Determination of Naphthenic Acid Profile in Ghana's Jubilee Oil Using Gas Chromatography-Mass Spectrometry

A thesis presented to the

DEPARTMENT OF NUCLEAR SCIENCES AND APPLICATIONS,
SCHOOL OF NUCLEAR AND ALLIED SCIENCES,
COLLEGE OF BASIC AND APPLIED SCIENCES,
UNIVERSITY OF GHANA

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BSc. (Ghana), 2011

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF

MASTER OF PHILOSOPHY DEGREE

IN

NUCLEAR AND RADIOCHEMISTRY

JULY, 2015

Table of Contents

DECLARATION

I, Ian Osuteye Jnr., do declare hereby that the work presented in this dissertation was carried out by me at the Department of Nuclear Science and Applications, School of Nuclear and Allied Sciences, College of Basic and Applied Sciences, University of Ghana, Legon, under the supervision of Dr. Dennis Kpakpo Adotey and Dr. Kwaku Kyeremeh.

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DEDICATION

This work is dedicated to **my Visionary Father, Mr. Osuteye Ian (Snr.)** and **my Cherished Mother, Mrs. Mercy Osuteye**, whose Prayers, Encouragement, Mentoring, Assistance and Hardwork have pivoted me this far.

ACKNOWLEDGMENT

My sincere gratitude goes to the Almighty God Jehovah for taking me through this Institution and for his guidance in making this project a success.

I am also grateful for the good will and generosity of my supervisors; Dr. Dennis Kpakpo Adotey and Dr. Kwaku Kyeremeh for their outstanding efforts in supervising me through their strong willed perseverance, sense of fairness and openness they exhibited. It is through them that the nucleus of this work was drawn. I also wish to extend the warmest of gratitude to Mr. Ian Osuteye Snr, Mrs. Mercy Osuteye, Ms Elaine Osuteye and Ms Naa Norkor Osuteye, whose support and prayer has brought me this far.

I will also like to thank the staff of Ghana Standards Authority (GSA), especially Mr. Samuel Adu, Mr. Samuel Kofi Mensah, Ms Millicent Kusi and Mr. Paul Osei-Fosu who assisted me in the analysis of my samples at the Petroleum and Pesticide Residue Laboratories.Finally, I would like to acknowledge the debt I owe my course mates and colleagues for their immense contribution towards this work especially Philip Odonkor, Charles Ansre, David Larbi, Suraj Sam Issaka, Randy Boateng, Maruf Abubakar, Abdullah Suhini, John Gyenfie, Frank Boakye-Antwi and Sylvester Ewordu. I would also like to express my appreciation to Mr. Samuel Larbi of Tema Oil Refinery (TOR). Their commitment, ideas and enthusiasm drove me to the completion of this work.

Thanks also to Mr. Clemence Yao Baba (Headmaster, Our Lady of Mercy Senior High School, Tema), for his support and perceptive advice.

LIST OF TABLES

Appendix

LIST OF FIGURES

LIST OF FIGURES (CONT.)

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
API	American Petroleum Institute
DCM	Dichloromethane
EPA	Environmental Protection Agency
ESI-FTICR-MS	Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
FH	Hexane Fraction
FPSO	Floating, Production, Storage and Offloading
FTIR	Fourier Transform Infra-red Spectrometer
GC-MS	Gas Chromatography-Mass Spectrometer
GSS	Ghana Statistical Service
GNPC	Ghana National Petroleum Company
KV	Kinematic Viscosity
LREI GC-MS	Low Resolution Electron Ionization Gas Chromatography Mass Spectrometer
NA	Naphthenic Acid
NFPA	National Fire and Protection Association

LIST OF ABBREVIATIONS (CONT)

OSPW	Oil Sand Processed Water
PP	Pour Point
RD	Relative Density
SC	Sulphur Content
SG	Specific Gravity
TAN	Total Acid Number
USEIA	United States Energy Information Administration
UV-Vis	Ultraviolet-Visible

ABSTRACT

Crude oil is the life-blood of the global economy. Its importance stems from the fact that it is a base product for a wide variety of goods [Drugs, Plastics, Liquefied Petroleum Gas (LPG)]. The oil discovery (over 3 billion barrel reserves in hydrocarbon and gas), about 60 km offshore between the Deepwater Tano and Cape Three Points Block in South western Ghana is a valuable natural asset and it has the potential of boosting the Ghanaian economy. During petroleum processing, various waste products are generated. One of such products is Naphthenic acids (NA). Naphthenic acids are organic acids naturally occurring in crude oil and a constituent of waste associated with oil refinery. Naphthenic acids serve as biomarkers for identification of the source of crude oil. The presence of Naphthenic acid in the aquatic environment causes toxic effects due to their weak biodegradable nature; the toxicity of Naphthenic acids depends on the class of Naphthenic acids present in the crude oil. The study assessed the profile of Naphthenic acids in Ghana's Jubilee crude oil using Low Resolution Electron Impact – Gas Chromatography Mass Spectrometry (LREI-GCMS) after isolation of Naphthenic acids in the Jubilee oil by a modified Kupchan's Partitioning Process. The Mass Spectrometric (MS) Work Station Software was used for the identification of the Naphthenic acids present in the Jubilee crude oil. The quality of the Jubilee oil was also evaluated through the use of some key physico-chemical parameters [Total Acid Number (TAN), Sulphur Content, Viscosity, Pour Point, Flashpoint, Water Content and Densities] based on the American Standards for Testing and Materials (ASTM, 2007). The Total Acid Number was determined by Colorimetric Titration (ASTM D974); Sulphur Content by X-ray Fluorescent Spectrometry (ASTM D4294); Pour Point by the use of the SETA cloud and

Pour Point Refrigerator Technique (ASTM D97); Viscosity by Gravity Timed Method (ASTM D445); Density by the Hydrometer Method (ASTM D1298); Flashpoints by the Pensky-Martens Closed Cup Method (ASTM D93); and Water Content by Distillation (ASTM D95). The results for the physico-chemical analysis revealed that, the Jubilee crude has a Flashpoint of > 80.5 ^{0}C, Density of 36.55 ^{0}API, Pour point of -15 ^{0}C and Sulphur content of 0.168 wt%. The Total Acid Number (TAN) for the Jubilee crude oil was 0.58 mg KOH/g crude; Viscosity of 3.899 cSt at 50 ^{0}C and a negligible Water content. Based on National Fire Protection Association (NFPA 30) and American Petroleum Institute (API) classification standards, the results for the physico-chemical parameters indicates that Ghana's Jubilee is combustible, light and sweet crude with relatively high Acid content, low Pour point and Viscosity. The analysed (using MS Work Station Software) LREI-GCMS chromatogram identified two Naphthenic acids, a couple of homologues belonging to the monocyclic ring family$(\boldsymbol{z = -2})$**.** The ${}^{\mathrm{m}}/_{\mathrm{z}}$ peaks of these acids were found at 168.1 and 184.1. These masses correspond to molecular formulas $(C_{10}H_{17}O_2)^-$ and $(C_{18}H_{17}O_2)$ respectively. The Naphthenic acids were identified as Metaethyl-3-cyclopentylpropanoic acid, $(C_{10}H_{17}O_2)^-$ and Metaethyl-3-cyclopentylbutanoic acid, $(C_{11}H_{20}O_2)$

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Crude oil is the life-blood of the global economy. Crude oil has been regarded as one of the important non-financial commodities in the world and it supplies 40 percent (40%) of the world's total energy needs (more than any other single commodity) [Hubbard, 1998]. Crude oil's importance stems from the fact that it is the base product for a number of indispensable goods, including gasoline, automobile components, liquefied petroleum gas (LPGs), medicines, polyesters, household interiors, jet fuel and plastics (Khaleef, 2011). Due to the pre-eminent role of crude in the global economy, crude oil makes for great investment.

Ghana discovered oil in 2007 in commercial quantities. The oil deposits which have a total proven reserve of about 3 billion barrels (480,000,000 m^3) are found in four main regions of sedimentary basins: Tano-Cape Three Points Basin (Western Region), Saltpond/Central Basin (Central Region), Accra-Keta Basin (Eastern Region) and the Voltarian Basin (Northern Region).

The oil field, named Jubilee, is located 60 km offshore between the Deepwater Tano and Cape Three Point block. Commercial production of the Jubilee crude oil started in 2010. The production is centered about 85,000 barrels per day (13,500 m^3/d) [Kokutse, 2007; Owusu and Nyantakyi, 2013].

Crude oil is not homogenous and its characteristics vary widely from oilfield to oilfield, from well to well in the same oilfield; the depth of the well, and the year of production. There is therefore the need for constant monitoring of the physicochemical properties of the crude oil including the Sulphur content, Flash Point, Water Content, Pour Point, Density, Total Acid Number (TAN) and Viscosity (Cao, 1992).

Understanding the physicochemical properties of crude oil is essential for quality assessment, formulation process such as production, refinery, storage, transportation, environmental behaviour monitoring and effects. Additionally, knowledge of the physico-chemical properties provide valuable insight into pressing environmental concerns globally because of toxic effects when crude oil invades aquatic ecosystems either from accidental spills or normal commercial activities (Martnez-Jernimo and Villase Cor, 2005).

Naphthenic acids are natural constituents of petroleum, where they were thought to have evolved from anaerobic microbial degradation of petroleum hydrocarbons (Tissot and Welte, 1978; Meredith et al., 2000; Watson et al., 2002). These are primarily the organic acids in crude oil (Meredith et al., 2000). Naphthenic acids account for as much as 4% of raw petroleum by weight (Barrow et al., 2003).

Naphthenic Acids (NA) are a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids with the general chemical formula $CnH_{2}n+_{Z}O_{2}$, (where n indicates the carbon number and z is a negative even integer signifying hydrogen deficiency (Holowento et al., 2002).

During petroleum processing, various waste products are generated. One of such products is Naphthenic acids (NA). NAs are responsible for certain problems observed in the refining of oil, such as the deactivation of the heterogeneous catalysts used in the refineries and their contribution to the salt deposits in the pipelines [$(RCOO)_2Ca$] {Nordli et al., 1991}. They are also the primary toxicants in wastewaters associated with oil refineries and oil sands extraction (Avinash, 2013). Naphthenic acids might enter surface water systems through mechanisms such as groundwater mixing, erosion of riverbank oil deposits in oil-producing regions and processes involved in the enhanced recovery of crude oil (Brient et al., 1995).

NA's act as natural emulsion stabilizers during degasification in oil production (Sjoblom et al., 2000). Their presence induces the decrease of the interfacial tension required for the formation of a stable emulsion. The chemical structure and the amount of NA's have an important role in regard to the interfacial tension (ɣ) values (Saab et al., 2005). They have surfactant properties and are the natural components in most petroleum sources including the bitumen present in the oil sands (Schramm et al., 2000; Lochte et al., 1955; Brient et al., 1995; Fan, 1991). NA's are considered as biomarkers related to oil maturation and biodegradation level of oil reservoir, because they are weakly biodegradable (Meredith et al., 2000; Headley et al., 2002; Dzidic et al., 1988).

The NA's are also useful for fingerprinting fuel spills in the environment because they are more resistant to weathering than the non-polar alkane, isoprenoid, and alkylcyclohexane hydrocarbons (Rostad & Hostettler, 2007). Naphthenic acids can be solubilized to produce metal salts (e.g., sodium and copper naphthenates) that have industrial applications such as surfactants and fungicides for wood preservation (Davis, 1967; Herman et al., 1994; St. John et al., 1998). They are used in textiles, emulsifiers, paint driers, and adhesion promoters in the manufacture of tyres (Brient et al., 1995).

Knowledge of the physicochemical properties and naphthenic acid profile of the Jubilee oil is essential in assessing the impact of the oil on aquatic habitat and refinery environments. Data on the naphthenic acid profile in Ghana's Jubilee is scarce and almost non-existent. It is therefore imperative that the naphthenic acids profile in Ghana's crude oil is characterized, as well as its physicochemical properties in order to provide reliable and accurate data, to enable governmental agencies like the Ghana National Petroleum Corporation (GNPC), Non-Governmental Organizations (with interest in oil exploration) and Environmental Protection Agency (EPA) regulate the activities of the oil exploration companies. In addition, such data will help interested agencies estimate the potential harmful effects of Naphthenic acids in the aquatic environment and the cost to be incurred during the refinery of the crude oil.

Naphthenic acids in crude oil differ from one origin to another. Knowledge of the acid origin, their extraction, the quantitative and structural study, the phase equilibria of the water-oil-carboxylic acid systems, and the interfacial activity is required to better understand the organic acid chemistry (Saab et al., 2005). Further, toxic action and corrosivity is determined by the structure of the naphthenic acid, hence identifying the type of naphthenic acid present in crude oil and the amount is essential (Lo et al., 2006; Hsu et al., 2000).

1.2 RESEARCH PROBLEM

The production of Jubilee crude oil holds the promise of boosting the economy of Ghana. A survey conducted by Reuters show that Ghana's economy could grow at about 14.7 % in 2011; one of the world's fastest growth rates, boosted by oil production (Ndaba, 2010). This will result in development in infrastructures in areas near the oilfield as well as provide manpower to meet the demands of production and possible refinery of the oil increasing government revenues by a quarter. It is going to impact local businesses and enhance tourism in suburbs of the oil field (Asafu-Adjaye, 2010).

However production of the oil has risk associated with it; such as oil spillage, fire hazards, and corrosion of refinery units and emissions of poisonous gases. These risks can be highly toxic and can cause a long-lasting, damaging impact to surrounding neighbourhoods, waterways, commercial, agriculture and industrial areas.

This proposed research aspires to explore some properties of the crude oil that affect production units, pollute the environment and pose health hazards to workers and the public. To achieve this, physico-chemical parameters of Ghana's Jubilee oil will be assessed to generate data. The data generated will help in the formulation of appropriate policy interventions to safeguard workers, indigenes, equipment, the environment and the ecosystem at large.

1.3 RESEARCH OBJECTIVES

1.3.1 Main Objective

The study endeavours to assess the naphthenic acid profile and to characterize the classes of naphthenic acids in Ghana’s Jubilee oil.

1.3.2 Specific Objectives

(a) To classify the quality of Ghana’s Jubilee oil based on its physico-chemical properties compared with global standards.

(b) To determine the naphthenic acids in Ghana’s Jubilee oil using Gas Chromatography coupled with Mass Spectrometry (GC-MS).

CHAPTER TWO

LITERATURE REVIEW

2.1 OVERVIEW OF NAPHTHENIC ACIDS

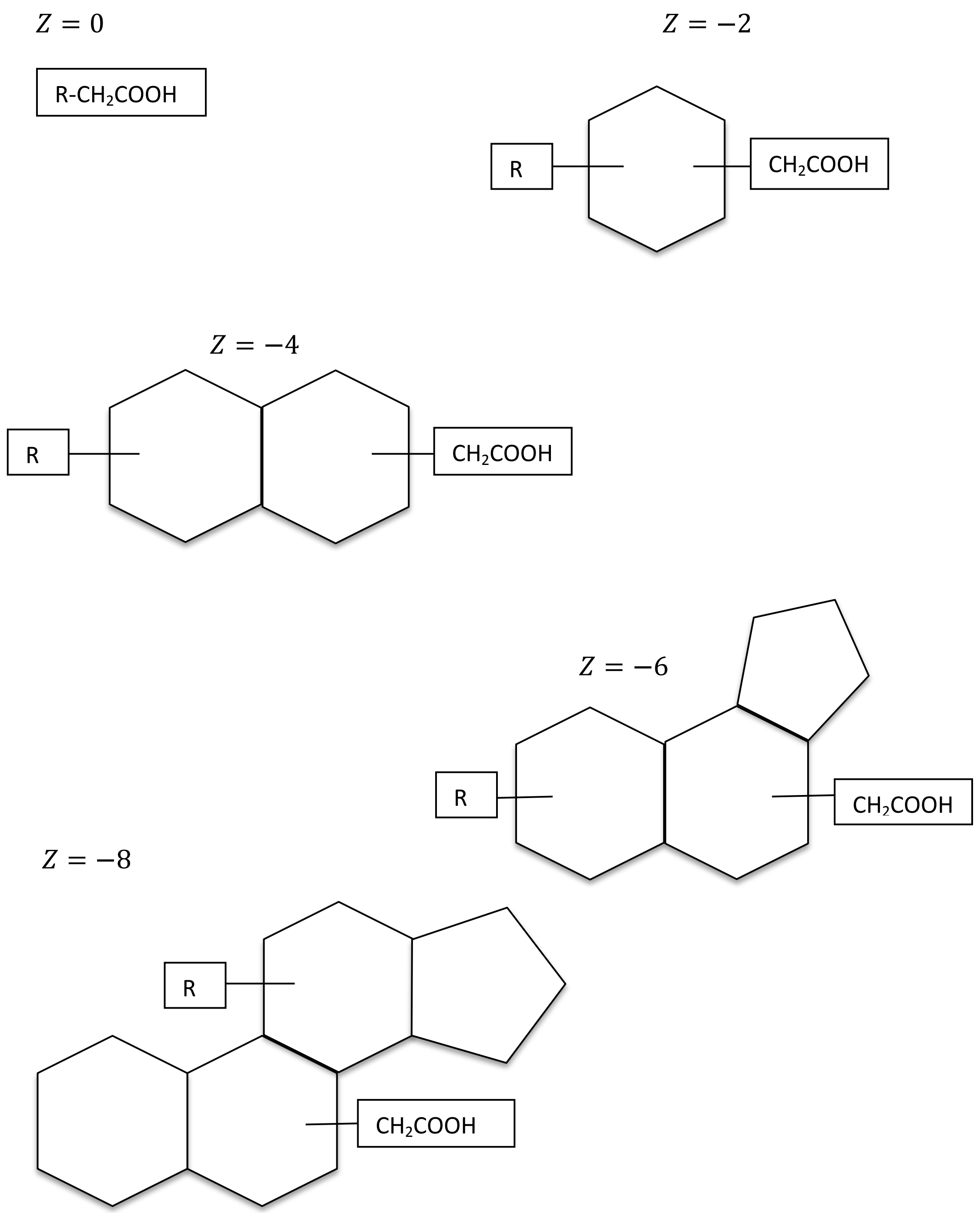
2.1.1 Naphthenic Acid Chemistry

International Union of Pure and Applied Chemistry (IUPAC) defines Naphthenic Acids (NAs) as acids, essentially monocarboxylic, derived from naphthenes. Naphthenes are primarily cycloalkanes particularly cyclopentane, cyclohexane and their alkyl derivatives (McNaught and Wilkinson, 1997). The cycloaliphatic acids include single rings and fused multiple rings. The carboxyl group is usually bonded or attached to a side chain rather than directly to the cycloaliphatic ring (Fig. 2.1) (Fan, 1991; Dzidic et al., 1988; CEATAG, 1998)

The components of naphthenic acids are commonly classified by their structures and the number of carbon atoms in the molecule. Naphthenic acids are represented by the general formula (Dzidic et al., 1988; Fan, 1991):

$$\mathbf{C_nH_{2n+z}O_2}$$

Where: **n** represents the carbon number and **z** is an even, negative integer corresponding to hydrogen deficiency mainly due to ring formation in the structure. Thus the absolute value of z divided by 2 gives the number of the rings in the compounds. A z-value of 0 means acyclic acids, which are believed to be highly branched (Rudzinski et al., 2002) rather than linear natural fatty acids. A z-value of -2 represents monocyclic or mono-unsaturated NAs; -4 represents bicyclic compound. The z-value may also include unsaturation in the chemical structure. The generality of the formula allows for a vast array of isomers for each value of n and Z. Fig 2.1 shows structural examples of what has been termed “classical NAs” by Grewer et al., (2010).



where R, represents an alkyl group

Fig 2.1 Examples of classical structures of NAs

Table 2.1 shows a review of the occurrence and fate of naphthenic acids with their molecular weights and families (Headley and McMartin, 2004).

Table 2.1 Molecular weights (M.W) of different 'z' series and 'n' families of Naphthenic Acids ($C_nH_{2n+z}O_2$).

No. of Carbon atoms	M.W (z = 0) (open chain)	M.W (z = -2) (1 ring)	M.W (z = -4) (2 rings)	M.W (z = -6) (3 rings)
10	172	170	168	166
11	186	184	182	180
12	200	198	196	194
13	214	212	210	208
14	228	226	224	222
15	242	240	238	236
16	256	254	252	250
17	270	268	266	264
18	284	282	280	278
19	298	296	294	292
20	312	310	308	306

Z= "hydrogen deficiency"

Table 2.2 (Brient et al., 1995; CEATAG, 1998; Herman et al., 1993; Headley et al., 2002) shows some general characteristics of Naphthenic acids

Table 2.2: Physical and Chemical Properties of Naphthenic Acids

Parameter	General Characteristics
Colour	Pale yellow, dark amber, yellowish brown, black
Odour	Primarily imparted by the presence of phenol and Sulphur impurities; musty hydrocarbon odour
State	Viscous liquid
Molecular weights	Generally between 140 and 450 amu
Solubility	(i) <50 mg/L at pH 7 in water (ii) Completely soluble in organic solvents
Density	Between 0.97 and 0.99 g/cm^3
Refractive Index	Approximately 1.5
pKa	Between 5 and 6
Log K_{ow}	(i) Approximately 4 at pH 1 (ii) Approximately 2.4 at pH 7 (iii) Approximately 2 at pH 10
Boiling point	Between 250 and 350 ^{o}C

Variation occurs in values with naphthenic acids source and composition. Values also vary between native and bitumen-extracted compounds (Brient et al., 1995; CEATAG, 1998; Herman et al., 1993; Headley et al., 2002). The pH of naphthenic acids show a relationship its solubility (Headley et al., 2002, CEATAG, 1998). Chemically, naphthenic acids behave like typical carboxylic acids with acid strengths similar to those of the higher fatty acids. Naphthenic acids are slightly weaker than low molecular weight carboxylic acids, such as acetic acid (Whelan and Farrington, 1992; Tissot and Welte, 1984; Snowdon and Powell, 1982). Metal salts can be produced from naphthenic acids that are soluble. These salts have industrial applications (Table 2.3) [Brient et al., 1995; St. John et al., 1998; Herman et al., 1994; Brient, 1998].

Over two-thirds of the naphthenic acids produced are converted to metal salts, the largest component of which is made into copper naphthenate used for the preservation of wood products. (Brient et al., 1995). Although the major commercial use of naphthenic acids has been in the production of metal soaps, they can also react to form esters, amine salts, amides, imidazolines, and other derivatives (Whelan and Farrington, 1992; Tissot and Welte, 1984; Stajner et al., 1998).

Table 2.3: Industrial uses of Naphthenic acids

Naphthenic acid metal salt	Industrial Application
Na salt	(i) Emulsifying agent for agricultural insecticide (ii) Additive for cutting oil emulsion breaker in oil industry
Ca naphthenate	Additive for lubricating oil
Fe and Mn naphthenate	Fuel additives for improving combustion, reducing corrosion
Pb and Ba salt	Catalyst for oil based paints
Cu and Zn naphthenate	Wood preservatives
Co naphthenate	(i) Curing agent in rubber and resins (ii) Adhesion promoter of steel cord to rubber
Mn, Pb, Co and Ca soaps	Oxidative catalyst

2.1.2 Sources of Naphthenic Acids

2.1.2.1 Raw Ore and Crude Oils

NAs are present naturally in crude oils (Seifert and Teeter, 1969; Tissot and Welte, 1978). They comprise part of the petroleum acids whose concentration varies from undetectable to 3% by weight depending on the source of oil (Lochte and Litman, 1955). Typically, oil sands crude oils contain NAs up to 4% by weight (Barrow et al., 2010).

2.1.2.2 Aqueous Presence

NAs are useful in the extraction of bitumen from the oil sands because they are natural surfactants released during The Clark Hot Water Process; a process that encourage bitumen liberation from the sand grains using hot water at 50 ^{o}C – 80 ^{o}C because the bitumen is less viscous (Masliyah et al., 2004). Under current practice, oil sands operators store all the process waters and tailings on site. NAs separated from bitumen during the extraction process dissolve in alkaline solution and accumulate with other waste products in the fluid tailings ponds. NAs are also present in surface water and groundwater. They are found to occur naturally in some surface waters that are in contact with the oil sand deposits in northeastern Alberta. The concentrations of NAs in surface water taken at various locations along the Athabasca River were in the range of 0.1 to 0.9 mg L^{-1} (Schramm et al., 2000). Near-surface aquifer water has been found to contain 2 to 5 mg L^{-1} NAs, which reflect natural contact with oil sands (CONRAD, 1998). NAs have also been found in natural groundwater with concentrations <4 mg L^{-1} and in basal and limestone aquifers at concentrations >55 mg L^{-1} (CONRAD, 1998).

2.1.2.3 Coal

Scott et al., (2009) proposed that a potential source of NAs in groundwater is coal. In their study, water from two domestic wells near coal deposits was extracted and analyzed by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FTICR-MS). The results unequivocally confirmed the presence of classical NAs with two oxygen atoms and other organic acids containing three, four, and five oxygen atoms. The reported NA concentrations using ESI- FTICR-MS in these two wells were 1 mg L^{-1} and 0.3 mg L^{-1}, respectively. Furthermore, leachates from distilled water percolated through three different crushed coals were shown to contain various organic acids, including NAs with concentrations reported at 0.7, 0.2 and 0.4 mg L^{-1}.

2.1.3 Ecological complications

NAs are toxic to aquatic algae and other micro-organisms. NA molecules possess hydrophilic and hydrophobic functional groups which allow them to penetrate the cell membranes and disrupt cellular function, eventually resulting in cell death (Frank et al., 2008). NAs in fresh fluid tailings can cause an acute toxic effect to aquatic organisms (LC50 <10% v/v for rainbow trout) and to mammals (oral LC_{50} =3.0 g/kg body weight). (MacKinnon and Boerger, 1986; United States Environmental Protection Agency, 1984) Herman et al., (1994) showed that acute toxicity of Oil Sand Processed Water (OSPW) by natural processes was reduced within one year while the removal of chronic toxicity required 2 to 3 years. More recent studies (MacKinnon, 2004) showed that the degradation of NAs in isolated tailings pond water occured at a rate of 16% per year over the first 5 years (from 130 to 24 mg L^{-1}), but further degradation of NAs beyond 5 years became insignificant. The degradation and detoxification rates have been shown by Han et al., (2009) to be related to structure. The most rapidly degraded NAs are the least cyclic (Z = 0 and Z = -2); whereas some of the more complex NAs can have half-lives in the order of 12.3 to 13.6 years. Thus, toxic effects do not relate to the NA concentration directly but are more a function of content and complexity of NAs (Brient et al., 1995; CONRAD Environmental Aquatics Technical Advisory Group, 1998; Lai et al., 1996) It is not well established which specific NAs are the most toxic due mainly to the presence of hundreds of these compounds in these sources (crude oil and waste water and oil sands). Even though the acutely toxic fraction of NAs can degrade naturally in experimental pits and wetlands, the lengthy residence time required makes it impractical for a direct environmental discharge of water. Moreover, NAs of high molecular weight are resistant to biodegradation hence can persist in reclaimed environments and pose a potential chronic toxicity risk (Zhao et al., 2012).

2.1.4 Methodological Challenges

Many analytical methods have been developed to characterize NAs, however, all the methods tend to be semi-quantitative, and lack the ability to identify individual isomers in the crude oil extract and water tailings. The challenges encountered include:

a. quantitation of the total concentration of NAs in a sample;
b. characterization of the structures of the compounds in the complex-poorly defined mixtures obtained using various sampling protocols;
c. determination of the concentration of each individual NA and other components in the mixture; and,
d. assessment of the toxicity of each of the components in the extracts (Zhao et al., 2012).

2.2 ANALYTICAL METHODS

2.2.1 Extraction of Naphthenic Acid

Jivraj et al., (1995) filtered tailing sample through a 0.45 µm millipore filter to remove suspended soilds. The filtrate was then acidified with H_2SO_4 to a pH of 2 to 2.5 to precipitate the NAs and the extracted the precipitate twice using dichloromethane (DCM) at a 1:2 solvent to water ratio. The dichloromethane extracts were combined and the solvent evaporated overnight to dryness. The residue was reconstituted in alkaline water (water with pH of 8 or 9) and subjected to ultrafiltration to separate the NAs (molecular weights of < 1,000 in general) from other organic acids which with higher molecular weights could skew analytical results. This method suited well for procuring smaller amounts of NAs for analytical purposes because filtration step is impractical for large water samples.

Rogers et al., (2005) used gravity settling of the suspended solids from non-acidified tailings samples for 3 days. The water was decanted acidified to pH2.5. The NAs were extracted with dichloromethane at a 1:2 solvent to water ratio. Rotary evaporation was used to recover and recycle the solvent. The organic extract was reconstituted using a 0.1 M sodium hydroxide (pH 13). The pH was reduced to 10 to produce insoluble organic acids which were removed by filtration using a 0.45 µm glass fibre micrrofilter. The filtrate was then subjected to a 1,000 MW cutoff ultrafiltration to help remove additional organic acids from NAs. The extraction efficiency of NA was reported to be 85 %. Gravity settling does not provide full clarification as compared with centrifugation or filtration. The modified procedure was simpler and was welcomed by other researchers (Barrow et al., 2010; Janfada et al., 2006) when dealing with a large sample size.

Bataineh et al., (2006), adjusted the tailings water to pH 11 using 2 M NaOH as the first step (Equation 2.1), and centrifugation was applied to remove suspended materials. The supernatant was recovered by using H_2SO_4 to lower the pH to <2 (Equation 2.2) and was then extracted three times with ethyl acetate containing 2% acetic acid by volume. The extracts were combined together and washed with saturated NaCl solution and dried over anhydrous Na_2SO_4. Rotary evaporation was employed to concentrate the sample. The residue was transferred to a small vial in ethyl acetate and taken to dryness under a gentle stream of nitrogen. Bataineh et al., (2006) centrifuged the samples for 20 min (15,000 g) and then adjusted the pH to 3 using formic acid. Solid phase extraction (Oasis HLB sorbent) cartridges were conditioned sequentially with ethyl acetate, methanol and 0.1 % formic acid prior to the addition of the acidified sample to the cartridge at a rate of 2 mL/min. Distilled water was used to rinse off all aqueous solution and the cartridges were dried under vacuum. The NAs were eluted with ethyl acetate. The extract was then dried by evaporating the ethyl acetate under nitrogen at 35 °C.

Mediaas et al., (2003), reported a method developed for Statoil (a leading energy company in oil and gas production based in Norway) to selectively isolate carboxylic acids from crude oils, distillates and other organic solvents. A sugar-based QAE Sephadex A-25 acid ion exchange resin was used. The hydrophilic acid ion exchange resin is more selective towards carboxylic acids than hydrophobic ion exchange resin.

The acid ion exchange resin exhibited excellent isolation efficiency and selectivity when used to recover carboxylic acids from crude oils and its distillates. Acid recovery from the distillates, the residue, and the crude oil are reported to be between 95 and 100 mol %.

$$RCOOH + NaOH \rightarrow RCOONa + H_2O \qquad 2.1$$

$$RCOONa + H_2SO_4 \rightarrow RCOOH + Na_2SO_4 \qquad 2.2$$

2.2.2 Quantification Analysis

Following sample preparation, Jivraj et al., (2005) analysed the acids using Fourier Transform Infrared spectroscopy method (FTIR) and the absorbance of the monomeric and dimeric forms of carboxylic groups were measured. The sum of the absorbances at the characteristic peaks was compared with the calibration curve obtained by commercially available NAs with known concentrations under the same analytical method to quantify the concentration of NA in sample (water). Hydrogen bonding occurs between adjacent carboxylic groups. The dimeric C=O bond of Naphthenic acids shows a single and sharp infrared photon absorbance near wavelength about 5,880 nm, or a wavenumber of 1,700 cm^{-1}. When diluted in dichloromethane, the dimeric form was in equilibrium with the monomeric form. The monomeric C=O bond absorbs at 1,743 cm^{-1}, whilst the dimer absorbs at 1,704 cm^{-1}. FTIR overestimates NA concentrations. This is due to the fact that, FTIR quantifies NA concentration in response to the absorbance of carboxylic groups, hence cannot identify the difference between classical naphthenic acids and the variety of non-classical NAs. In addition, the calibration curve which is often obtained from commercial NAs, may not represent the real NAs extracted from crude oil and tailings samples (Grewer et al., 2010; Yen et al., 2004).

Mohamed et al., (2008) reported that Ultraviolet-Visible (UV-Vis) absorption and fluorescence emission spectrophotometry are potentially inexpensive and fast methods for screening of oil sands NAs, and for the semi-quantification of NA concentrations. There are components in the NA complex have various levels of unsaturation and aromaticity and contain carboxylic acid functional group that can absorb UV-Vis radiation and also generate an intense fluorescence emission.

Holowenko et al., (2002) employed Gas Chromatography- Mass Spectrometry (GC-MS) with electron impact ionization to characterize nine water samples derived from oil sands extraction processes. For each sample, a valley between groups of NAs with carbon numbers <21 and carbon numbers >21 was found in the three- dimensional bar graphs based on the abundance of NAs to the corresponding carbon number and Z families. The group of NAs with carbon numbers 22 to 33 in Z families 0 to -12 was singled out and defined as “C22+ cluster”. This was a useful means of comparing composition distribution in NAs from various OSPW and with various degrees of acute toxicity.

Headley et al., (2009) noted that unit-resolution MS was not providing a correct interpretation of the compounds being formed. Rather than an increase in C22+ there was actually an increase in concentration of the oxy-NAs, which increased the mass but when using the classical NA formula resulted in a misclassification of the NAs that were present in the sample (Bataineh et al., 2006; Clemente and Fedorak, 2004). Dzidic et al., (1988) developed a method based on negative ion chemical ionization mass spectrometry using fluoride ions produced from NF_3 as the reagent gas in the characterization of NAs in California crude oils and refinery wastewaters. NAs in the presence of other compounds, such as hydrocarbons, can be selectively ionized through an aid-base reaction in the gas phase where the base (F^-) reacts with the acid (RCOOH) to form RCOO- and the acid HF as shown below:

$$F^- + RCOOH \rightarrow RCOO^- + HF \qquad 2.3$$

The spectra exhibit only the single $RCOO^-$ carboxylate ions and nonacidic compounds such as hydrocarbons cannot be ionized by F^- ions. Thus, the spectrum is simplified.

2.3 Physico-chemical Parameters.

All the methods described for the physico-chemical parameters were referenced from the American Standard for Testing and Materials, (ASTM, 2007).

The viscosity of the oil is important for optimum storage, handling and operational conditions (ASTM, 2007). It affects the rate at which spilled oil will spread, the degree to which it will penetrate shoreline substrates, and the selection of mechanical spill countermeasures equipment. An extensive laboratory investigation of crude oil properties when exposed to weathering was used by Brandvik et al., (1990) for predicting the behaviour of oil spilled on the sea. Physical and chemical properties were used to recover crude oil from oil-saturated rubber particles (Aisien et al., 2010). The quality of many petroleum products is related to the amount of sulphur present (ASTM, 2007).

The density of crude oil is necessary for the conversion of measured volumes to volumes or volume to masses or both at the standard reference temperature during custody transfer. Density, RD and API gravity is a factor in governing the quality and pricing of crude oil, with high gravity oils commanding higher prices (Appenteng et al., 2003). Density is also an important indicator for automotive, aviation and marine fuels where it affects storage, handling and combustion. When used in connection with bulk oil measurements, volume correction errors are minimized. This is done by observing the hydrometer reading close to the bulk oil temperature.

Pour point is used to define the cold flow properties of the crude oil taking into account the gravity. TAN, an industry measurement standard, though limited, is useful in predicting problems in refineries. Knowledge about TAN values will help classify the level of the organic acid content of crude oil as either high or low. High acid crude have TAN between 0.5to 1 mg KOH/g crude whilst high acidic crude has TAN >1.0 mg KOH/g crude (Norman, 2006).

Flashpoint is a factor in assessing the flammability hazard of a material. This property is used in shipping and safety regulations to define combustible and flammable materials; thus description of the crude oil's property in response to heat and test flame under controlled laboratory conditions.

The quality of many petroleum products is related to the amount of sulphur present. Combustion of high Sulphur containing crude oil generates dangerous levels of Sulphur dioxide (SO_2) with severe environmental and human health effects. SO_2 has respiratory impacts such as lung irritation, increased breathing rates, and suffocation. It also contributes to the formation of acid rain, which may cause extensive damage to materials and terrestrial ecosystems, aquatic ecosystems, and human populations (Appenteng et al., 2003). Sulphur helps predict the performance, handling and processing of crude oil. In some cases, the presence of sulphur is useful to the product to be achieved (ASTM, 2007).

The water content is relevant in the refinery. The presence of water causes rusting of refinery units, hence has influence on the sale and transfer of crude oil. (ASTM, 2007)

CHAPTER THREE

METHODOLOGY

3.1 GHANA’S CRUDE OIL

3.1.1 Jubilee Oil

Ghana is a country with an estimated population of about 24.6 million people (GSS, 2012). It lies in the Western part of Africa along the coast of Gulf of Guinea. Ghana has been prospecting for oil since 1890 (Owusu and Nyantakyi, 2013). Ghana shares geographical boundaries with Ivory Coast on the west, Republic of Togo on the east, Burkina Faso on the north and the Gulf of Guinea on the south. Ghana is located geographically on latitude 8^0 00´ north of the Equator and longitude 2^0 00´ West of Greenwich Meridian (Owusu and Nyantakyi, 2013).

Fig 3.1 and Fig 3.2 shows the map of the deposit in Ghana as well as the eleven blocks auctioned in Ghana’s offshore waters, the various explanatory wells drilled in those blocks between 2004 and 2008 (Bermudez-Lugo, 2006). The fields recoverable reserves are estimated to be more than 370 million barrels with an upside potential of 1.8 million barrels. It is located at a water depth of 1,100 m (Kable, 2015).

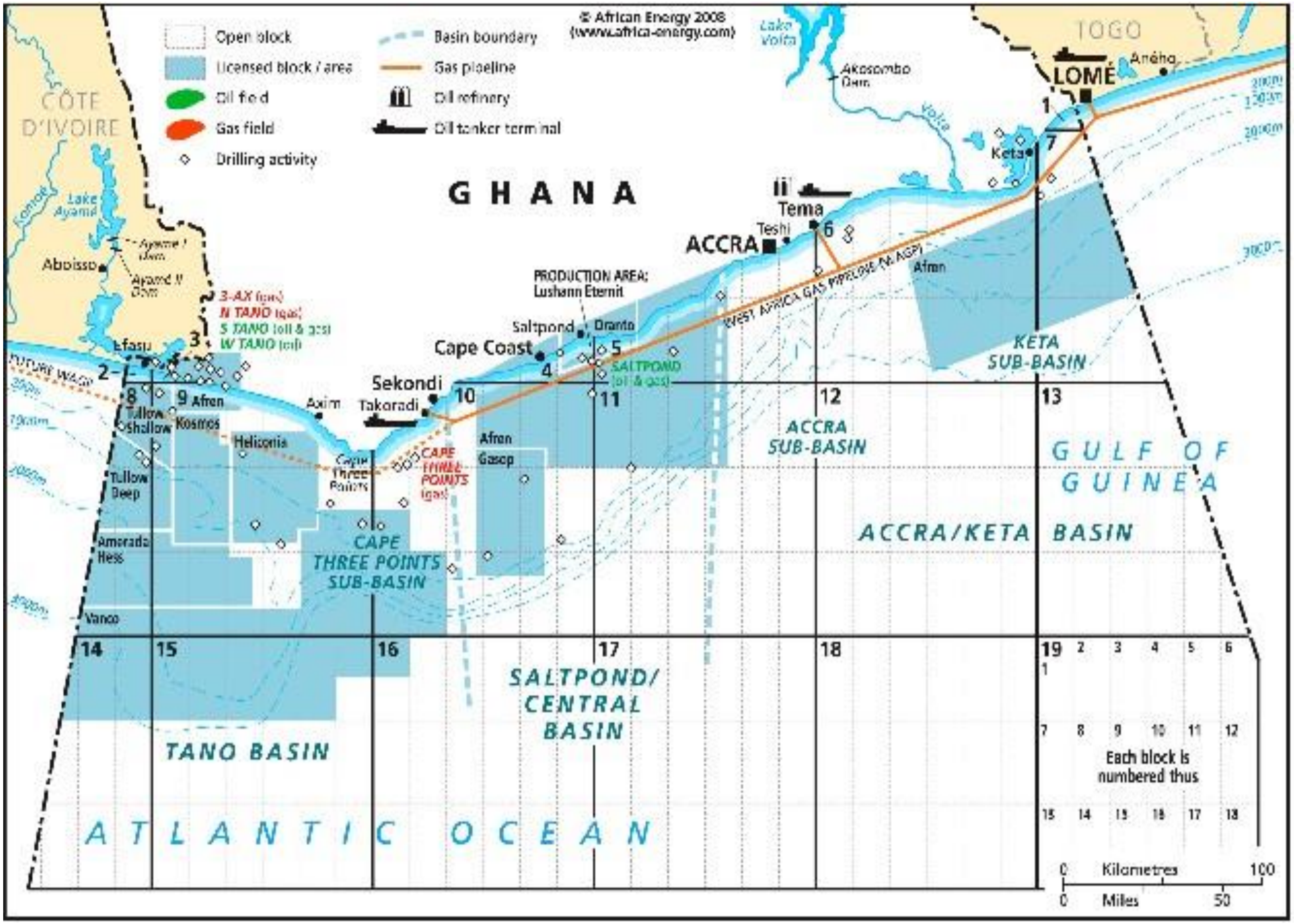


Fig 3.1: A map showing the eleven blocks auctioned in Ghana's offshore waters

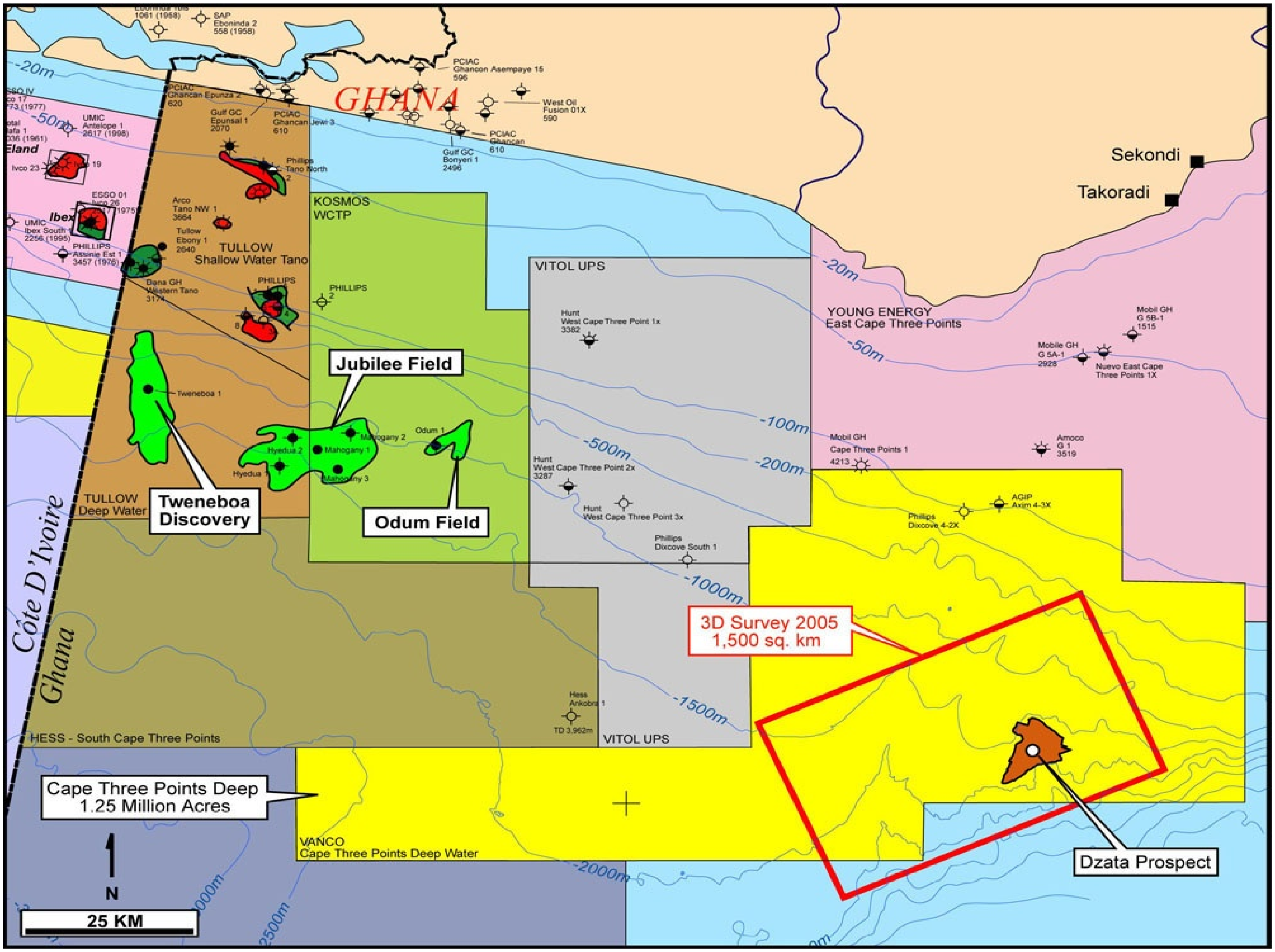


Fig 3.2: A map showing the geographical position of the Jubilee oil field

3.1.2 Location of Ghana's Jubilee oil field

The Jubilee field connects the Deepwater Tano and West Cape Three Points (WCTP) blocks. It is about 63 km from the Ghanaian coast and 132 km southwest of the city of Takoradi. The coordinates of the offshore field is 4.49278, -2.9 16667 (Wikipedia, 2014; Pennwell Corporation, 2009).

3.1.3 Geology of the oilfields

The geology o the Jubilee oilfields is a deepwater cretaceous sandstone (Pennwell Corporation, 2009).

Jubilee's geology has ideal hydrocarbon with turbidite reservoirs deposited in giant stratigraphic traps conditions which are highly effective seals to preserve oil and gas for exploration and exploitation. The field is also rich in gas with reserves estimated to be between 800 billion and 1.2 trillion cubic feet. The estimated size of Jubilee oil's reserve is between 600 million and 1.8 billion barrels of oil (Owusu and Nyantakyi, 2013).

3.2 COLLECTION OF CRUDE OIL SAMPLES

Jubilee oil from Ghana and Bonny light crude oil from Nigeria were obtained from the Quality Control laboratory (QC lab) of the Tema Oil Refinery Company, (TOR), Ghana. TOR obtained the crude oil sample from the FPSO (Floating, Production, Storage and

Off-loading) vessel. The Bonny light crude oil sample from Nigeria was a ship composite from MT NIPPON PRINCESS.

The crude oil samples obtained from TOR for analysis are presented in Fig 3.3a and Fig 3.3b.

According to the Quality Control (QC) officer at TOR, running sample technique was employed onshore. With this technique, a representative sample of the crude was obtained by lowering a corked sampling bottle to the level of the bottom of the outlet connection or swing line. The sampling bottle was opened and returned to the top of the oil at uniform rate such that the sampling bottle was three-fourths full when drawn from the oil in the storage tanks in the oil ship vessel. A composite sample was formed by blending the various tank samples volumetrically to achieve homogeneity.

The composite blend of the Jubilee oil and Bonny light crudes were stored in plastic container and aluminium can, respectively, for analysis.

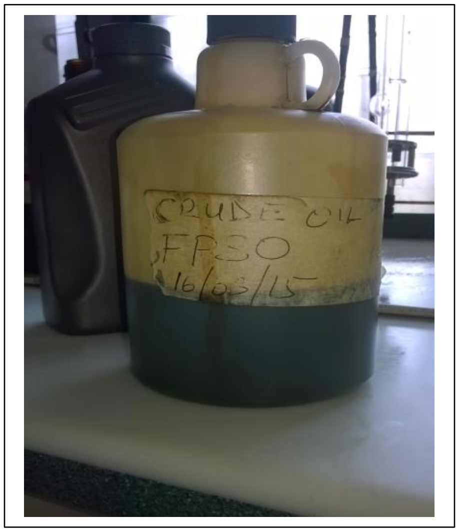


Fig 3.3a FPSO crude oil in sample container

Fig 3.3b Bonny light crude oil in sample container

3.3 ANALYSIS OF CRUDE OIL SAMPLES

Analysis of the crude oil samples were divided into two (2) parts. The first part involved the determination of the physico-chemical parameters of crude oil (Sulphur Content, TAN, Pour Point, Density, Flash Point, Water Content and Viscosity).

The second part of the analysis involved the determination of the NA profile and classes of NA in the crude oil samples.

3.3.1 Physico-Chemical Parameters

All physico-chemical analysis were done at the Petroleum laboratory of the Ghana Standards Authority (GSA).

3.3.1.1 Determination of Sulphur Content Using X-ray Fluorescence Spectrometry (XRF)

Principle

The method is based on premise that every element has a unique atomic structure allowing a unique set of peaks on its X-ray spectrum. The test sample is placed in a beam of X-rays from an X-ray source. The incident beam excites a lower, inner electron, creating an electron hole. An outer electron from a higher energy shell fills the electron hole. The difference in energy between the higher energy shell and lower energy shell may release a radiation in a form of X-rays, thus, the energies of X-rays are characteristic atomic structure of the element of interest and their energy difference. The number and energy of the X-rays emitted are measured by an energy dispersive spectrometer to determine the elemental composition of the specimen, and for that matter Sulphur (Goldstein et al., 2003).

Apparatus

Energy dispersive X-ray Fluorescence Spectrometer (Sulfur meter RX-620SA). These include source of X-ray excitation, X-ray detector which detects the emission of X-ray, Jigs for sample preparation, filters for discriminating between Sulphur Kα and other X-rays of higher energy, Signal conditioning and Data handling electronics which are responsible for X-ray intensity counting, background corrections, conversion of Sulphur X-ray into percent Sulphur concentrations and Display, which reads concentration of Sulphur in mass percent (%).

Reagents and Materials

Di-n-Butyl Sulphide (DBS), which is a high purity standard with certified analysis for Sulphur content for calibration of the Spectrometer, X-ray transparent film which would resist chemical attack by sulphur-containing sample and some high aromatic compounds, Sample cells which meet the Spectrometer’s geometry requirement and also offers resistance to sample attack, and pipette for measuring a fixed volume of the sample into the sample cell.

Experimental Procedure (ASTM D4294)

The instrument was set up for the recording of the net Sulphur X-ray intensity. About 5 mL of DBS (Sulphur standard) was pipetted into the sample cell. The cell was sealed with an X-ray film and jigs for the sample preparation (Fig 3.4b). The cell containing the standard was placed in the XRF instrument (Sulfur meter RX-620SA) [Fig 3.4a], and the measurement for Sulphur taken at a counting rate of 300 seconds. Two additional readings were obtained on the standard using freshly prepared cells and fresh portions of the standard. Having analyzed the standard to obtain an optimum calibration curve based on the net Sulphur counts, the crude oil samples were analyzed for Sulphur content. About 5 mL aliquot of Ghana's Jubilee oil sample was transferred into a fresh sample cell (Fig 3.4c), and prepared for Sulphur content analysis. Readings were taken for three different measurements at a counting rate of 300 seconds each. The same procedure was repeated for Bonny light crude oil and the concentrations, automatically calculated from the calibration curve.

Fig 3.4a Sulphur meter RX – 620 SA

Fig 3.4b Jigs for sample preparation

Fig 3.4c Sample being prepared using jigs

3.3.1.2 Determination of Flashpoint Using Pensky-Martens Closed Cup Method

Principle

This method is based on the premise that every liquid has a vapour pressure and the vapour pressure of any liquid is a function of its temperature. As temperature increases, the concentration of vapour of the liquid in the air increases till a certain concentration of vapour needed to sustain combustion. That point is the lowest temperature at which there will be enough flammable vapour to ignite when an ignition source is applied (NFPA 30, 2003).

Apparatus

The Pensky-Martens Closed Cup Apparatus, (Automated–FP93 5G2); this apparatus include a test cup, test cover and shutter, stirring device, heating source and ignition source.

Reagents and Materials

Toluene

Experimental Procedure (ASTM D93)

An aliquot of the Jubilee crude oil sample was dispensed into the test cup to the calibrated mark. Excess test sample (crude oil) was removed using pipette. The assembly (test cover and cup) was securely fastened into the apparatus (Fig 3.5a). The apparatus was switched on and temperature set at 60.5 ^{o}C to see if the concentration of vapour pressure of the crude will cause an ignition when an ignition source is applied (Fig3.5b). This was to determine if the crude oil was flammable or combustible. The toluene was used to rinse the test cup and the procedure repeated for Bonny light crude oil.

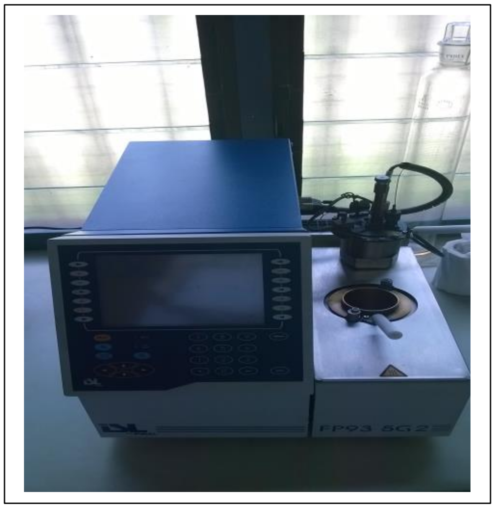


Fig 3.5a Pensky-Martens closed cup apparatus

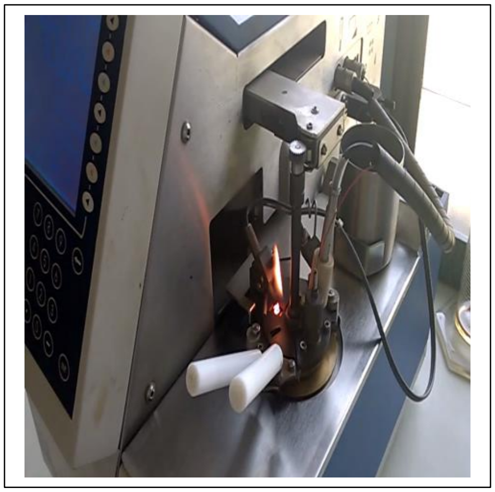


Fig 3.5b Fire application in the sample test during Flashpoint determination

3.3.1.3 Determination of Water Content Using the Dean and Stark Method

Principle

This method determines the quantity of water contained in crude oil using changes in either volume or mass of the oil. The crude oil is heated under reflux with a water-immiscible solvent. This causes both the water and solvent to distil together from the sample. The condensed water and solvents are continuously collected but separated in the glass trap with the water collected beneath because it is denser than the immiscible solvent. This causes the immiscible solvent to return to the glass still. The water content is calculated by the ratio of volume of water collected at the trap to the total volume of crude oil [Equation 3.1] (ASTM, 2007).

Apparatus

Glass still, Heating mantle, Reflux condenser, Measuring cylinder, Graduated glass trap and Retort stand.

Reagents and Materials

Solvent carrier solvent (toluene), Silicone lubricant and Running water

Experimental Procedure (ASTM D95)

About 100 mL aliquot of crude oil sample was measured using a measuring cylinder and transferred into a glass still. The oil adhering to the sides of the measuring cylinder was rinsed with a total of 100 mL (one 50 mL portion and two 25 mL portions) of the toluene (the solvent-carrier liquid). The glass still was placed in the heating mantle and the water trap connected and supported (Fig 3.6b). The tip of the reflux condenser was lubricated and fixed to the glass trap which was in turn connected to a running tap through the jacket of the condenser (Fig 3.6c). Loose cotton was plugged into the top of the condenser to prevent condensation of atmospheric moisture inside it. Heat was applied to the glass still adjusting the rate of boiling so that the condensed distillate discharges from the condenser at a rate of two to five drops per second (Fig 3.6a). Distillation continued until no water was visible in any part of the apparatus except in the trap; and volume of water in the trap remains constant for 5 minutes. The trap and contents were allowed to cool. The water content of the solvent was determined by distilling an equivalent amount of the same solvent used for the crude oil in the distillation apparatus and testing (solvent blank).

The water content {WC}, [% $\left(\frac{V}{V}\right)$], was calculated from the relation:

$$WC = \frac{(volume\ \ in\ water\ trap,\ \ ml) - (water\ in\ solvent\ blank,\ \ ml)}{volume\ in\ test\ sample\ (crude\ oil\ )} \cdot 100\% \qquad 3.1$$

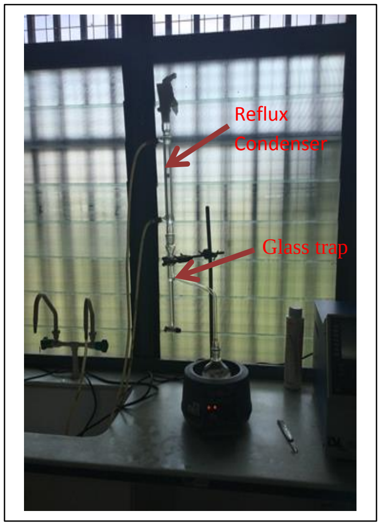


Fig 3.6a Dean and Stark set-up

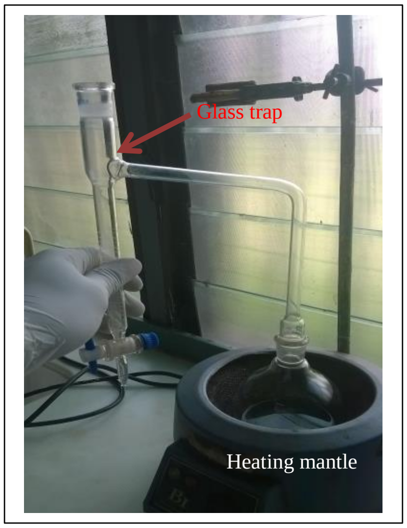


Fig 3.6b Glass trap at point of insertion with glass still

Fig 3.6c Reflux condenser at point of insertion with glass trap

3.3.1.4 Determination of Pour point

Principle

This method is centered on the flow characteristics, thus the lowest temperature under gravity for which the oil ceases to flow (ASTM, 2007).

Apparatus

The SETA Cloud and Pour Point Refrigerator. The refrigerator is made up of a bath with a groove to hold the jacket firmly in place and a cylindrical, watertight, metal jacket. Underneath the attached jacket is a solvent of technical rating suitable for low-temperature bath media or refrigeration. The instrument could refrigerate to a temperature as low as -51 ^{o}C.

Reagents and Materials

Clear, flat-bottomed test jar; High pour thermometer; Cork

Experimental Procedure (ASTM D97)

An aliquot of the test sample (crude oil) was placed into the test sample jar till the recommended mark (Fig 3.7b). The cork was fitted tightly to the jar and a Hg-in-glass thermometer (-100 ^{0}C to 30 ^{o}C) was immersed (approximately 3 mm) into test sample. This was followed by placing the test into the jacket of the Pour point refrigerator (Fig 3.7a). At regular timing intervals (3 minutes) the test jar was tilted to see if the test sample would flow. This was repeated until there was no flow when the test jar was held in a horizontal manner (for about 5 seconds). The temperature at the point where the crude oil did not flow was recorded as the pour point temperature (Fig 3.7c).

Fig 3.7a SETA Cloud and Pour point refrigerator

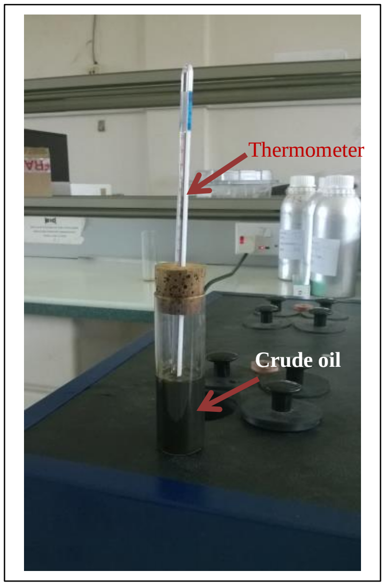


Fig 3.7b Crude oil in a test jar with thermometer for analysis

Fig 3.7c Pour point determination in progress

3.3.1.5 Determination of Density by Hydrometer Method

Principle

The method involves taking the temperature of the test sample at an equilibrated temperature reading and taking the hydrometer reading on of the test sample. The reading is taken on the basis that the specific gravity of a liquid varies directly with the depth of immersion of the hydrometer (floating body) in it. Using a standard reference chart, the density is recorded at 15 ^{o}C, 0 ^{o}C or any referenced temperature (ASTM, 2007).

Apparatus

Hydrometer

Reagents and Materials

Thermometer, Measuring cylinder, Retort stand

Experimental Procedure (ASTM D1298)

About 80 mL of the crude oil was poured into a measuring cylinder. A thermometer was supported by a retort stand and lowered gently to take the reading of the crude oil (Fig 3.8a). The hydrometer was lowered gently into the crude oil taking care to avoid wetting the stem above the level at which it floated freely. The hydrometer was depressed (above two scale divisions) into the crude oil and released. This allowed a rest, floating freely from the walls of the measuring cylinder (Fig 3.8b). This also enhanced the migration of air bubbles to the surface. This was followed by the reading of the hydrometer and the temperature. Using a Reference Table, the density was found at 15 ^{o}C. The procedure was repeated using distilled water (Fig 3.8c).

The relative density and API (American Petroleum Institute) gravity was mathematically calculated as indicated below:

The relative density (R.D)/ Specific Gravity (SG) is given as

$$SG = \frac{\rho_{crude\ oil}}{\rho_{water}} \qquad 3.2$$

Where:

ρ = density

The formula to obtain API gravity of petroleum liquids, from Specific Gravity (SG), is:

$$API\ gravity = \frac{141.5}{SG} - 131.5 \qquad 3.3$$

Where:

SG = specific gravity

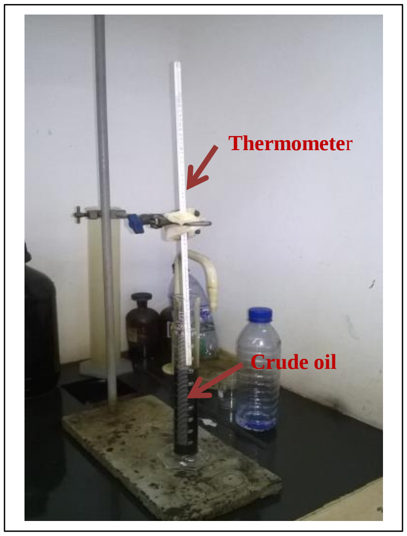


Fig 3.9a Determination of reference temperature of crude oil before density determination

Fig 3.9b Density determination of crude oil sample

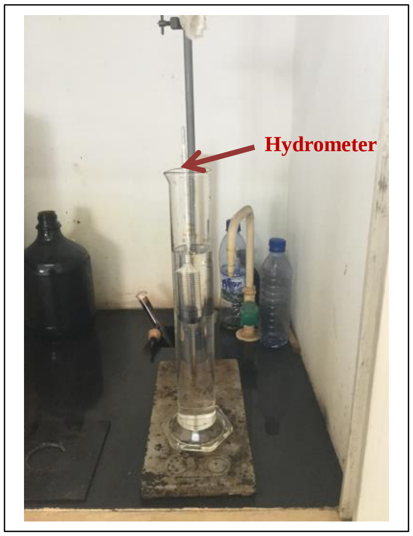


Fig 3.9c Density determination of distilled water

3.3.1.6 Determination of Total Acid Number (TAN) Using Colour-Indicator Titration

Principle

This method measures the total amount of acids in a sample and not the specific quantities of different acidic compounds in the crude sample. The test is based on colour change of the test sample mixed with a titration solvent (a mixture of toluene, water and anhydrous isopropyl alcohol) when titrated with a standardized alcoholic acids or base (ASTM, 2007).

Apparatus

Two 50 mL Burettes and a Double clamp

Reagents and Materials

(a) A 0.1 M standardized alcoholic Potassium Hydroxide (KOH) solution ; **(b)** Titration solvent [Toluene: Water: Anhydrous Isopropyl Alcohol in the ratio 100: 1: 99] ; **(c)** A 0.1 M standardized alcoholic Hydrochloric acid (HCl) solution ; **(d)** α-naphtholbenzein indicator ; **(e)** Pipette ; Conical flask and Chemical balance.

Experimental Procedure (ASTM D974)

The standardized alcoholic KOH was introduced in one of the burettes and the standardized HCl in the other. About 1 g of the crude oil was weighed in an Erlenmeyer flask (Fig 3.10a). About 100 mL of the titration solvent (Fig 3.10b) was added followed by the addition of 0.5 mL of the indicator (Fig 3.10c). The resulting solution and swirled to ensure complete dissolution. Based on the colour change, the solution was titrated with the standardized acid first or the standardized base. (If the mixture turned yellow-orange, titration was done with the alcoholic KOH first with small increment shaking vigorously until end point is reached, a colour change from orange to green or green-brown). The mixture, however, turned greenish-brown on addition of the indicator for both samples. This was then followed by titration with the alcoholic HCl until a colour change from greenish-brown to orange colour which persisted for about 15 seconds (Fig 3.10d). The volume of HCl required to change the colour of the titrand from green to orange were 0.11 mL and 0.13 mL for Jubilee and Bonny light crude oils respectively. A blank titration was performed on the 100 mL titration solvent and 0.5 mL indicator solution using the 0.1 M alcoholic KOH. About 0.08 mL of KOH was required to change the colour of the blank from yellow to green.

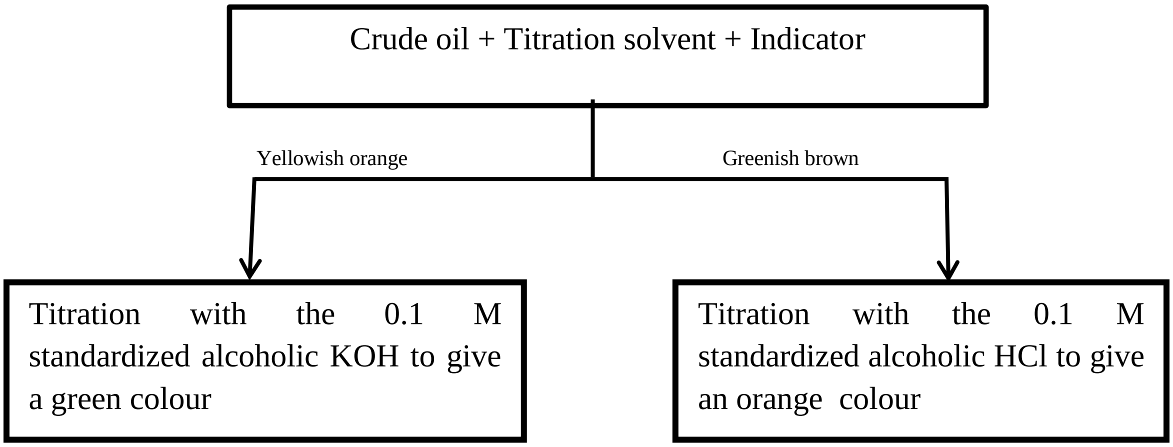


Fig 3.10 Schematic diagram for TAN determination

The TAN was calculated using the formula: mg of KOH/g

$$TAN = \frac{[(Em + FM) + 56.1]}{W} \tag{3.4}$$

Where:

E = HCl solution required for titration of the sample, mL

m = molarity of the HCl solution

F = KOH required for titration of the acid number blank, mL

M = molarity of the KOH solution

W = sample weighed, g

Fig 3.11a Weighed and labelled crude oil sample

Fig 3.11b Standard Reagents

Fig 3.11c Titrands

Fig 3.11d Titration with std. alc. KOH

3.3.1.7 Determination of Viscosity Using Viscometers

Principle

This method is based on the time a fixed volume of liquid flows under gravity through a calibrated working capillary of a viscometer (ASTM, 2007).

Apparatus

Viscometer, Viscometer holders, Temperature measuring device ranging from 0 ^{o}C -100 ^{o}C, Temperature control, Temperature bath, Timing device (KV-6)

Reagents and Materials

Silicone oil (fluid bath), pipette filler, rubber stoppers

Experimental Procedure (ASTM D445)

The viscometer bath was adjusted and maintained at a temperature of 50 ^{o}C (Fig 3.12a). Using pipette filler, an aliquot of the crude oil was drawn into the working capillary and timing bulb of a 2C viscometer (Fig 3.12b). Rubber stoppers were placed into the tubes to hold the test portion in place. The viscometer was then inserted into the holder placed on the bath. The viscometer was left in the bath for an hour. Suction was used to adjust the head level of the crude oil through the lowest capillary tube. Suction was done some few millimeters above the above the first timing mark. With the sample flowing freely under the force of gravity, timing is made in 0.1 seconds from the point it passes the orifice of the first mark in the capillary to the second timing mark. The Kinematic and Dynamic viscosity was calculated as:

The Kinematic viscosity,

$$v = \frac{cP}{\rho} \qquad 3.5$$

Where:

C = calibration constant of the viscometer

t = flow time (s).

Hence, dynamic viscosity (cP) is given as;

$$cP = \rho v \quad 3.6$$

Where:

ρ = density (g/cm^3) at same temperature as kinematic viscosity,

v = kinematic viscosity(cSt).

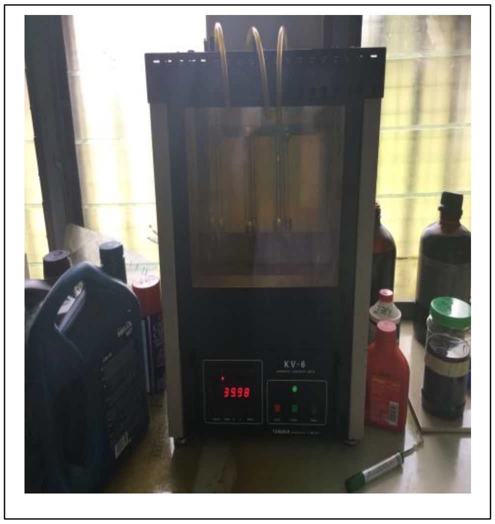


Fig 3.12a Viscometer with other components

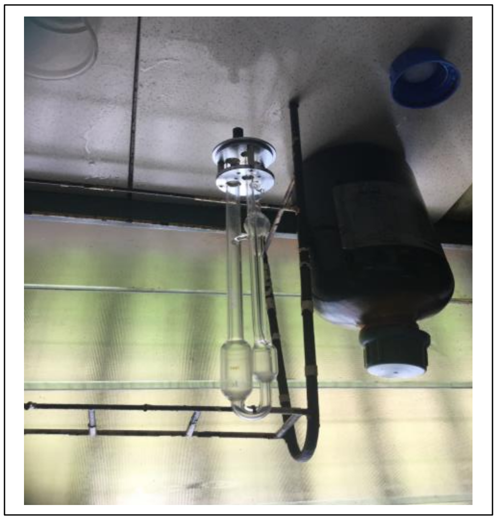


Fig 3.12b Viscometer

3.3.2 Determination of Naphthenic Acids

3.3.2.1 Extraction of Naphthenic Acids (NA's) from Crude Oil Sample

The determination involved the extraction of NA with a mixture of dichloromethane (CH_2Cl_2) and water (ratio 1:1), followed by derivatization of the NA to ester and subsequent clean-up of the extract. The profile and classes of NA in the derivatized extract was determined by GC-MS.

3.3.2.2 Extraction of NA

The general scheme extraction, derivatization, clean-up and determination are presented in Fig 3.13. The detailed experimental procedure is presented after the general scheme.

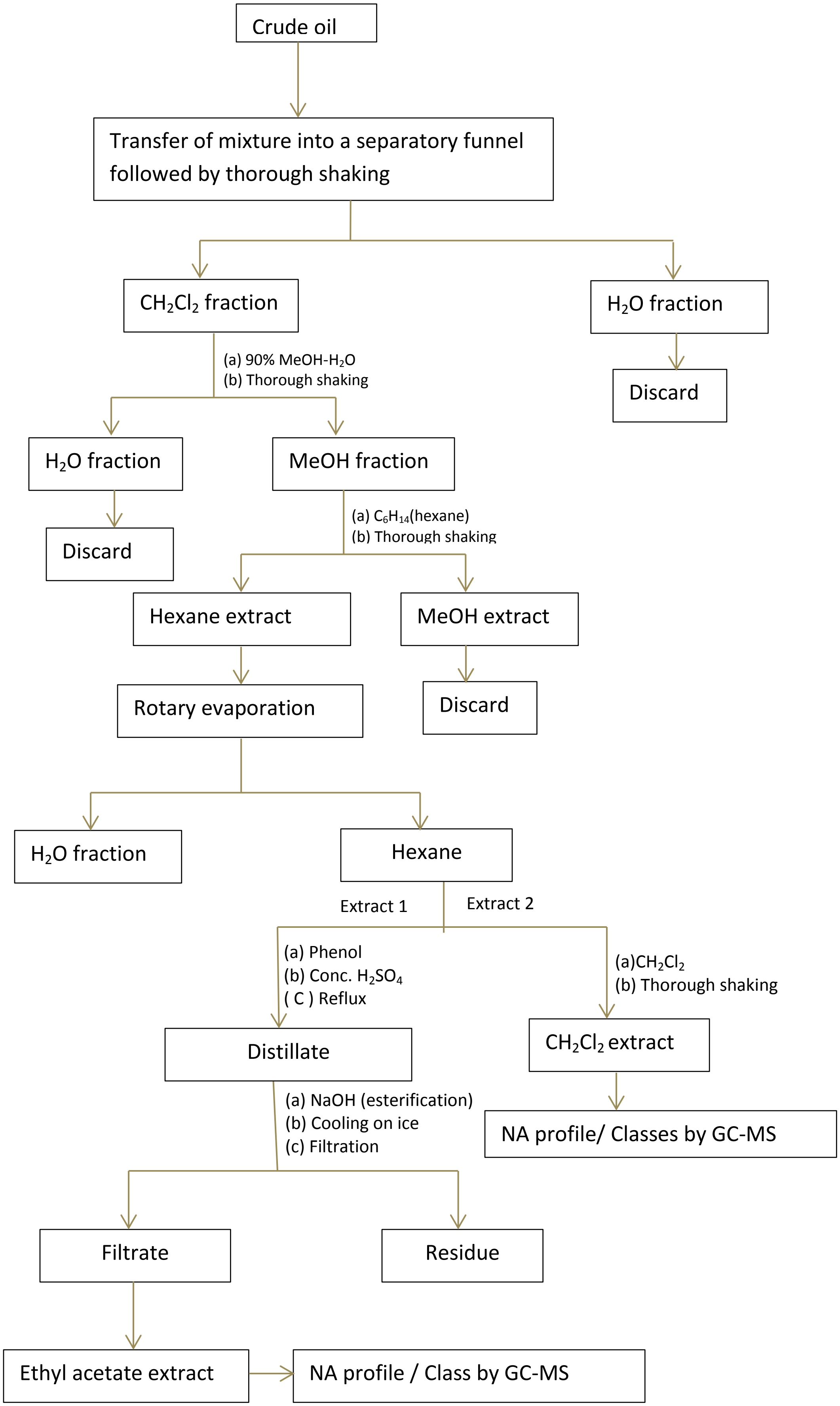


Fig 3.13 Flow chart for the extraction, derivatization and sample clean-up and, the NA profile and Classes

Apparatus

Beaker, Measuring cylinder, Separatory funnel, Rotary evaporator, Retort stand

Reagents and Materials

Dichloromethane (DCM), Distilled water, Methanol, Hexane

Experimental Procedure

About 2.012 g of the Jubilee oil was weighed in a beaker, and 150 mL of water (a 100 mL and 50 mL portions) was added to the oil. This was followed by 150 mL of DCM (a 100 mL and 50 mL portions).

The mixture was poured into a separatory funnel (Fig 3.14a), corked and shaken for a uniform dissolution. Whilst shaking mechanically, the separatory funnel was tilted periodically and vented. This was done for about 25 minutes. The solution was then clamped and allowed to separate for 48 hours.

Two phases were formed; an aqueous phase and an organic phase. The aqueous phase was drained off. The organic phase (DCM) was again extracted with 150 mL of 90%-10% methanol-water followed by extraction with 150 mL hexane. The Polar phase which was the hexane phase was on top. This was identified by putting a drop of hexane in the mixture. It dissolved in the top layer. The hexane layer was separated and rotary evaporated (Fig 3.14b) to dryness (Fig 3.14c). Part of the extract was dissolved in an aliquot of DCM in a 10 mL glass vial for GC-MS analysis.

Esterification of the extract

A 100 mL round bottomed flask (3-neck) was clamped and placed in a steam bath (at a temperature of 100 ^{o}C). About 1 g of the extract was put into the flask and 15 mL of freshly prepared 1.0 M Phenol was added. Boiling chips were added to the flask and a reflux condenser attached for heating under reflux on the steam bath. The condenser was attached to a cooling water bath (set at 10 ^{o}C). Slowly, 5 mL of concentrated sulphuric acid (assay 95-97%) was added using Pasteur pipette through one of the necks of the flask. The two open necks were sealed and the mixture refluxed for 4 hours (Fig 3.14d).

After 4 hours, the reaction solution was then cooled, poured into a mixture of 10% aqueous sodium hydroxide (50 mL) and ice (approximately 50 g). The mixture was left for about 20 hours to see if there would be crystallization. The mixture was filtered with no observed crystals formed.

A clean up was done on the Jubilee crude extract and the esterified extract for GC-MS analysis (Fig 3.14f). This was done by drawing a few drops (about 5) of one of the extract into a glass vial (Fig 3.14e) using a Pasteur pipette. The sample was then topped up with ethyl acetate to about 3⁄4th the volume of the glass vial whilst dissolving to give a homogenous mixture. It was then sealed. This same procedure was repeated for the esterified extract. The samples in the vials were sent to GSA for GC-MS analysis.

The GC-MS operated was a Varian CP-3800 GC and Saturn 2200ms/ms system with column type HP-5, having dimensions, length: 30 m, width: 0.25 µm and depth: 0.25 µm. The gas for operation was Helium. The oven condition for the analysis was set at 50 ^{o}C for 2 minutes and increased at 10 ^{o}C/min till 300 ^{o}C. This temperature was then held for 8 mins. It was set at a mass range from 30-650 m/z. The injection volume was 2 μL. The temperature at which injection was made was 270 °C and set at a flow rate of 1.0 mL/min.

Fig 3.14a Separatory funnel for extraction of NA

Fig 3.14b Concentration of hexane phase using rotary evaporator

Fig 3.14c Concentrate extract

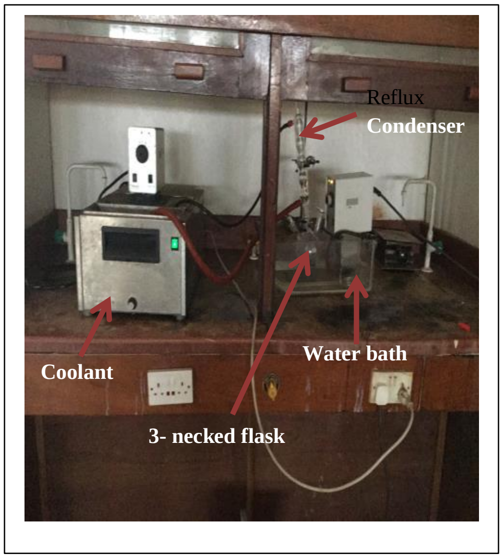


Fig 3.14d Set-up for esterification reaction (coolant, water bath, reflux condenser, clamp and a 3-necked flask)

Fig 3.14e Glass vials containing extract and ester for GC-MS analysis

Fig 3.14f GC-MS instrument Varian CP-3800

CHAPTER FOUR

RESULTS AND DISCUSSION

In this chapter, the results obtained for the physico-chemical analysis and the NA profile and classes are presented and discussed.

4.1 Physico-chemical Parameters

The results obtained for the physico-chemical properties of the crude oils (Jubilee and Bonny light) are presented in Table 4.1

Table 4.1 Results of Physico-chemical Properties of Crude oil

Parameter	Jubilee oil	Bonny light
Density at 15 °C (kg/m^3)	842	862
Relative Density	0.842	0.862
Density (°API)	36.55	32.65
Pour point (°C)	-15	-18
Flashpoint (°C)	> 80.5	> 66
Sulphur content (wt %)	0.168	0.320
Water content (%)	negligible	negligible
Kinetic Viscosity at 50 °C (cSt)	3.899	3.032
Dynamic Viscosity at 50 °C (cP)	3.283	2.613
TAN (mg KOH/ g crude)	0.58	0.70

The data on the Physico-chemical parameters of Crude oils from other parts of the world were obtained from Chevron Crude Marketing Company (2001). The detailed data is presented in Appendix C. The country of origin of the crude oils are presented in Table 4.2

Table 4.2 Country of origin of crude oils

Crude oil	Country of origin [Continent]
Bonny light	Nigeria [Africa]
Medanito	Puerto–Rosales [Argentina]
Hibernia	Canada [North America]
Captain	Aberdeen, Scotland [Europe]
Nemba	Angola [Africa]
Eocene	Middle- East [Asia]
Azeri	Central Asia

4.1.1 American Petroleum Institute (API) Gravity

Jubilee and Bonny Light Crude Oils

The American Petroleum Institute (API) gravity indicates the grade or quality of crude oils. API classifies crude oil based on density and viscosity. Crude oil samples with API gravity higher than 31.1^{o}API are classified as light crude oils, those with API gravity between 22.3-31.1^{o}API are classified as medium crude while those with API gravity of 22.3 ^{o}API and below are classified as heavy crude oil (AP1, 2011). A comparison of the values of API gravity obtained for the Jubilee crude oil (36.55) and Bonny light crude oil

(32.65) with that of API Standard classification (2011) indicates that both crudes are light crude oils.

Comparison with Other Crude Oils

From Fig 4.1, Eocene and Captain crude oils from Middle-east and Aberdeen respectively are below 22.3^{o} hence classified as heavy crude oils. Jubilee oil from Ghana, Bonny light from Nigeria, Medanito from Latin America, Hibernia from North America, Nemba from Angola and Azeri from Central Asia are above 31.1^{o} hence all are light crude with the lightest being Nemba from Angola having an API gravity of 39.79. None of the crude oil was medium.

Light crude oil samples are in high demand and are of high market value because it is easier to handle as compared to heavy crude which is tougher because it is too thick to pump easily through pipelines unless diluted with light crude.

The heavier the oil, the more difficult it's refining. Refining is expensive in the production of the useful petroleum products such as petrol, diesel and aviation fuel.

This indicates less cost in the refining of Ghana's Jubilee oil as well as the use of it as a blend in refining heavy oils.

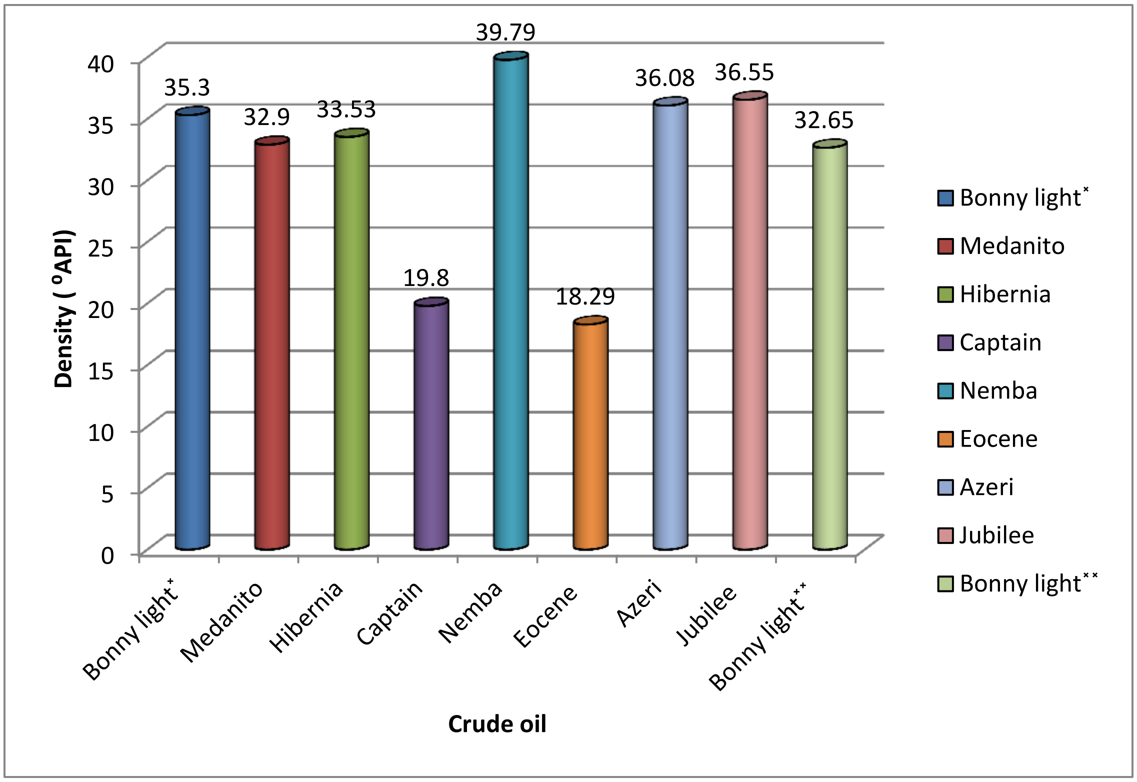


Fig 4.1 Comparison of API gravity of Jubilee and Bonny light crudes to other crudes in the world

* Bonny light information from literature
** Bonny light information from study

4.1.2 Sulphur Content

Jubilee and Bonny light crude oils

The Sulphur content in crude oil is also used in the classification of crude oils. Crude oils with Sulphur content concentration less than 0.5% wt are “Sweet”. Sweet crude oils have low Sulphur content. Crude oils that have Sulphur concentration greater than 0.5% wt are known as “Sour”. Sour crude oils have high Sulphur content (API, 2011). Sulphur content in Jubilee crude oil and Bonny light crude oil are 0.168% and 0.320% wt respectively (Appendix B), indicating that the two crude oils are sweet.

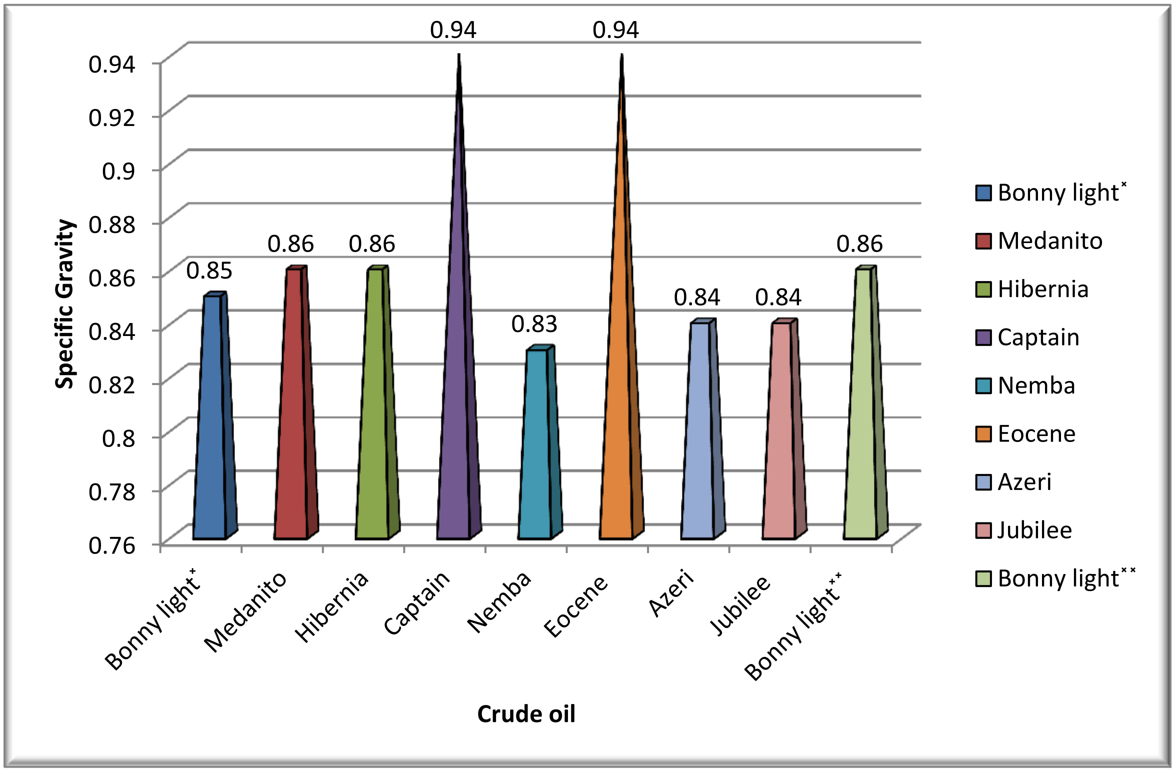


Fig 4.2 Comparison of Specific Gravity of Jubilee and Bonny light crudes to other crudes in the world

Comparison with Other Crudes

Eocene crude oil from the Middle-east, Hibernia from North America and Captain from Aberdeen, Europe are "Sour" crudes with Eocene having the highest sulphur content value of 4.57% wt (Fig 4.3). Bonny light crude oil from Nigeria, Medanito from Latin America, Nemba from Angola, Azeri from Central Asia and Jubilee from Ghana are "Sweet". The sweetest crude are from Azeri and Bonny light (Fig 4.3).

Sulphur is relatively a heavy element. Its presence will add to the specific gravity of oil samples, thus reducing the API. The API Gravity of crude oil is known to increase as the Specific Gravity decreases (Riegel and Kent, 2007). Sulphur content of crude oil is therefore known to increase as the Specific Gravity increases. Fig 4.2 confirms that; Eocene and Captain which have the lowest API Gravity of 18.29 and 19.80 respectively, and have the highest Specific Gravity of 0.94 (same for each). They also have the highest sulphur content of 4.57 and 0.64 % weight respectively.

Sulphur is corrosive and cause rapid asset deterioration with associated cost at the refinery (Smith and Craig, 2005). Captain and Eocene crude oils will be very cost intensive in refining as compared to the other crudes due to the corrosive nature of sulphur and its ability to inhibit the activity of catalyst during refinery.

Geographical locations of crude oil cause variation in the proportions of the hydrocarbon elements, sulphur content, viscosity among other properties. Whereas heavy crude oil samples are reported in abundance are also associated with high deposits of sulphur-rich rocks, light crude oil samples are found mostly in areas with low deposits of sulphur rocks (Nehb et al., 2006; Riegel and Kent, 2007; USEIA, 2011).

Sweet crude oils are generally preferred to Sour because it has less corrosion; and has a lower pollution potential which leads to low cost of production. It is therefore more suited for the production of the most valuable refined products such as gasoline, petroleum naphtha (Volk et al., 2006).

The result of this study therefore confirms that, Ghana’s Jubilee crude oil and Bonny light from Nigeria generally are of low sulphur content and are also predominantly of light crude oil category as compared to Eocene, Hibernia, Captain, Medanito and Bonny light crudes. This infers good quality which enhances their preferences in the oil market and refinery operations (Dickson and Udoessien, 2012).

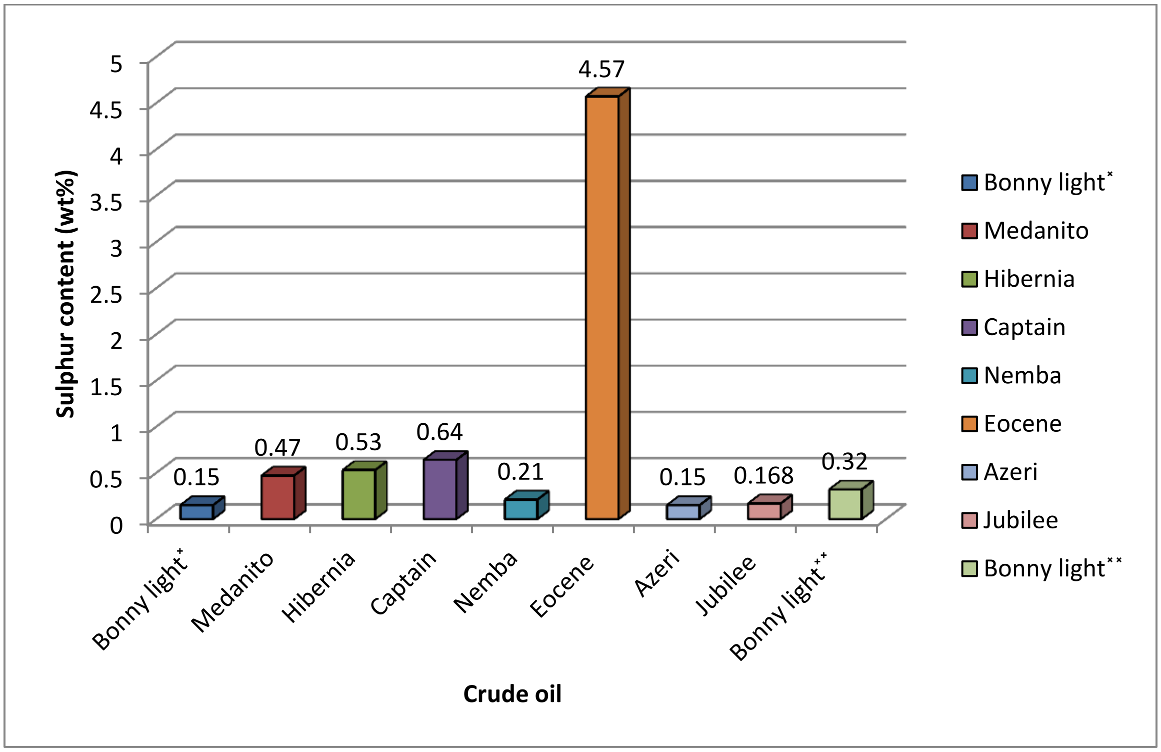


Fig 4.3 Comparison of the Sulphur content in Jubilee and Bonny light crudes to other crudes in the world

4.1.3 Water Content

Water lowers the API gravity and reduces the selling price of crude oil. Water contents were appreciably low in the samples. Drops of water with a diameter of about 0.01 mm were formed on the walls of the glass trap during the water content determination using distillation. This could not be collected, in order to quantify. It was therefore reported as negligible for both Jubilee and Bonny light crude oil. Appenteng et al., (2013) reported a value of 0.05 mm in Jubilee crude oil in a similar study using the distillation method.

Knowledge of Water and Nitrogen content (%N) of any crude oil is important in the refining, purchase and sales of crude oil because of corrosion problems associated with these parameters (Kurt et al., 2005; Udoessien, 2003). However, the % N could not be measured because of the lack of equipment. The low water content of the crude oils also indicates that, they are of high selling price. Rusting due to presence of water on metals in refinery pipes will also be minimal during refining (Kurt et al., 2005; Udoessien, 2003).

4.1.4 Flashpoint

The lowest temperature at which enough crude oil can evaporate to form a combustible concentration of gas (flashpoint) were reported to be above 80 ^{o}C (176 ^{o}F) for Jubilee crude oil after 44 applications of fire and above 66 ^{o}C (140 ^{o}F) after 30 applications of fire for Bonny light crude oil. The flashpoint is used to distinguish flammable liquids from combustible liquids. Flammable liquids are more dangerous than combustible liquids. Liquids having flashpoints less than 37.8 ^{0}C (below 100.0 ^{0}F) are flammable whilst liquids with flashpoints between 37.8 ^{0}C and 93.0 ^{0}C (100.0 ^{0}F and 200.0 ^{0}F) are combustible (Wikipedia, 2014; NFPA, 2013). Results obtained from the study indicate Jubilee and Bonny light crudes as combustible liquids.

In the determination of the flashpoints of the crude oil, soot was formed on the Pensky-Martens test cup apparatus; hence a precise temperature was not recorded. This was due to the fear that, the instrument which was used to determine the flashpoint of crude oil distillates at GSA would breakdown.

4.1.5 Pour Point

Pour point of a petroleum specimen is an index of the lowest temperature at which a liquid still behaves as a fluid (Dickson and Udoessien, 2012). In this study, the determined Pour Point was -15 ^{o}C for Jubilee crude oil and -18 ^{o}C for Bonny light crude oil. Appenteng et al., (2013) and Chevron Crude Marketing (2001) quoted -3 ^{o}C and -11.48 ^{o}C for Jubilee crude oil and Bonny light crude oil respectively. The observed variation may be due to the fact that the crude oils were from different wells in the same field. These temperatures are the point for which wax is separated from the oil. From Fig 4.4, Captain and Eocene crudes had the lowest pour point values of -32.48 ^{o}C and -32.02 ^{o}C respectively, implying their richness in mixtures of saturated n- and iso- alkanes, naphthenes and alkyl- and naphthene- substituted aromatic compounds, no wonder they are heavy crude oils (Danilovic et al., 2013). The viscosity of the oil affects Pour Point. A low Pour Point value means a highly viscous oil or high wax content in crude (Jokuty, 2001).

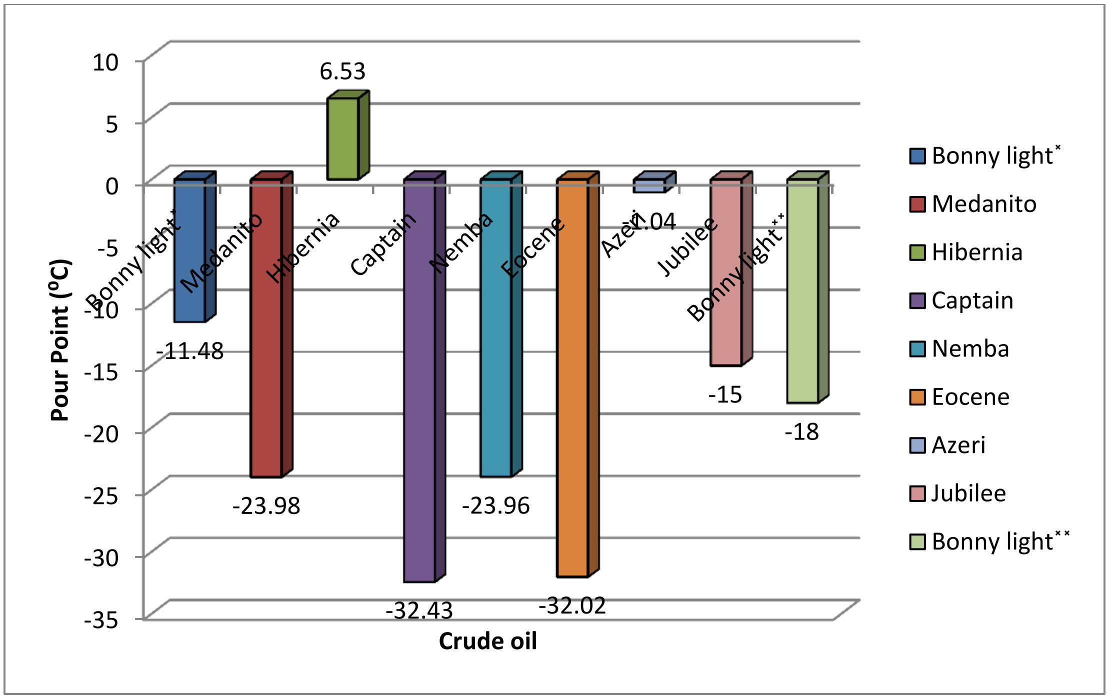


Fig 4.4 Comparison of Pour Point of Jubilee and Bonny light crudes to other crudes in the world

Knowledge of the Pour Point value gives an indication of factors such as size and shape of the container, the physical structure of the oil; that must be considered in a spillage response from a spillage (Jokuty, 2001).

Further comparison with other crude oils (Fig 4.4) indicates a high Pour Point value of 6.53 ^{o}C for Hibernia crude oil (a light crude oil).

4.1.6 Viscosity

Viscosity is a measure of internal friction of a liquid, and it indicates the flowing ability of crude oil from one point to another (Kurt et al., 2005); or the fluid's resistance against either tensional stress, or shear stress. The viscosities of the crude oil are described as dynamic viscosity, (when external force is applied) and, kinematic viscosity (the ratio of dynamic velocity to density, a quantity in which no force is involved), at a specific temperature.

Bonny light had a kinetic viscosity of 2.73 cSt whilst Jubilee crude oil had a kinetic viscosity of 3.9 cSt. The viscosity of Jubilee crude (3.90 cSt) is higher than some African crudes as Bonny light (2.73 cSt) and Nemba (3.19 cSt) (Fig 4.5). The low viscosities of Bonny light and Nemba crudes indicate that they can easily flow when transported through pipes thus making them easy for transportation as compared to Jubilee oil (Abarasi, 2013). The implication however is that, the crude oil samples Bonny light and Nemba from Nigeria and Angola respectively, have greater ability to readily flow into the environment in events of oil spillage than Ghana's crude and the other crudes sampled across the world. Knowledge of the viscosity of the crude oil with respect to transportation is important in engineering construction of pipelines. It is also important in studying the energy loses during production. Viscosity also plays an important role in reservoir simulations as well as in determining the structure of liquids (Abdulkareem and Kovo, 2006).

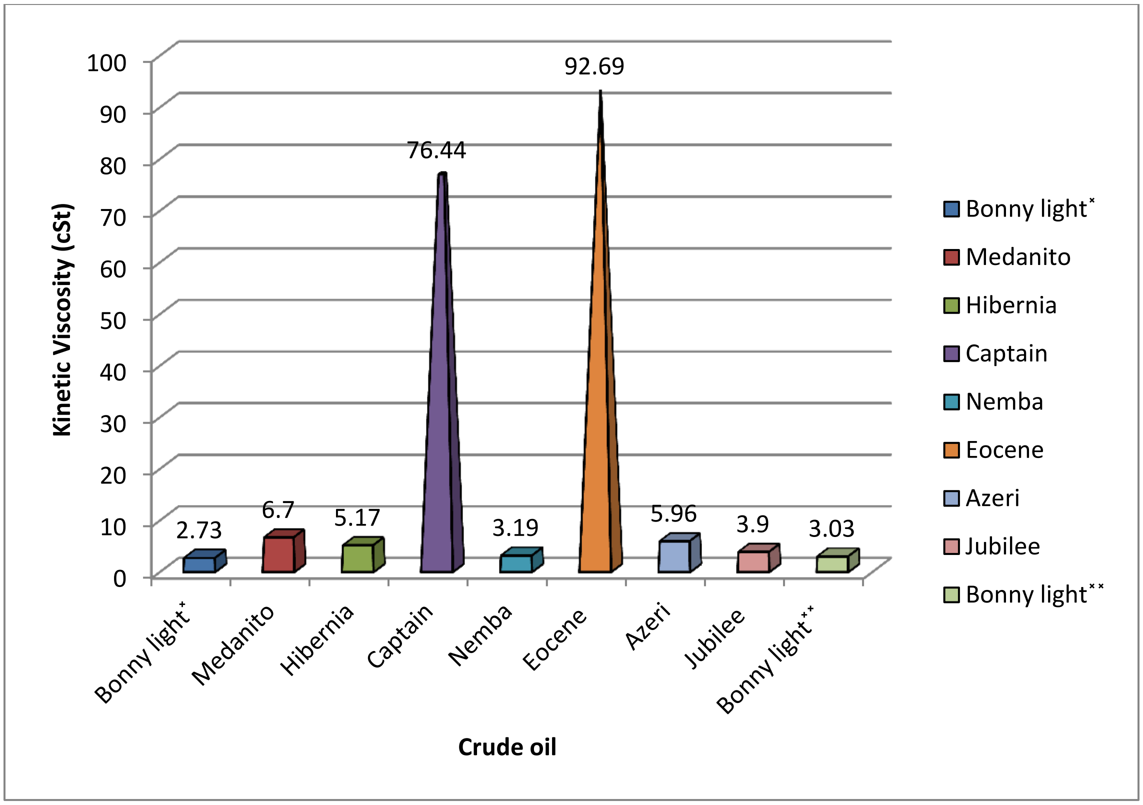


Fig 4.5 Comparison of the Kinetic Viscosities of Jubilee and Bonny light crudes to other crudes in the world

4.1.7 Total Acid Number (TAN)

A generally accepted criterion for oil acidity is TAN. TAN is the amount in milligrams of KOH required to neutralize the acidity of 1 g of crude oil. Oils with a total acid number (TAN) between 0.5 mg KOH/g and 1.0 mg KOH/g are classified as high acid oils; whereas oils with a TAN above 1 mg KOH/g are classified as high acidic oils (Ravi et al., 2014). Eocene, Bonny light from Chevron, Hibernia, Azeri and Nemba have low acid numbers, less than 0.5 (Fig 4.6). The high acid oils are Medanito, Jubilee (Appendix A) and Bonny light** having TAN values between 0.5 and 1. However, the high acidic oil is Captain with a total acid number of 1.91.

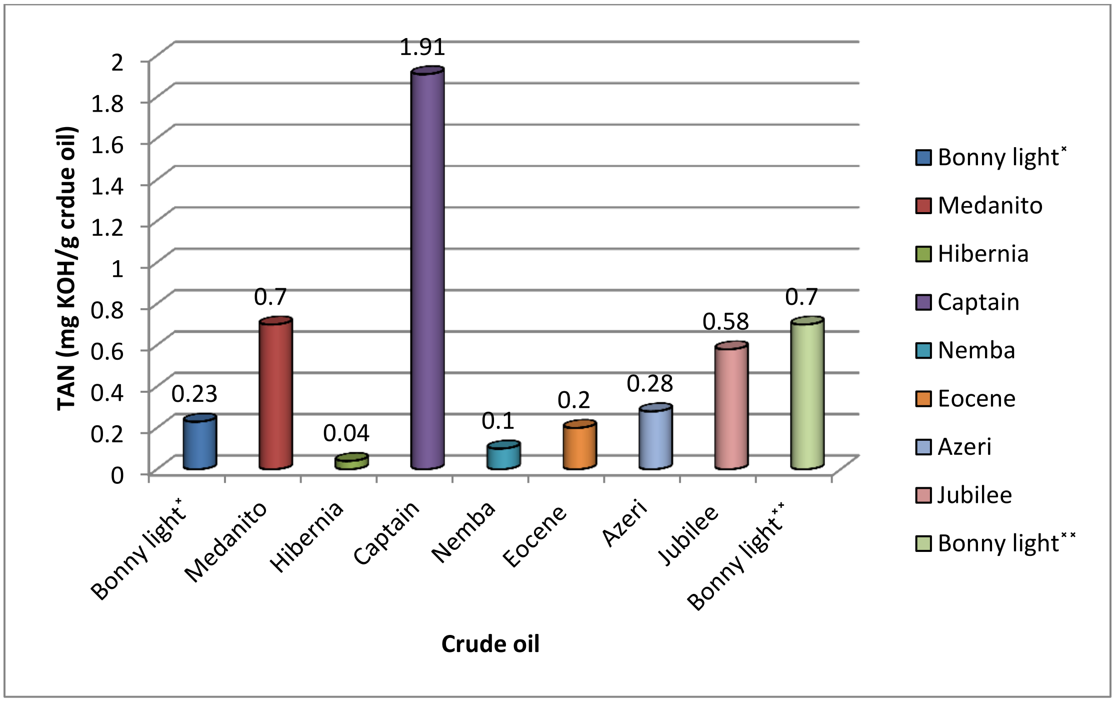


Fig 4.6 Comparison of the TAN of Jubilee and Bonny light crudes to other crudes in the world

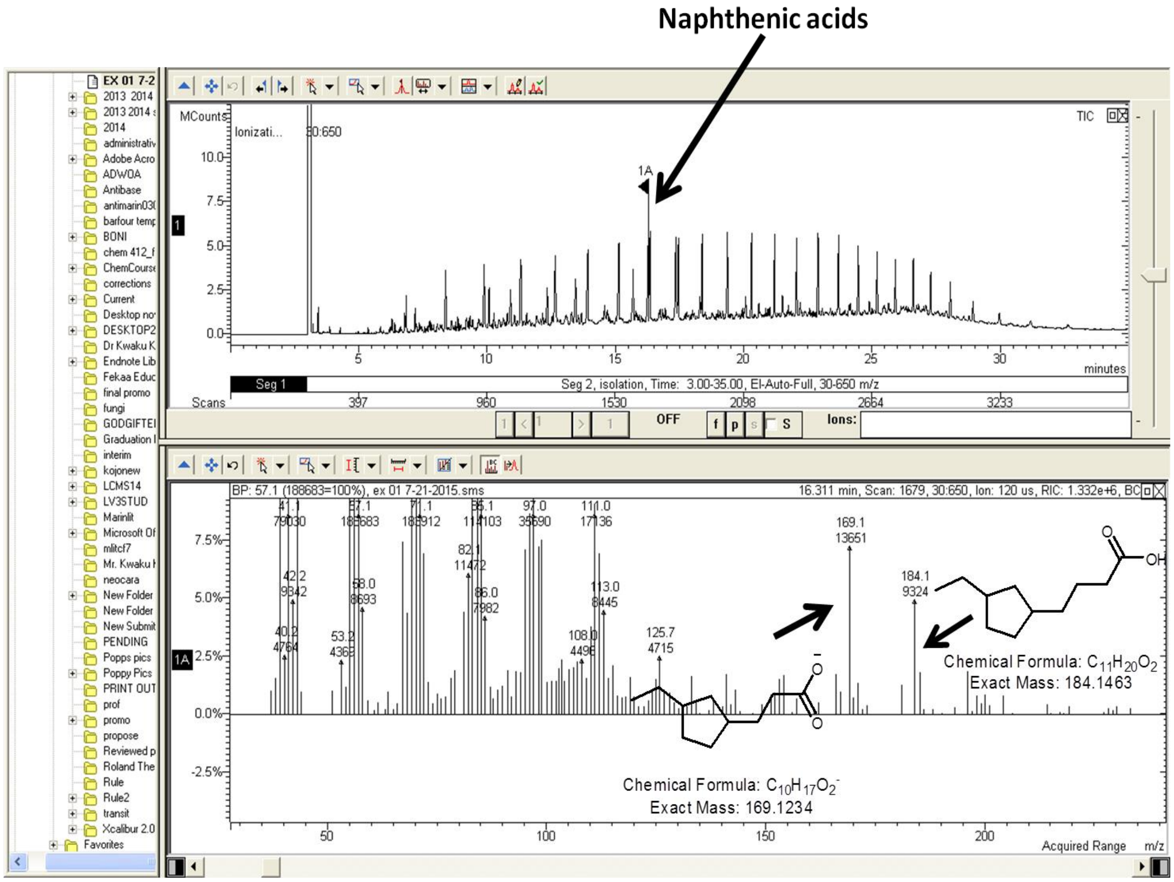
4.2 Low Resolution GC-MS profile of Naphthenic Acid in Ghana's Jubilee Crude

Crude oil is a cocktail of different homologous series of hydrocarbons starting from the very simple methane, ethane and propane to the rather complex and large molecular weight substances like asphaltenes.

A modified version of the Kupchan's partitioning process was employed from which, an FH fraction (hexane fraction) containing mainly the fatty and less polar components (carboxylic acids) of the oil was obtained.

The spectrum of the Low Resolution Electron Impact Gas chromatography Mass Spectrometry (LREI-GC-MS) of the Jubilee crude oil is presented in Fig 4.7. A careful analysis of the data obtained for the FH fraction showed a whole range of low molecular weight fatty components of the crude oil that included two (2) homologues of naphthenic acids at m/z = 169.1 and 184.1 (Fig 4.7). Structural confirmation of these two homologues was achieved by analysis and interpretation of the similar fragmentation patterns seen for the two molecules (Fig 4.8).

Further analysis of the remaining peaks in the GC-MS chromatogram showed that, the two homologues identified are the main forms in which naphthenic acid exist in the Jubilee crude oil (Fig 4.7).



Seg 2, isolation, Time: 3.00-35.00, EI-Auto-Full, 30-650 m/z

BP: 57.1 (188683=100%), ex 01 7-21-2015.sms

16.311 min, Scan: 1679, 30:650, Ion: 120 us, RIC: 1.332e+6, BC

Fig 4.7 Naphthenic Acid peaks and structure elucidation from MS workstation software, showing small hydrocarbon component profile of Ghanaian's Jubilee oil

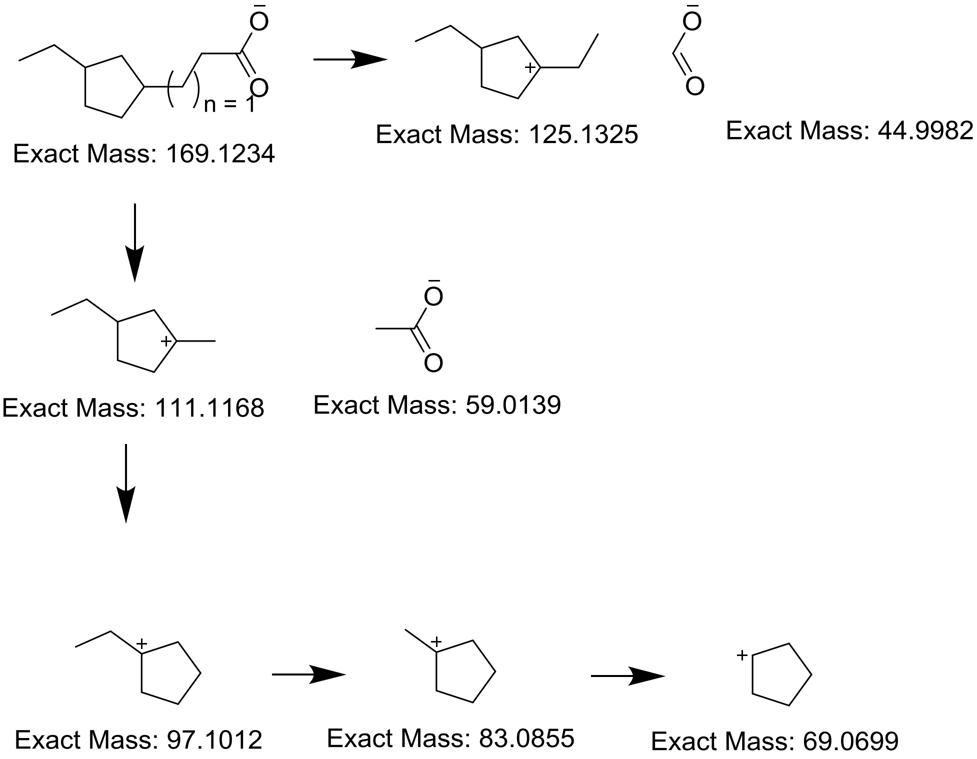
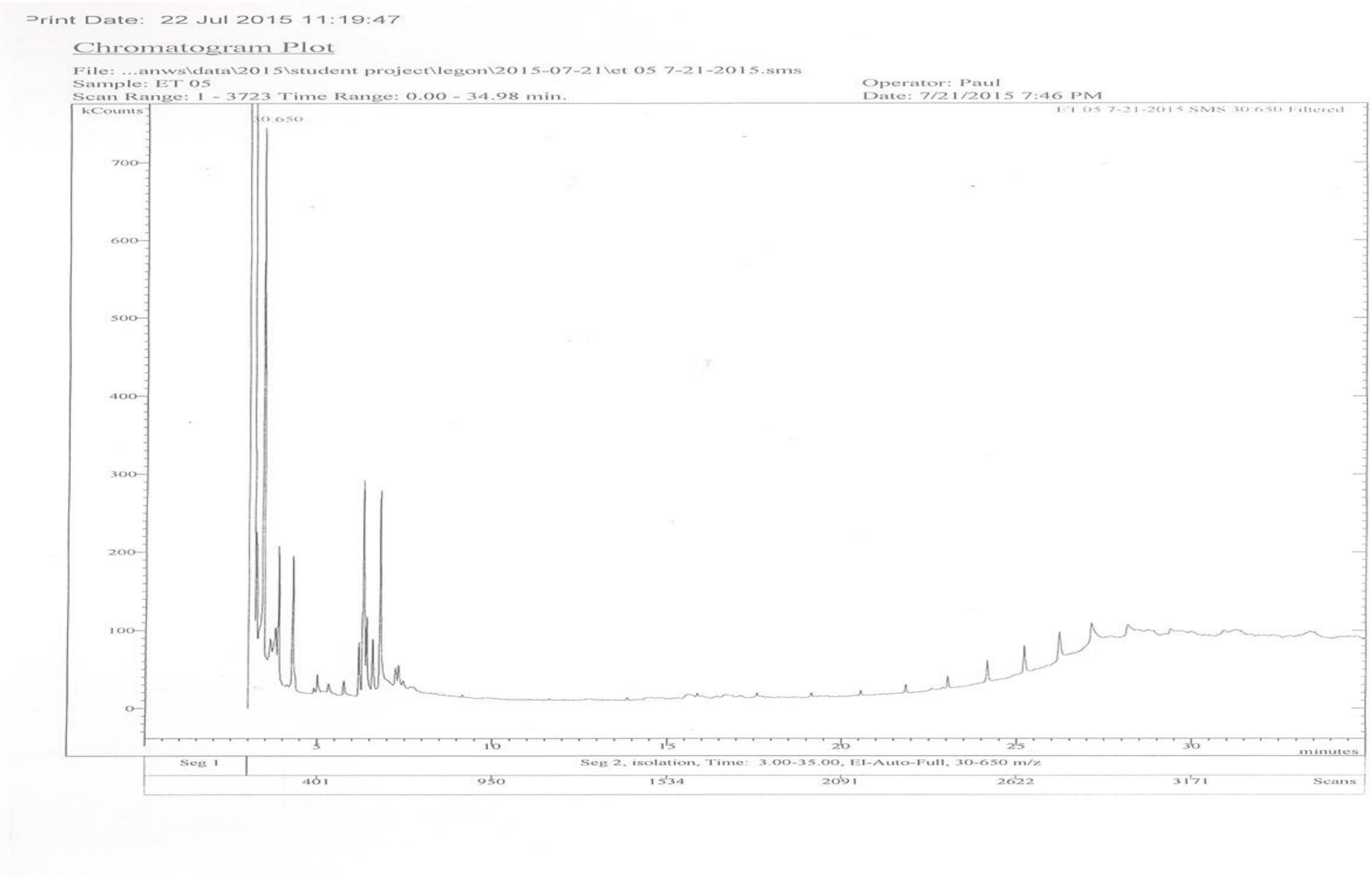


Fig 4.8 Schematic diagram of the fragmentation patterns and their corresponding masses

Also, it appears as if the two homologues of naphthenic acid were present in similar quantities compared to the other low molecular weight hydrocarbons present in the oil sample. However, the lack of a UV absorption chromophore in the structure of these two naphthenic acid derivatives made it difficult to isolate by any UV-detection HPLC method. In order to achieve complete quantification of these naphthenic acid derivatives, chemical reactions were therefore set up to take advantage of the presence of the carboxylic acid moiety and synthetically introduce a chromophore on to these structures using Phenol. Phenol, a benzene ring derivative (an OH group) was used as a base in the esterification reaction. Though it behaves like an acid, with pKa = 10, the alkoxide group makes it possible for the reaction to take place. However, the esterification was not successful. A naphthenic acid precipitate which was expected was not obtained. A GC-MS analysis which was undertaken (Fig 4.9) showed the absence of peaks corresponding to the masses of the benzene ring and naphthenate ions.

The Naphthenic Acid compounds identified with the aid of the **MS workstation software** are: metaethyl-3-cyclopentylpropanoic acid with molecular formula $C_{10}H_{18}O_2$ and metaethyl-3-cyclopentylbutanoic acid with molecular formula, $C_{11}H_{20}O_2$.

They are monocyclic aliphatic compounds belonging to the NA class, with $z = -2$ series ($z =$ hydrogen deficiency).



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Chromatogram Plot

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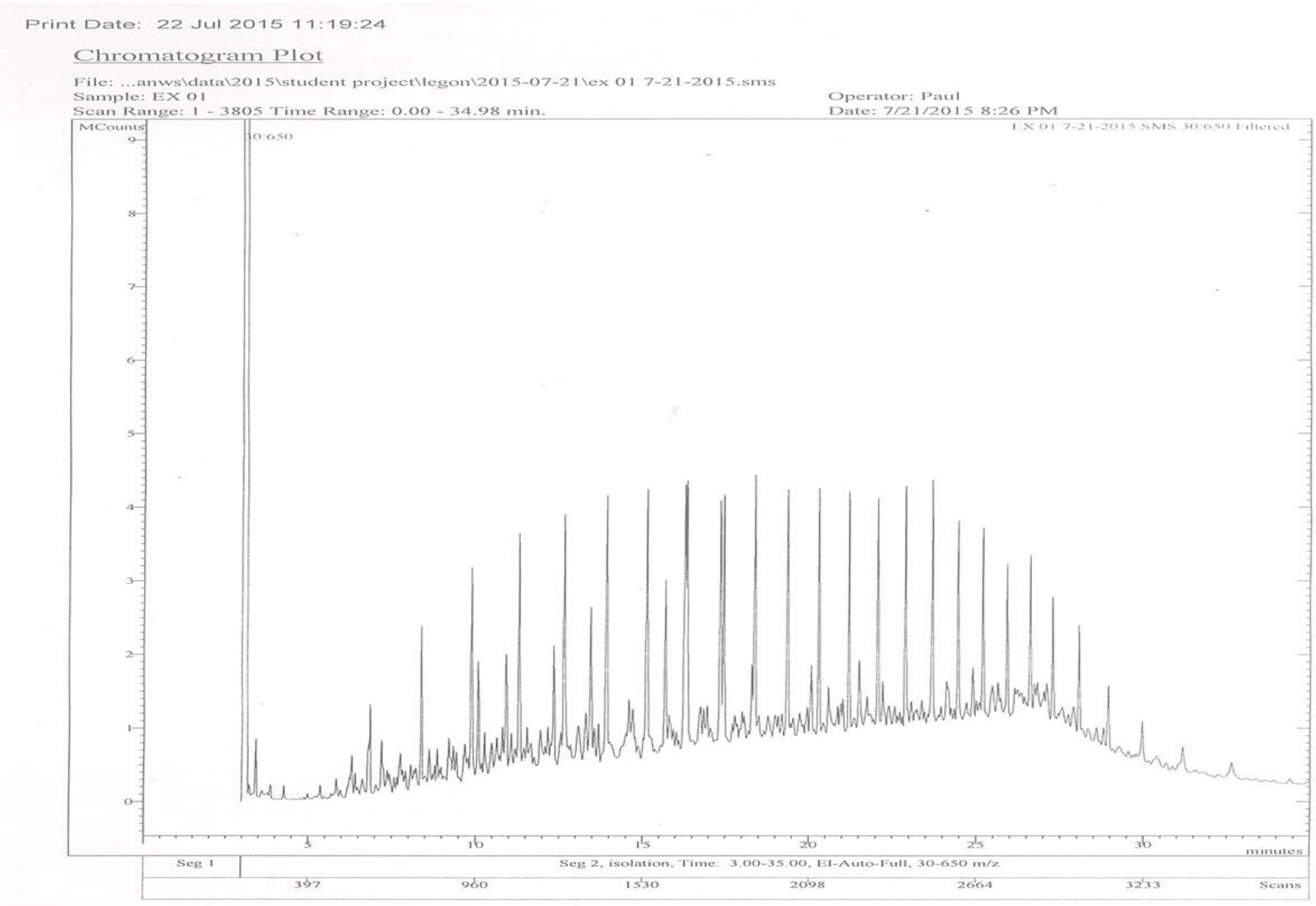
Sample: ET 05
Scan Range: 1 - 3723 Time Range: 0.00 - 34.98 min.
Operator: Paul
Date: 7/21/2015 7:46 PM

Fig 4.9 A chromatogram of the esterified hexane extracts



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Chromatogram Plot

File: ...anws\data\2015\student project\legon\2015-07-21\ex 01 7-21-2015.sms
Sample: EX 01
Scan Range: 1 - 3805 Time Range: 0.00 - 34.98 min.
Operator: Paul
Date: 7/21/2015 8:26 PM

Fig 4.10 A chromatogram of the hexane extract

4.3 Relationship Between Physico-chemical Parameters and Naphthenic Acid (NA)

4.3.1 Sulphur content and NA

In contrast, crude oils having sulphur content between 2 and 3% form a protective layer against naphthenic acid corrosion (Jayaraman et al., 1986). Sulphur content in a crude oil is an important factor in naphthenic acid corrosion, mainly due to a competition between the two kinds of processes, naphthenic attack and hydrogen sulphide attack according to the following equations: (Babaian-Kibala et al., 1993; Slavcheva et al., 1999)

$$Fe + 2RCOOH \rightarrow Fe(RCOO)_2 + H_2 \qquad 4.1$$

$$Fe + H_2S \rightarrow FeS + H_2 \qquad 4.2$$

$$Fe(RCOO)_2 + H_2S \rightarrow FeS + 2RCOOH \qquad 4.3$$

Eq. (4.1) represents the direct attack of naphthenic acid on iron (carbon steel), while Eq. (4.2) represents the corrosion by hydrogen sulphide. A highly significant difference is that, the corrosion product, iron naphthenate, is very soluble in oil, while iron sulphide tends to form a protective film on the metal. Eq. (4.3) represents the case where hydrogen sulphide reacts with the soluble iron naphthenate to produce iron sulphide, precipitated in the oil. Naphthenic acid is regenerated by this reaction. In order to form the protective layer, crude oils need to have 2–3% sulfur content, if this film is not removed. Therefore, a crude oil with a relative high naphthenic acid number and low sulfur content seems to be more corrosive at high temperature than a crude oil with the same naphthenic acid content and high sulfur content. Naphthenic acid corrosion occurs in distillation units where the oil temperature is in the range of 220–400 °C.

4.3.2 TAN, Sulphur content and NA

TAN values are high and the total sulfur contents are low in both Jubilee and Bonny light crude oils. These results could give the impression that, even though the TAN is higher in the Jubilee crude, it would be less protected against naphthenic acid corrosion because the sulphur content is nearly zero at distillation temperatures below 200 °C (Jayaraman et al., 1986)

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study endeavours to assess the naphthenic acid profile and to characterize the classes of naphthenic acid in Ghana's Jubilee oil.

The results from this study have shown that crude oil obtained from Ghana's Jubilee field contains low level of sulphur (0.168 wt %), hence a sweet crude oil according to API classifications standards. Ghana's crude oil belongs to the category of light oil grade, with a density of 36.55 ^{o}API. Accordingly, it can therefore be used as a crude oil blend to heavy- sour crude oils such as Eocene or Captain from the Middle – East and Europe respectively (to make them light or reduce their high sulphur content). In addition, Ghana's Jubilee crude is a high acid oil and a combustible liquid, with a flashpoint above 80.5 ^{0}C.

The viscosities obtained for Jubilee oil were 3.899 cSt for kinetic, and 3.283 cP for dynamic at 50 ^{o}C. The low values of viscosity, obtained for Jubilee oil indicates that, it can flow easily. This makes it easy for transportation through pipelines without the necessary addition of diluents at regular intervals often associated with heavy crude oil samples. However, the low viscosity of the Jubilee oil implies that it can easily flow and spread out rapidly into the environment in event of oil spillage. The water content of the Jubilee oil was negligible.

The TAN value of 0.58 mg KOH/g crude for Jubilee oil indicates high acid content, hence corrosive due to refinery is conceivable, but however the almost negligible water content will minimize the rate of corrosion (ASTM, 2007). The low levels of water content, relatively high TAN, low Pour Point, low viscosities, and relatively high density indicates that, Ghana's crude oil has characteristics which enhance their first choice in the oil market and refinery operations, according to API and NFPA classifications.

The Naphthenic acids identified in Ghana's Jubilee oil are a couple of homologues belonging to the monocyclic ring family ($z = -2$). The *m/z* peaks of these acids were found at 168.1 and 184.1. These masses corresponds to molecular formulas $(C_{10}H_{17}O_2)^-$ and $(C_{11}H_{20}O_2)$ respectively (Headley and McMartin, 2004). The Naphthenic acids were identified as Metaethyl-3-cyclopentylpropanoic acid and Metaethyl-3-cyclopentylbutanoic acid.

5.2 Recommendations

In other to acquire adequate baseline data on Naphthenic acids in Ghana's Jubilee oil, further studies should be carried out to:

i. determine the suitable way of reducing the concentrations of Naphthenic acid in the crude before or during refining.

ii. constantly monitor the levels of Naphthenic acid in the areas affected by the activities of the oil and gas industry.

iii. assess the human health hazards posed by the discharge of effluents from the oil and gas industry.

Government agencies such as Environmental Protection Agency (EPA) and Ghana National Petroleum Company (GNPC) should link up with academia to develop research projects on Ghana's crude oil in order to generate reliable and accurate data on NA in Jubilee oil to:

a. develop sensitization platforms for the broader public education on petroleum issues and reforms as well as build capacities to understand the Petroleum sector. This will enhance public and civil society participation.

b. establish broad consultations with coastal communities in the Western Region regarding the shared use of the sea; establishing zones that are off limits to oil and gas development, wildlife reserves and forests.

c. facilitate a strong Freedom of Information Act so as to aid researchers gain good and strong background to studies in the petroleum sector.

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APPENDICES

APPENDIX A

Table A: Titre Values for Total Acid Number (TAN) calculation

Titration	Volume of Acid/Base used (mL)					
	Blank		Jubilee		Bonny light	
	HCl	KOH	HCl	KOH	HCl	KOH
Titre 1	0.14	0.08	0.1	0.04	0.12	0.10
Titre 2	0.16	0.08	0.1	0.08	0.14	0.10
Titre 3	0.16	0.08	0.12	0.08	0.14	0.06
Average ± StDev	0.15±0.01	0.08±0.00	0.11±0.01	0.07±0.01	0.13±0.01	0.09±0.02

APPENDIX B

Table B: Sulphur Content measurement (XRF)

Run	Sulphur content (wt %)		
	Standard	Jubilee	Bonny light
1st	0.0242	0.168	0.320
2nd	0.0244	0.168	0.321
3rd	0.0250	0.168	0.320
Average ± StDev	0.0246±0.00041	0.168±0.00004	0.320±0.00031

The standard used is Di-n-Butyl Sulphide

APPENDIX C

Table C: Data on some Crudes in the world

Crude oil		Parameters					
Name	Country of origin/ Continent	API	SG	SC	TAN	PP	KV
Bonny light	Nigeria/ Africa	35.5	0.85	0.15	0.23	-11.48	2.73
Medanito	Puerto-Rosales/Latin America	32.9	0.86	0.47	0.7	-23.98	6.7
Hibernia	Canada/North America	33.53	0.86	0.53	0.04	6.53	5.17
Captain	Aberdeen, Scotland/Europe	19.8	0.94	0.64	1.91	-32.43	76.44
Nemba	Angola/Africa	39.79	0.83	0.21	0.10	-23.96	3.19
Eocene	Partitioned zone of Kuwait and Saudi Arabia, Middle east/Asia	18.29	0.94	4.57	0.2	-32.02	92.69
Azeri	Azerbaijan/ Central Asia	36.08	0.84	0.15	0.28	-1.04	5.96
Jubilee	Ghana/ Africa	36.55	0.84	0.17	0.58	-15	3.90

SG (Specific Gravity) **SC** (Sulphur Content) **PP** (Pour Point) **TAN** (Total Acid Number) **KV** (Kinetic Viscosity) **API** (American Petroleum Institute)

Source : www.crudemarketing.chevron.com (2012)