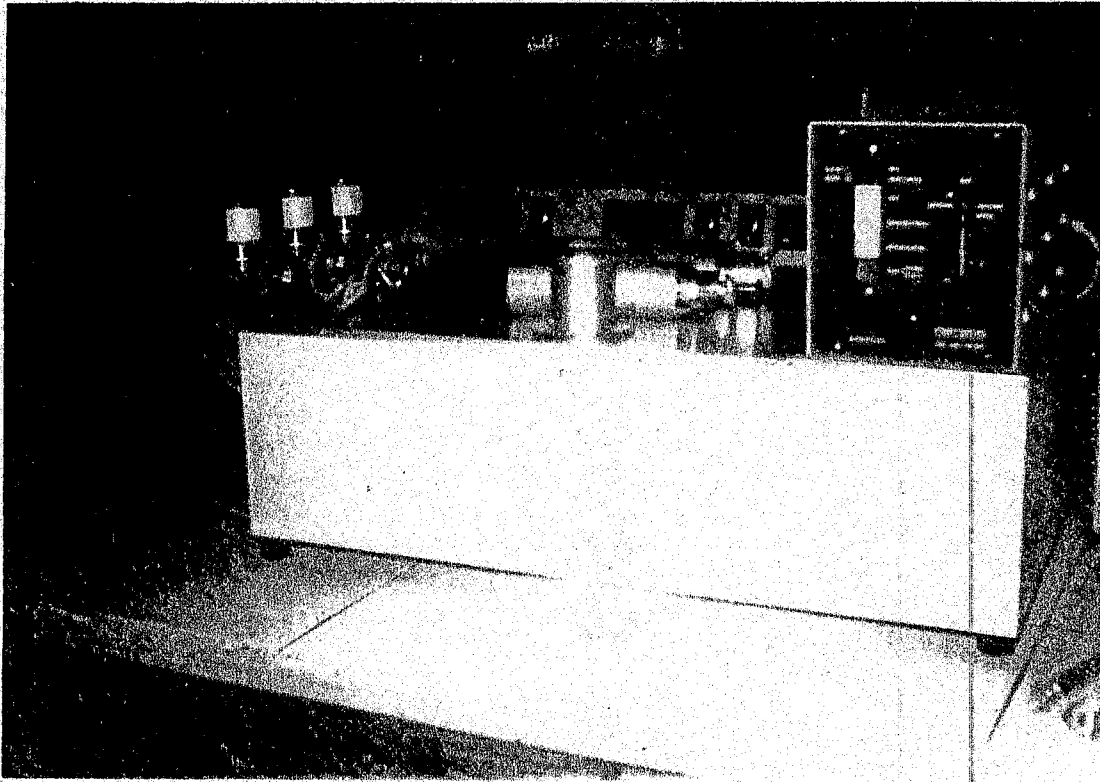
x + w = 40.587g

w = 40.587 - 40.551 = 0.036g

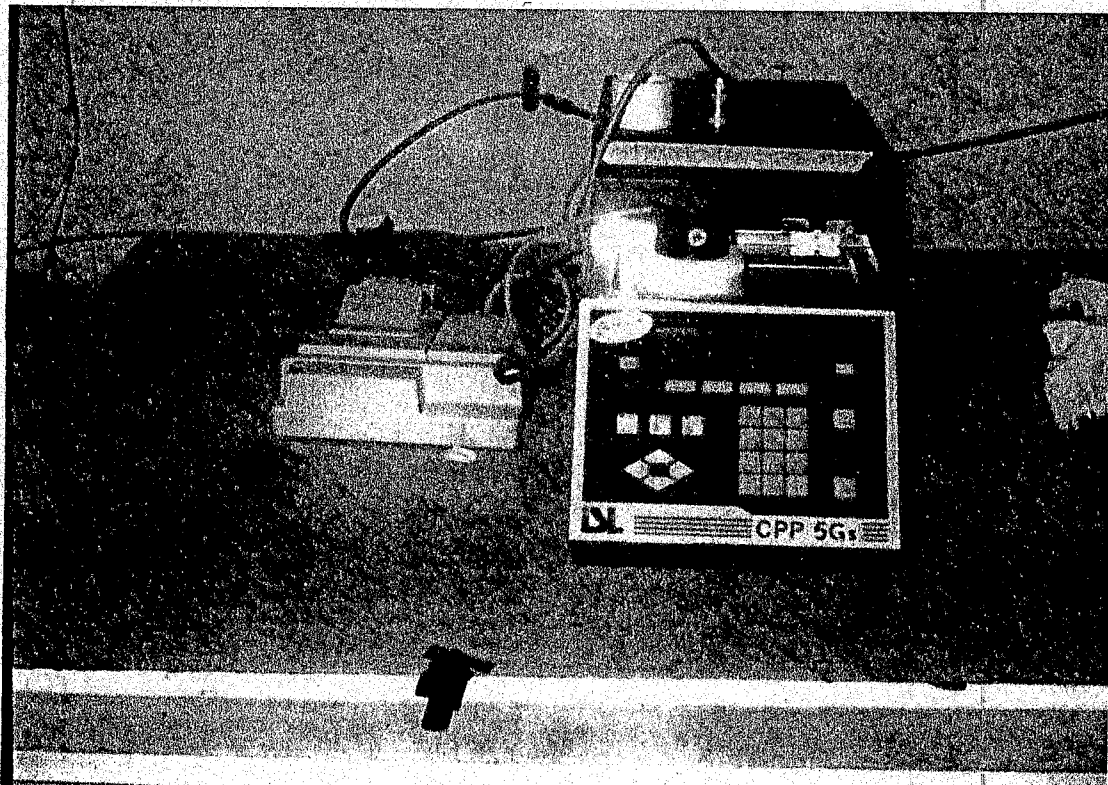
% ash content =  $\frac{w}{W} \times 100$   
=  $\frac{0.036}{10.148} \times 100$   
= 0.35wt%



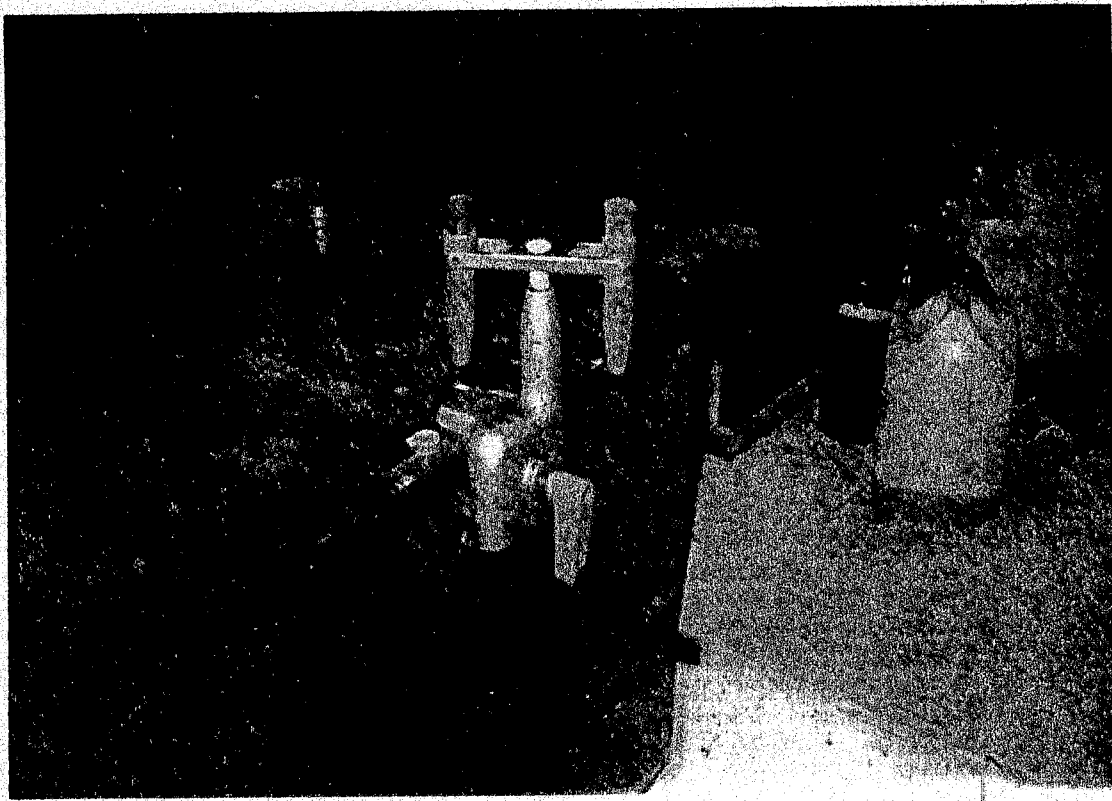
**Automated Viscometer**



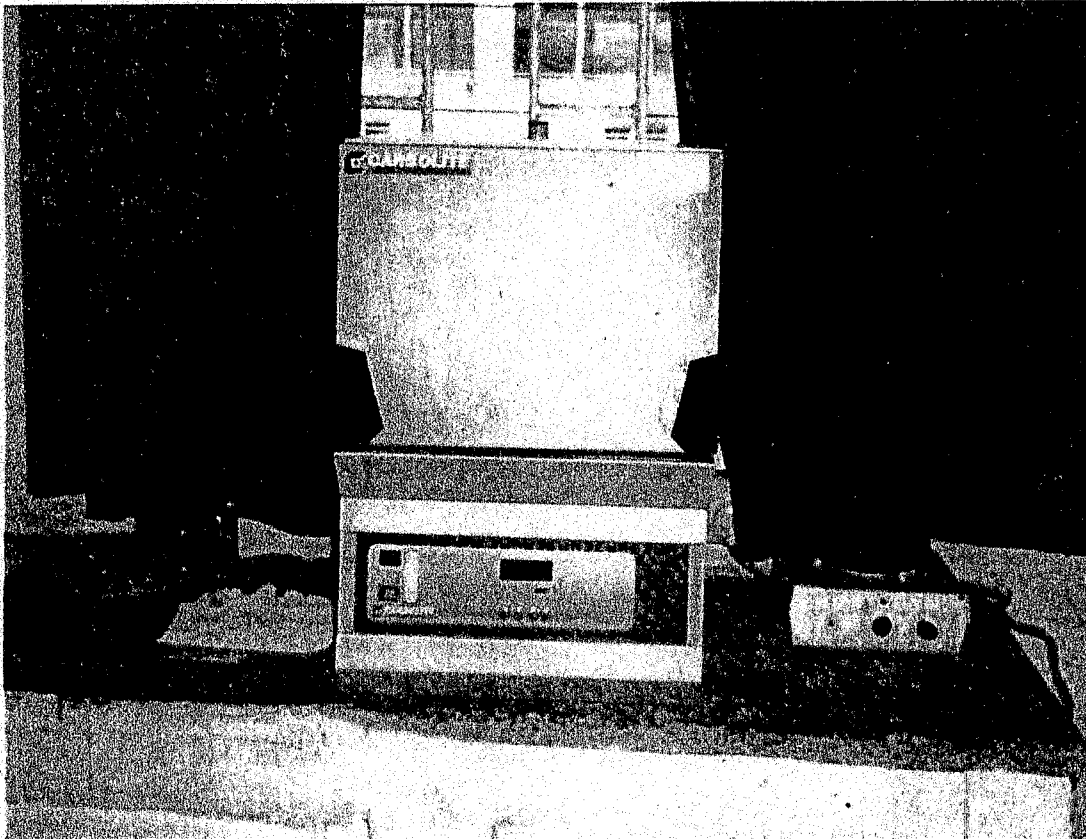
**Reid Vapor Pressure Apparatus**



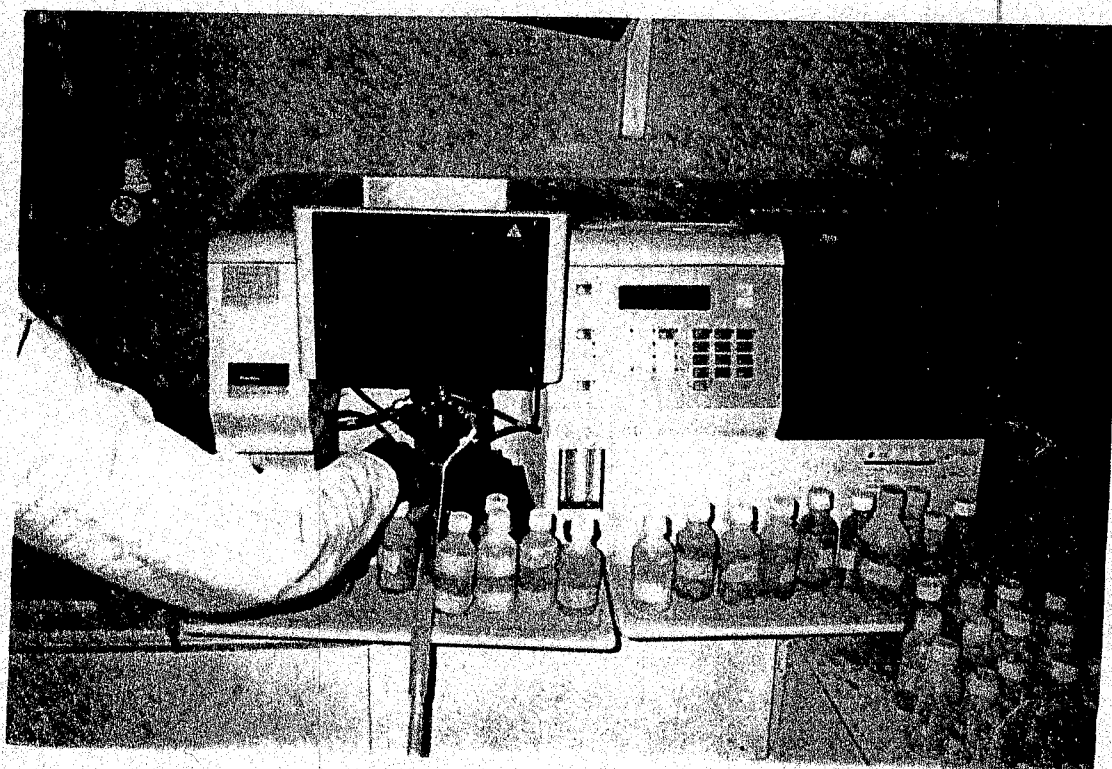
**Automated Pour Point Apparatus**



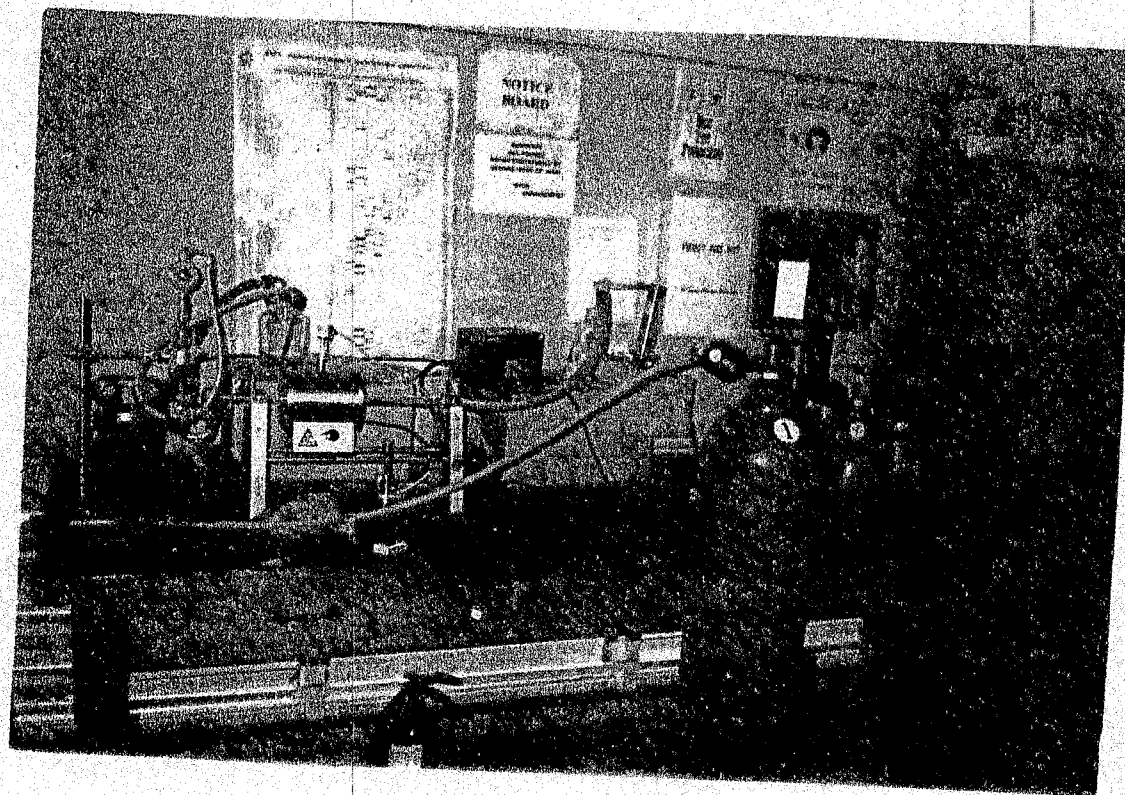
**Centrifuge Apparatus (manual)**



**Muffle Furnace**



**Atomic Absorption Spectrometer (AAS)**



**Sulfur Analyzer**