

**CHARACTERIZATION AND MODELLING OF  
NIGERIAN CRUDE OIL SPILLS ON CALM WATER.**

**BY**

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DEPARTMENT OF CHEMICAL ENGINEERING,  
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**FEBRUARY, 2009.**

## DECLARATION

I hereby declare that this thesis titled "CHARACTERIZATION AND MODELLING OF NIGERIAN CRUDE OIL SPILLS ON CALM WATER" is a record of my own research findings. It has not been presented partially or wholly on any previous work for the award of any degree. Any quotations and sources of information are acknowledged by means of reference.



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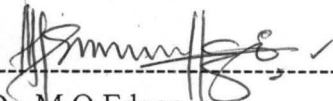
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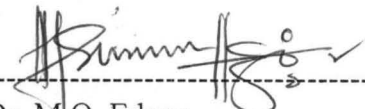


## CERTIFICATION


This thesis titled: "CHARACTERIZATION AND MODELLING OF NIGERIAN CRUDE OIL SPILLS ON CALM WATER" by AJADI, ADEOLA GRACE (MNG/SEET/2005/1140) meets the regulations governing the award of the Degree of Master of Engineering of the Federal University of Technology, Minna and is approved for its contribution to scientific knowledge and literary presentation by

  
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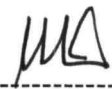
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## DEDICATION

This thesis is dedicated to God Almighty.

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## ABSTRACT

The target of this study was to carry out a detailed characterization of Nigerian crude oils from various oil fields as well as develop a spreading rate regression model capable of predicting rate of spread of crude oil spills on Nigerian waters. Crude oil samples from different oil fields were detailly characterized at specified temperature so as to determine the major factors responsible for spreading rate of crude oil on waters. These included surface tension, viscosity and specific gravity. The spreading rate of each crude oil was determined by artificially spilling it on laboratory calm/stagnant water in a rectangular tank and their averages were also computed. These averages were used to develop a regression model equation for spreading rate. Results obtained show that the crude oils possessed similar physicochemical properties. They were mainly light, sweet naphthenic crude oils. They contained very low metal content averaging 0.4wppm for vanadium and 3.0wppm for nickel; total acid number (TAN) of about 0.4mgKOH/g and salt content were within the same range of 2-4lb/1000b with average pour point of 15.5°C. The model developed gave an average spreading rate of 3.3528cm/s at 37.5°C and the predictive regression model as

$$R = 5.7199 + 0.3151X_1 + 0.6242X_2 + 1.2278X_3 + 2.5603X_4 + 0.0144X_{12} - 0.024X_{13} \\ + 0.1543X_{14} - 0.0336X_{23} + 0.3256X_{24} + 0.7001X_{34} - 0.0059X_{123} + 0.004X_{124} \\ + 0.0253X_{134} + 0.0122X_{234} - 0.0186X_{1234}$$

This model was found suitable for most of the crude oils examined since they possessed similar physicochemical properties

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## CHAPTER ONE

### 1.0

## INTRODUCTION

Petroleum is a word coined from two latin words petri meaning stone (rock) and oleum meaning oil which literally means oil from rock. Scientifically, petroleum is a naturally occurring complex rock oil mixture predominantly hydrocarbons and hydrocarbon derivatives ranging in molecular weight from methane to heavy bitumen (Edoga,2008). Apart from the hydrocarbons, it contains sulphur, nitrogen, oxygen, vanadium, nickel and arsenic compounds which are regarded as impurities. Also, petroleum contains water, inorganic salts, suspended solids and water-soluble trace metals, which are the unwanted products. These unwanted products can be removed during the pretreatment process using various techniques. Some crude oils also have a higher sulfur content, an undesirable characteristic with respect to both processing and product quality which must be removed via a desulphurizing unit in the down stream processing.

Principally, petroleum is the major source of primary energy, which is obtained from various products of petroleum namely premium motor spirit (PMS) or gasoline, dual-purpose kerosene (DPK), diesel, liquefied petroleum gas (LPG), lubricants, tar, asphalt, petroleum coke. Normally, the hydrocarbons do exist in the three physical states of matter namely solid, liquid and gas, but the majority of the deposits occur as an oily inflammable liquid. Regardless of the physical states, the hydrocarbons possess unique physicochemical properties which may vary from location to location and from field to field. Diverse properties possessed by different crude oils do have great influences on the refining route and product quality as well as determine the type of remediation when oil spill occurs.

The appearance of Nigerian petroleum ranges from black or dark brown to yellowish or even greenish depending on their location and composition (Wikipedia, 2007). Its texture is oily and are either light or viscous. For the Nigerian crude oil the yields from various processing route gave 37% paraffin, 28% by volume of naphthenes and 9% aromatics, (Robert and Francis, 2000) implying that it is a less dense (light) paraffinic petroleum. The paraffinic crude oils generally have a higher content of light hydrocarbons (higher value product) that can be recovered with simple distillation. The denser crude oils produce greater content of low valued products with simple distillation and require additional processing to produce the desired range of products. Based on another finding by Adebayo (1989), it was revealed that the Nigerian crude oils contain 54% by volume of naphthenes with octane number of 60, API gravity by approximation as 36, sulphur content as 0.2% by weight. In view of the above findings, it is therefore obvious that there are contradictions in respect of the composition of the Nigerian crude oils which demands urgent attention. Recently the country has been under pressure to revive her refinery into a functional state of which the knowledge of the detailed physicochemical properties of each crude oil peculiar to a particular oil deposit would provide a lasting solution to this challenge.

As long as crude oil and other petroleum products are transported across the world's oceans, there will always be a risk of oil spill incidence. In addition, pipeline blowouts, tanker loading and unloading, and other offshore industrial operations will also generate oil spills. Therefore, this work was conceived with the aim of assessing the qualities and hence compare and contrast the similarities and differences among the crude oils with a view to developing a model that will be unique in determining the spreading rate of crude oil when Nigeria oils spill on sea water.



## 1.1 Aim and Objectives

The aim of the present study therefore was to characterize the Nigerian crude oils taken from various fields and locations. Specifically, the aim was to carry out a detailed assessment of the physicochemical properties of the Nigerian crude oils, with the objective to study how at fixed temperature, specific gravity, viscosity and surface tension properties of the oils affect the spreading rate of the oils on water. More so, how these factors interact, and how their interactions affect the spreading rate of the crude oils in a natural environment. Subsequently to develop an oil spill spreading rate model using the result obtained from the experiment based on a  $2^k$  factorial experimental design which was ultimately validated so as to ascertain the similarities and differences in the behaviour of our crude oil on the sea after an oil spill accident. These findings (properties) were used in developing some models that were used to determine spreading rate of oil on waters as well as proffer solution to oil spill.

## 1.2 Approach

In order to achieve the above objectives, the following procedures were undertaken starting from the collection of various crude oil samples from kolo creek bonny light, nembe well bonny light and Idu ekpeye in Bayelsa state; Obagi well 35, obagi well 40, and Umuchem in Rivers state; qua iboe light enang and qua iboe light Upenek in Akwa Ibom state, ogara and forcados in Delta state Owaza well 22 and Owaza well 23 in Abia state, Oguta and Egbema Opakate in Imo state.; the detailed characterization of the above crude oil samples so as to determine their properties. These properties include specific gravity, API gravity, kinematic viscosity, pour point, Reid vapour pressure (R.V.P), sulphur content, nickel, vanadium, iron copper and lead contents, conrandson carbon residue, salt content, basic



sediments and water contents, ash content, total acid number (TAN), paraffinic naphthenic and aromatic nature. Finally, these properties were further used in developing model for oil spill spreading rate. In this study, full factorial experiment (FFE) was used to efficiently screen variables in the experiment. This permitted the determination of the degree and nature of the interaction between factors involved in the spreading rate of crude petroleum.

### **1.3 Justification**

Crude oil characterization can be of great value in assessing the properties/qualities of the oils which in turn can enhance their applicability in oil spill management and hence a better environmental engineering management. During an oil spill incident, the properties of the spilled oil must be known immediately. Unfortunately, the properties routinely measured by oil producers and refiners are not the ones that the on scene commanders need to know most urgently rather the properties the oil possess at the instant the spill occurs. Thus this work will reveal the exact properties of this oil at the instant of oil spill so long as the temperature of sea water is known, how these properties will interact to produce an effect which will predict the spreading rate of the crude oil. Oil producers and refiners do not know to what extent their oil will evaporate and how quickly it will spread as well as to what extent the oil would have spread after time (t). It is the target of this work therefore to answer the question whether the oil is likely to sink or submerge; provide the viscosity of the oil at ambient temperatures, as some crudes evaporate to volatile organic compounds due to slight change in ambient temperature. The knowledge of this study will provide right response for on-site personnel against health hazard and the toxicity to marine or aquatic organisms.

In the light of the unverified similarities and differences in the behavior of our crude oils on the sea, it is therefore necessary to review the detailed properties of each crude oil peculiar to

each field. This will reveal the similarities and differences of these oils, if any of these is determined hence we can provide information for standard classification cum spreading rate for oil spill remediation.

#### **1.4 Study Constraint/Limitation**

Most of the equipment, materials and reagents needed to carry out the experiments proposed in this research work were not available in our laboratories and as such the search for such equipment was a constraint towards achieving the aims/objectives of the work. The library was equally not well stocked with relevant literatures. This was also a constraint.

Finally, lack of sufficient fund could be taken to be the major constraint since with enough fund all those equipment, materials and reagents that were not previously there in our laboratories could have been procured within the shortest available time

## CHAPTER TWO

### 2.0

### LITERATURE REVIEW

Petroleum is the world's major source of energy and is a key factor in the continued development of world economies. It is essential for future planning that governments and industries have a clear quality assessment and standard properties of petroleum available for production. To achieve such an assessment, it is imperative that the industries adopt a consistent manner for assessing the current and future qualities and quantities of petroleum expected to be recovered from naturally occurring underground accumulation. Such qualities normally refer to the standard properties of petroleum whereas the quantities are defined as reserves, and their assessment is of considerable importance to governments, international agencies, economists, bankers, and the international energy industry. In almost all ramifications, crude oils have no inherent value without a petroleum refining industry to process them into usable specification products. The rare exceptions are very light crude oils or condensates that may be burned as low quality fuels in locations with very loose or non-existent environmental restrictions. However, as a result of the refining industry, crude oil is one of the most significant categories among the commodities in the world.

The American Petroleum Institute, API, has considered classification of petroleum and definitions of various petroleum and petroleum product. Since then, the evolution of classification has yielded more precise engineering methods to determine their properties and has intensified the need for an improved quality to achieve consistency among

professionals working with refinery. These have become the preferred standards for petroleum classification across the industry.

Both natural and accidental pollutions including oil spillage affect aquatic and terrestrial habitat as well as the physical and chemical nature of the sea surface and environment. The world production of crude oil is about 3 billion tons per year and half of it is transported by sea (Clark, 1992). During the transportation, a significant amount of the oil is spilled into the sea due to operational discharges of ships as well as from accidental tankers collisions and grounding (Clark, 1992). The incidence of oil spills resulting from tanker traffic, offshore drilling, and associated activities will increase in years to come as the world's demand for petroleum and petroleum products continues to rise.

In Nigeria, these oil activities take place in the Niger Delta, (being strategically positioned in the south - south region of the country), oil production, shipping and refinement are crucial industries for the Nigerian economy but are also potential threats to the coastal marine environment. An example of this was the recent oil spill in October, 1997, in Singapore strait between the Indian and Pacific Oceans, caused by the collision of two tankers: "Evoikos" and "Oraphin Global", when approximately 28,000 tons of marine fuel oil was accidentally discharged into the Straits. Similarly in Nigeria, the local says they cannot fish on river; they can neither farm as their land has been devastated, this is the story of communities in the Niger delta region of Nigeria". (Adesina, 2002) At present, it is not possible to determine the location, extent, thickness and type of oil – pollutant using just one single model.

$$R(t) = \left[ 11.23 - 1.07 \left( \frac{S + 2\gamma_o - 1.285(\gamma_w \gamma_o)^{1/2}}{0.05539 (\gamma_w \gamma_o)^{1/2}} \right) + \frac{1}{3}V \right] t^{0.87}$$

Njobuenwu, and Abowei obtained the equation above as the new comprehensive empirical model for the prediction of the spreading of a finite quantity of oil spill on a placid aquatic medium. (Njobuenwu, et al 2003). where  $\gamma$  is the free energy per unit area of new surface. Dimensionally, this is  $\text{erg/cm}^2$ ,  $\text{dyne/cm}$ ,  $\text{nN/m}$  or  $\text{g/s}^2$ . component  $w$  constitute the substrate (water),  $o$  the spreading oil  $S$  is the surface tension.  $V$  velocity.

The regression model presented here is expected to provide a practical solution to oil spill responses as well as remediation action to be taken. It is hoped to be applicable to continuous use for in-situ monitoring of the inherent spreading rates of oil spills on sea. Moreover, such surface spreading properties constitute the requisite input data for modeling the spreading rate of oil spill. In general, the spreading of large oil mass is chiefly driven by specific gravity, vapour pressure, temperature, viscosity and surface tension properties of the oil. In the event of unintentional release of oil into coastal waters, oils form slicks and can have deleterious impacts on biota in exposed ecosystems. Their effects will depend to a large extent on the ultimate location of the oil as well as on its chemical composition at the time of interaction with aquatic biota. Oil slicks usually spread rapidly to a large area because of the lower specific gravity and low viscosity, therefore a quick response to ameliorate the damage has to be initiated.

Five clean-up strategies that frequently receive consideration include; mechanical clean-up or recovery, burning, bioremediation, treatment with chemical dispersants, and adsorption. The morphology of the slick near its leading edge and over the entire covered area in the terminal stages of spreading is strongly affected by surface tension forces (Camp and Berg, 1987).

Another critical factor that affects the spreading rate of spilled oil is temperature which invariably affects viscosity of the spilled oil (Lily, 2008), the viscosity of oil is influenced by the ambient temperature, that is, if it is warm the spilled oil will be less viscous so it will spread more rapidly.

The surface properties in particular, surface and interfacial tensions of the water body themselves are equally of key importance. Such information is crucial for determining the actual or potential pollution pathways of crude oil spills. The microlayer surfactants present in sea water (unlike artificial sea water) originate from several sources – petroleum deposits, biological activity of plankton, terrestrial material or atmospheric precipitation (Hunter and Liss, 1981), and can affect the way oil spreads on water. In addition, the presence of surfactants in both the aqueous and oil phases can lead to interfacial tension gradients giving rise to Marangoni stresses (Bauget et al. 2001) that could also initiate and drive the spreading process (Craster and Matar, 2006). An understanding of the structure of liquids adjacent to other surfaces, and of how surface wettability is governed by interfacial forces or phenomena, is important in many technological, industrial, chemical and biological situations (Adamson and Gast, 1997)



especially in oil spill and remediation.

In this work, we reviewed recent experimental progress, provided a conceptual framework within which the majority of the spreading experiments could be understood and evaluated, and pointed out relationship between experiment and theory, and finally developed predictive models that could describe the spreading rate of Nigerian crude oil spill on sea waters.

## **2.1 Petroleum in Nigeria**

Exploration for oil in Nigeria began as long as 1908, although surveying using modern techniques were not carried out until 1937 and there was not a cessation of operations during the 1939 to 1945 war. The first commercial accumulation of light oil was discovered at Oloibiri (1955). The age of the reservoir was tertiary, and this at once directed attention to the reservoir rock potentialities of the tertiary sandstone in the deltas of the Niger and Benue rivers. The coastal sedimentary basin in this area has been the scene of three distinct depositional cycles between mid-cretaceous and recent times, the third of which starting in the eocene marked the continuing growth of the main Niger Delta.

The output from Oloibiri was in fact somewhat disappointing, but its discovery was soon followed by a number of others in the Port Harcourt and Afam areas, of which Imo river, Bomu, Umechem Koro proved to be the most prolific. Other onshore discoveries were made in the Mid-west region for example, at Olomoro and Uzera. A number of important

off shore fields were also discovered for example, Okan, Okubie. In this part of West Africa, the slope of the continental shelf is very gentle, so that a large area of shallow water is accessible for exploration.(Robert, 1980).

Production from most of these Nigerian fields comes from very porous tertiary sand stones of the Agbada series, which sometimes contains oil and associated gas and sometimes only non-associated gas.

The Niger Delta basin, in which the oilfields are located, covers an area of some 75,000km<sup>2</sup> and is part of the much larger southern Niger – basin. It is separated on the west from the Dahomey (Benin) Basin by the Okitipupa (High) and is bounded on the east by the line of Cameroon volcanic on the north the niger basin transects the older cretaceous Anambra basin. The sedimentary fill consist of a tertiary regression classic sequence which is some 12,000m thick maximum. (Robert, 1980)

The Eastern or Bonny division has production centered in seven groups of oilfields, with the largest being Nembe (production capacity 120,000bbl/d). The other groups are Cawthorn Channel (70,000bbl/d), Ekulama (50,000bbl/d), Imo River (25,000 bbl/d), Kolo Creek (25,000 bbl/d), Adibawa (20,000bbl/d) and Etelebou (20,000bbl/d).

Nigeria, 10th largest oil producer in the world, the third largest in Africa and the most prolific oil producer in Sub-Saharan Africa, has about 250 oil and gas fields of which some 120 fields are producing. It contains estimated proven oil reserves of 22.5 billion barrels and produces 90 million tons per year (2 million barrels per day, 2 mmbbl/d) of



crude oil, mostly from the Niger-Delta. Present plans are to increase that daily production to 4 mmbbl/d, and reserve amount to 40 billion barrels, all by 2001, through further prospecting, mainly offshore. Its crude oils have a gravity between 21 deg. API and 45 deg. API. Its main export crudes are Bonny Light (37deg. API) and Forcados (31 deg. API). About 65% of Nigeria's oil is above 35 deg. API with very low sulphur content.

In the late nineties there are four major oil refineries: the Warri Refinery and Petrochemical Plant which can process 125,000 barrels of crude per day, the New Port Harcourt Refinery which can produce 150,000 barrels per day (there is also an 'Old' Port Harcourt Refinery with negligible production), as well as the Kaduna Refinery. The Port Harcourt and Warri Refineries both operate at only 30% capacity. It is estimated that demand and consumption of petroleum in Nigeria grows at a rate of 12.8% annually. (wikipedia, 2002) However, petroleum products are unavailable to most Nigerians and are quite costly, because almost all of the oil extracted by the multinational oil companies is refined overseas, while only a limited quantity is supplied to Nigerians themselves.

New discoveries raise Nigeria's gas reserves, fresh discoveries in Nigeria in the last two years have raised the country's gas reserves according to statistics released by the NNPC at the on going 17th World Petroleum Congress (WPC), Rio de Janeiro, Brazil.

Most Nigerian crude oils are light and they possess a low sulphur content property by implication they are sweet. They therefore have very high yield of gasoline and other light ends of the barrel. This quality has made the Nigerian crudes to be in high demand in US and West European markets. In 1979, 48.92% of NNPC crude oil export went to US, while 36.92% went to Western Europe, 9.6% of the export went to the Caribbeans

and 2.77% to Africa. As from 1980, the Nigerian government decided to diversify the direction of its crude oil exports. This move, coupled with the increase availability of heavy, low quality but much cheaper crude oil from Mexico and Alaska close to the location of the market led to the rapid decline of the share of the Nigerian crude oil into the US. This declining share was aggravated by the increasing installation of cracking facilities in refineries in the US; a development that has led to increase share of the Persian/Arabian Gulf vis-à-vis the light crude. Also, the North Sea crude oil, which is of comparable quality to Nigerian crude oils but priced much lower, effectively competed or replace Nigerian crude oils in the US market. The bulk of the Nigerian crude oils have therefore shifted to the West European market. In 1980, 53.9% of Nigerian's crude oils as against 36.9% in 1979 went to Western Europe.(economy and corporate planning division NNPC, 2000)

**Bonny light:** This crude oil is produced in Nigeria from Chevron Texaco and Shell concessions. Chevron Texaco's exports are throughput and loaded from the Shell-operated Bonny Terminals. The API gravity for Bonny Light is 35 degrees and the sulfur content is 0.2%. Specifications are: API 35.4°, specific gravity (S.G.) 0.85, Sulphur 0.14, Pour point -18°C, TAN 0.27 mg KOH/g, Nickel 3.6 wppm, Vanadium 0.4 wppm, viscosity (Visc.) (50°C) 2.9 cSt.

**Qua iboe:** The crude oil is produced from numerous offshore fields in the Bight of Biafra in south-eastern Nigeria, east of the Oso field. The API gravity for Qua Ibo is 36 degrees and the sulfur content is 0.1%. The Qua Iboe terminal is operated by ExxonMobil specific gravity (S.G.) 0.8487, Sulphur 0.1175, Pour point 60°F, TAN 0.32 mg KOH/g, Nickel 4.1 wppm, Vanadium 0.3 wppm, Visc. (20°C) 5.71 cSt.

**Brass river:** The crude is a typical Nigerian high-quality West African gasoline and gasoil - oriented crude. Its gravity has become heavier over the past few years. The crude has a low metal content and a high yield of gasoline and middle distillates with acceptable cetane index. Naphtha with an  $N+2A > 70$ , the naphtha is a good feedstock for gasoline production. Specifications are: API 36.25°, S.G. 0.845 conversion rate 7.46, Sulphur 0.13 mass%, Pour point -36 °C, TAN 0.29 mg KOH/g, Nickel 2.0wppm, Vanadium < 2 wppm, Visc. (40°C) 5.2 cSt.

**Escravos:** The crude is produced in Nigeria and loaded from the ChevronTexaco-operated at Escravos. API gravity of 33.0-33.5 degrees and a sulfur content of 0.17-0.18%. Other specifications are: S.G. 0.85 conversion rate 7.54, Sulphur 0.15 mass %, Pour point 7 °C, TAN 0.53 mg KOH/g, Nickel 4.8 wppm, Vanadium 0.5 wppm, Visc. (40°C) 4.75 cSt.

**Forcados:** Forcados terminal is on the Niger Delta. Forcados is Nigerian crude with a low sulphur and low metals content. It is rich in distillates and has low fuel content. Loading location is Forcados terminal. This crude has a larger distillate refining profile. Its API gravity is 30 degrees and has a sulfur content of 0.2%, Pour point -27 °C, TAN 0.34 mg KOH/g, Nickel 3.9 wppm, Vanadium 1.0 wppm, Visc. (50°C) 4.6 cSt.

### 2.1.1 Extraction

The most common method of obtaining petroleum is extracting it from oil wells found in oil fields. After the well has been located, various methods are used to recover the petroleum. Primary recovery methods are used to extract oil that is brought to the surface by underground pressure, and can generally recover about 20% of the oil present. After

the oil pressure has depleted to the point that the oil is no longer brought to the surface, secondary recovery methods draw another 5 to 10% of the oil in the well to the surface. Finally, when secondary oil recovery methods are no longer viable, tertiary recovery methods reduce the viscosity of the oil in order to bring more to the surface.

### 2.1.2 Uses

The chemical structure of petroleum is composed of hydrocarbon chains of different lengths. Because of this, petroleum may be taken to oil refineries and the hydrocarbon chemicals separated by distillation and treated by other chemical processes, to be used for a variety of purposes. Examples are ethane and other short- chain alkanes which are used as fuel, diesel fuel, fuel oils, gasoline, jet fuel, kerosene, liquefied petroleum gas (LPG).

Certain types of resultant hydrocarbons may be mixed with other non-hydrocarbons, to create other end products:

- Alkenes (olefins) which can be manufactured into plastics or other compounds
- Lubricants (produces light machine oils, motor oils, and greases, adding viscosity stabilizers as required).
- Wax, used in the packaging of frozen foods, among others.
- Sulfur or Sulfuric acid. These are useful industrial materials. Sulfuric acid is usually prepared as the acid precursor oleum, a byproduct of sulfur removal from fuels.
- Bulk tar.
- Asphalt

- Petroleum coke, used in speciality carbon products or as solid fuel.
- Paraffin wax Aromatic petrochemicals to be used as precursors in other chemical production

**2.1.3 Classification based on location** The oil industry classifies "crude" by the location of its origin (e.g., "West Texas Intermediate, WTI" or "Brent") and often by its relative weight or viscosity ("light", "intermediate" or "heavy"); refiners may also refer to it as "sweet," which means it contains relatively little sulfur, or as "sour," which means it contains substantial amounts of sulfur and requires more refining in order to meet current product specifications. Each crude oil has unique molecular characteristics which are understood by the use of crude oil assay analysis in petroleum laboratories.(wikipedea encyclopedia)

Barrels from an area in which the crude oil's molecular characteristics have been determined and the oil has been classified are used as pricing references throughout the world. These references are known as Crude oil benchmarks and are listed;

- Brent Crude, comprising 15 oils from fields in the Brent and Ninian systems in the East Shetland Basin of the North Sea. The oil is landed at Sullom Voe terminal in the Shetlands. Oil production from Europe, Africa and Middle Eastern oil flowing west tends to be priced off the price of this oil, which forms a benchmark.
- West Texas Intermediate (WTI) for North American oil.
- Dubai, used as benchmark for Middle East oil flowing to the Asia-Pacific region.

- Tapis (from Malaysia, used as a reference for light Far East oil)
- Minas (from Indonesia, used as a reference for heavy Far East oil)

Numerous attempts have been made to devise a system to classify crude oils into types, based on the predominant hydrocarbon series which is present; such attempts have only partially succeeded, however, because many crude oils exhibit changes, in dominant type in different regions of their distillation ranges. The US Bureau of mines correlation index method attempted to deal with this difficulty by quoting the preponderant types in two nominated fractions in the distillation range, giving crude oil classifications such as naphthenic – naphthenic, naphthenic – paraffinic, etc. Other type descriptions becomes common, such as intermediate and intermediate wax bearing, indicating the difficulties of classifying very complex mixtures. .(wikipedia encyclopeda)

A relatively simple approach, to give comparism of the characteristics of the crude oils over the whole distillation range, is by means of a graph relating the densities of distillate fractions to their mid-boiling-point. The level of the density at boiling point is indicative of the relative proportion present of the three principal hydrocarbon series diminish in the order aromatics > cyclo-alkanes > alkanes. Some crude oils contains preponderance of cyclo alkanes (i.e. naphthenic) through out, there are many which change over at about 250°C towards the paraffinic and waxy area. (NNPC Handbook on organization and function of oil company,1980)



#### **2.1.4 Grading differential and pricing**

There are a number of factors, sometimes conflicting; involved in determining the relative value or advantage a crude oil may hold in a particular oil market. Each crude oil has its own unique characteristic and properties that will determine the product it will yield and in what quantities, after refining. A refinery configuration will also inevitably influence the sort of yield a barrel of a specific crude oil will provide. An ideal crude oil may exist for a given refinery's configuration, but may not prove suitable because of its cost, or because it no longer can yield sufficient quantities of new key product required for the refinery's traditional market. Product demand in a refinery's domestic markets can vary considerably, for seasonal, economic and environmental reasons, which may affect the kind of crude or mixture of crude a refiner will seek to buy.

Refiners therefore constantly have to make compromises over the type of crude or mixture they produce because of availability of specific types of crude oil, crude market prices, actual refinery configuration and shifts in product demand. The attractiveness of certain types of crude oil for refiners will vary from market to market depending on the kind of product demand patterns that have been developed. In any calculation of the attractiveness or advantages a specific crude oil has in a market, a dominant consideration will be its price.

**2.1.5 API gravity:** In the course of its growth, the oil industry has developed ways of grading the much different crude oil that exist, to provide some sort of brand measure for the market. One of the widest used is the American petroleum institute's grading system

based on specific gravity. Each crude oil is given an API degree rating in relation to its specific gravity compared to that of water. For the purposes of the API scale, water has been given a measure of  $10^{\circ}$  API, with crude lighter than water being given a higher degree. Arabian light crude with a  $34^{\circ}$  API grading is therefore over three times as light as water. The higher the degree, the lighter the crude oil. Broad classifications of crude according to API degree vary considerably with the traditions of each market, and therefore differ from region to region and even between countries. However, very broad crude oils, such as those from North African, with  $40^{\circ}$  to  $45^{\circ}$  API are said to be very light and those with grades above  $30^{\circ}$  API are generally considered light crude in the  $22^{\circ} - 30^{\circ}$  API range are classed as medium, while those below  $22^{\circ}$  are referred to as heavy crude.

Crude oil below  $10^{\circ}$  API are heavy they will sink in water and their cost of production with current technology is so high that they are not yet being produced commercially in large quantities. However, huge reserves of such heavy crude exist, as in the Orinoco belt of Venezuela, where a number of pilot projects are using different enhanced recovery techniques to develop economic methods for their exploitation. Once their extraction and processing becomes economically attractive, they will form an important additional world energy resource.

The higher the degrees API, the lighter (less dense, thinner) is the crude oil, and in general the more desirable, say medium gravity 30 - 40 degree API. However, it is the composition of the crude, not really the specific gravity, which is the desirable issue for the production of high octane gasoline and diesel fuel.



### **2.1.6 Sulphur content.**

Besides being graded according to specific gravity, the level of impurities, contained in each crude allows attractiveness or not. One of the most important common elements that determines a crude's quality is its level of sulphur content. The higher the percentage of sulphur present, the less attractive the crude oil is because of its corrosive quality in a refinery and because of the strict environmental regulations that exist in many markets.

Also the lower the sulphur, the "sweeter" (less polluting from processing) the crude. 0.50% mass or less of sulphur is considered sweet crude; otherwise sour (hence more cost to process sulphur removal), but not to exceed 2%. The sulphur content in crude oil can vary from as little as 0.1% in weight to as high as 7% in a very sour crude. On this basis a 34<sup>0</sup>API crude oil with a 0.3% sulphur content can expect a slight price advantage over a similar grade crude with a 0.7% sulphur content produced in the same region. The level of other impurity such as metals like vanadium may also affect the quality and attractiveness and thus the price of one crude oil relative to another. (Robert et al, 2000)

**2.1.7 Geographical location:** another important element that affects the relative value or differential between crude oils is the geographical location of its production and its distance from specific market places light crude produced in North Africa have a considerable price advantage on this basis over crude oil produced in the Gulf area, which have to travel much further to reach European market. The nearness of a crude oil's point of production to the market adds a measure of value to it. Extra light crude producers such as Algeria and Nigeria are therefore able to charge more for their crude oils in Europe than producers of heavier crude oil in South American or the Arabian

Peninsula. Compared to crude oils in the 34<sup>0</sup> API range produced in the Gulf area, lighter crude oil from North Africa, with 44<sup>0</sup> API gravity and a low sulphur content of around 0.3 %, are expect to command a higher price between crude oil and their differentials, therefore are based on their specific gravity (lightness or heaviness); the level of impurities present (mainly sulphur) and the cost of transportation. (wikipedia encyclopaedia)

The price of a barrel (which is 42 gallons) of oil is highly dependent on both its grade (which is determined by factors such as its specific gravity or API and its sulphur content) and location. The vast majority of oil will not be traded on an exchange but on an over-the-counter basis, typically with reference to a marker crude oil grade that is typically quoted via pricing agencies such as Argus Media Ltd and Platts. Other important benchmarks include Dubai, Tapis, and the OPEC basket. The Energy Information Administration (EIA) uses the Imported Refiner Acquisition Cost, the weighted average cost of all oil imported into the US as their "world oil price".

The Organization of the Petroleum Exporting Countries (OPEC) is an international organization made up of Algeria, Angola, Indonesia, Iran, Iraq, Kuwait, Libya, Nigeria, Qatar, Saudi Arabia, the United Arab Emirates, and Venezuela. Since 1965 its international headquarters have been in Vienna, Austria. It is considered to be a cartel by many observers. OPEC fixes oil prices. Petroleum and mineral oil products include a broad range of hydrocarbon-based substances of varying chemical compositions and a wide variety of physical properties such as density, viscosity, kinematics viscosity, surface tension, and specific gravity. For this reason, specifications for petroleum and mineral oil products vary widely, depending on the specific product. The proper selection

of a petroleum and mineral oil product must also take application requirements into account.

The International Standards Organization (ISO) maintains standards for petroleum and mineral oil products. For the petroleum industry, ISO works in partnership with the American Petroleum Industry (API) to internationalize standards. ASTM International (formerly called the American Society for Testing and Materials (ASTM) Committee D02 also maintains standards for petroleum and mineral oil products, many of which are harmonized with ISO standards.

#### **2.1.8 Crude oil assay**

A crude oil assay is essentially the chemical evaluation of crude oil feedstocks by petroleum testing laboratories. It is a compilation of the results of numerous analyses conducted on the whole crude oil or its fractions. Each crude oil type has unique molecular, chemical characteristics. No crude oil type is identical and there are crucial differences in crude oil quality. The results of crude oil assay testing provide extensive detailed hydrocarbon analysis data for refiners, oil traders and producers. Assay data help refineries determine if a crude oil feedstock is compatible for a particular petroleum refinery or if the crude oil could cause yield, quality, production, environmental and other problems. The assay tests can be extensive. Testing can include crude oil characterization of whole crude oils and the various boiling range fractions produced from physical or simulated distillation by various procedures. Information obtained from the petroleum

assay is used for detailed refinery engineering and client marketing purposes. Feedstock assay data are an important tool in the refining process. These tests characterize a crude oil and enable refiners to evaluate the feasibility and economics of processing a given crude in their refinery or competitors refineries.

Crude oil assays vary widely in the degree of details, however, qualities of interest with respect to the whole crude will be emphasized in this research ([www.crudeoil.org](http://www.crudeoil.org)).

## **2.2 Classification of Crude Oils**

### **2.2.1 US bureau of mines classification**

This classification is based upon the specific gravity of two distillation fractions of the crude oil, and the specific gravity limits for these two fractions define nine types of crude oil. The crude oil is subjected to a standardized analytic distillation, first at atmospheric pressure and then in vacuum at a pressure of 40mmHg; this is the Hempel distillation. Fractions are collected over intervals of 25°C and the two key fractions in which the classification is made are: 250 – 270°C at atmospheric pressure in the kerosene range and 275 – 300°C at 40mmHg pressure in the lubricating oil range

### **2.2.2 Characterization factor (K)**

Since crude oil is a mixture, the actual properties are always an average values that depends on the components present in the mixture. The most significant physical properties are the boiling point, (T), specific gravity (S) and the viscosity. These properties can be readily tested and measured and its value related to the chemical composition of the oil. In most cases, comparison and classification of crude oil are by means of the characterization factor (K) given by

$$K = \frac{(T+460)^{1/3}}{S}$$

S

Where S = specific gravity

Note that the specific gravity at 60°F (15°C) applies, T implies the average boiling point at atmospheric pressure. For K= 12.5 to 13.0, crude oil is paraffinic, for K= 11.0 to 12.0, crude oil is naphthenic and for K= 9.5 to 11.0 crude oil is aromatic. For K between mixed crude (paraffinic – naphthenic), thus, crude oil are classified into four groups according to the percentage of the classes of these hydrocarbon types present in the crude oil.

### 2.2.3 Tissot and Welte's classification

Tissot and Welte 1978 have proposed a classification system based upon the crude oil's content of various structural types of hydrocarbon. These types include alkanes, naphthenes, aromatics including heteroatomic molecules, asphalts and resins. The sulphur content of the crude oil is also determined by modern analytical techniques on the part of the crude oil with a boiling point above 210°C at atmospheric pressure.

**1. Paraffinic oils:** these will have saturated open chain hydrocarbon content of greater than 50%, they are light, their specific gravity is normally below 0.85 and their resinous – asphaltic component less than 10% with a very low sulphur content.

#### **2. Naphthenic oils:**

Saturated cyclic compound account for 50% or more of the crude oils, many of them are degraded oils with less than 20% of the n- and iso alkanes which were originally paraffinic or paraffinic-naphthenic oils prior to biodegradation.

### 3. Paraffinic-naphthenic oils:

These contains more than 50% saturated molecules with a sulphur content of normally less than 1%, often in benzothiophenes. While the aromatic 25-40% of the hydrocarbon and the asphalts and resins vary between 5 and 15%. They are slightly more dense and viscous than paraffinic oils.

4. **Aromatic-intermediate oils:** contains 40-70% aromatic compound, many of which are of steroid origin. Sulphur is normally less than 1% and occurs in thiophene derivatives which can be more than 25% of the aromatic compound present. Resins and asphalt 10-30% of the oil, they are heavy with a specific gravity above 0.85.

5. **Naphthenic- aromatic oils:** these oils are biodegradable, sulphur content less than 1%, but contain significant amounts of resins (often 25%).

6. **Aromatic-asphaltic oils:** these oils are mostly biodegraded aromatic – intermediate oils, sulphur content greater than 1% and can reach 9%. Their resin and asphaltene content varies between 30 and 60%

### 2.3 Behavior of Crude Oil on the Sea Surface

When the crude oil is released on the seawater surface, it undergoes certain processes, which contribute to its ultimate fate over a period. Initially, oil starts floating on the surface of the seawater at the vicinity of the point of release (Cormack, 1999). Further, it undergoes various weathering processes that alter the properties of the crude oil. The weathering process includes (Jenkins et al., 1991):

- Spreading
- Evaporation

- Dissolution
- Dispersion
- Photochemical oxidation
- Flushing due to wave energy
- Emulsification
- Microbial biodegradation
- Adsorption to suspended matter
- Sedimentation

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### 2.3.1 Spreading

As soon as the crude oil is spilled, it starts spreading on the sea surface. The speed of spreading mainly depends upon the oil characteristics and volume of the spilled oil (Doerffer, 1992). It increases the overall surface area of the spill and enhances the mass transfer through evaporation and dissolution (Doerffer, 1992). The crude oil tends to spread to a mean thickness of approximately 0.1 mm with some thicker oil patches (Mackay and McAuliffe, 1988). The crude oil with relatively high wax contents spreads rapidly in sunlight, although at night it typically solidifies (Lee et al., 1981). Spreading behavior of crude oil is a complex process, due to the influence of various forces, interfacial tension, and sea state effects (Mackay and McAuliffe, 1988). The principal forces influencing the lateral spreading of oil on the calm sea are frictional, inertial, gravitational, and surface tension (Doerffer, 1992).

The volume of spilled oil has a direct impact on rate of spreading, because of the gravitational force, hence, large spills spread faster than small ones (Doerffer, 1992).



However, the rate of spreading decreases eventually, when the surface tension becomes major spreading force (Doerffer, 1992). Surface tension decreases with increasing temperature and increases the rate of spreading (Doerffer, 1992). Light crude oils have low specific gravity and therefore great potential to spread (Doerffer, 1992). Spreading exposes more oil to the underlying sea water and promotes dispersion of the oil into the sea by wave action (Cormack, 1999). The rate and extent at which these processes proceed depend on the physical and chemical properties of the crude oil (Daling, 1996). Jenkins et al. (1991) stated that spreading, evaporation and emulsification are the three processes that significantly influence the properties of the crude oil. Fundamental knowledge of these three processes is therefore necessary to predict the behavior of the spilled oil. Other processes such as photo-oxidation, microbial biodegradation, dissolution, and sedimentation also influence the behavior and fate of spilled oil, but to a lesser extent (Daling, 1996).

#### **2.4 Effect of Oil Spill:**

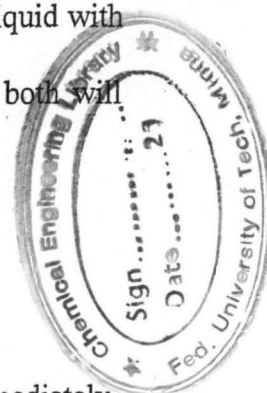
Oil spills occur in oceans, lakes, and rivers all over the world. Some of these spills are large and very damaging to nature while some are small and occur regularly. Examples of small spills are: used oil from automobiles that is poured down storm drains and the discharge of oil from outboard motors on boats. The extent of damage a spill does to the environment is related to the oil type, size of the spill, weather conditions, location of the spill, and the timing of the spill. Winds, tides, and waves will all have an effect on where the oil goes and how much damage it does. The oil from a spill can effect the marine environment by:

- \* coating the substrate and organisms living on nearby shorelines with oil.
- evaporating into the atmosphere to become an aerosol that is transported by the wind.
- breaking into smaller particles in the water that are ingested by zooplankton and small fishes and enters the food chain.
- coating the fur and feathers of mammals and birds, destroying their insulating ability, reducing buoyancy, and harming the animals when the oil is ingested as they clean themselves. Animals die from exposure, drowning, suffocation, or from ingestion of oil.

When an oil spill accident occurs, the oil floats on top of the water. This is because the oil is less dense than the water. Density is a measure of how much mass an object contains for a specific volume. It can be expressed by the formula:  $Density = Mass/Volume$ . Seawater has a density of  $1.025 \text{ g/cm}^3$ , freshwater =  $0.998 \text{ g/cm}^3$ , and oil's density is typically  $0.83\text{-}0.95 \text{ g/cm}^3$ . A liquid with a lower density will float on top of a liquid with a higher density. Freshwater and oil have lower densities than seawater and both will form a layer on top of the seawater unless some force acts to mix the two.

## 2.5 Effect of Crude Oil Properties on Spreading Rate of Oil on Water

During any oil spill incident, the properties of the spilled oil must be known immediately. Unfortunately, the properties routinely measured by oil producers and refiners are not the ones that on-scene commanders need to know most urgently. Oil producers and refiners typically do not know to what extent their oils will evaporate and how quickly; to what extent dispersibility will occur naturally, or be enhanced with dispersants; whether emulsions will form; if the oil is likely to sink or submerge; the viscosity of the oil, at ambient temperatures, as it evaporates; the health hazard to on-site personnel from



volatile organic compounds; and the toxicity to marine or aquatic organisms. (Jokuty *et al*, 2008)

### **Reid vapour pressure**

Vapour pressure is an important physical property of volatile liquids. It is the pressure that a vapour exerts on its surroundings. Its units are kilopascals, corrected to one atmosphere (101.3 kPa). For volatile petroleum products, vapour pressure is used as an indirect measure of evaporation rate. Vapour pressure can be measured by a variety of methods including Reid, dynamic, static, isoteniscopic, vapour pressure balance, and gas saturation. The most commonly used method for crude oils has been the Reid vapour pressure, as determined by ASTM method D 323 - Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method), (ASTM, 1996a). This test method determines vapour pressure at 37.8<sup>0</sup>C (100 <sup>0</sup>F) of petroleum products and crude oils with initial boiling point above 0<sup>0</sup> C (32<sup>0</sup> F). It is measured by saturating a known volume of oil in an air chamber of known volume and measuring the equilibrium pressure which is then corrected to one atmosphere (Jokuty *et al*, 2008).

### **Density**

Density is defined as the mass per unit volume of a substance. It is most often reported for oils in units of g/mL or g/cm<sup>3</sup>, and less often in units of kg/m<sup>3</sup>. Density is temperature-dependent. Oil will float on water if the density of the oil is less than that of the water. This will be true of all fresh crude oils, and most fuel oils, for both salt and fresh water. Bitumens and certain residual fuel oils may have densities greater than 1.0

g/mL and their buoyancy behaviour will vary depending on the salinity and temperature of the water. The density of spilled oil will also increase with time, as the more volatile (and less dense) components are lost. After considerable evaporation, the density of some crude oils may increase enough for the oils to sink below the water surface.

Two density-related properties of oils are often used: specific gravity and American Petroleum Institute (API) gravity. Specific gravity (or relative density) is the ratio, at a specified temperature, of the oil density to the density of pure water.

The API gravity scale arbitrarily assigns an API gravity of  $10^0$  to pure water. API gravity is calculated as: **specific gravity**  $(141.5/131.5 + ^\circ\text{API})^T = \text{temperature,}$

Oils with low densities, and hence low specific gravities, have high API gravities. The price of a crude oil is usually based on its API gravity, with high gravity oils commanding higher prices. API gravity, and density or specific gravity at  $15^0\text{ C}$ , can be interconverted using Petroleum Measurement Table (American Petroleum Institute, 1982).

Density is measured using an Anton Parr DMA 48 digital density meter, and following ASTM method D 5002 - Density and Relative Density of Crude Oils by Digital Density Analyzer (ASTM, 1996a). In this way, densities can be measured to 0.0001 g/mL with a repeatability of "0.0005 g/mL.

## Viscosity

Viscosity is a measure of a fluid's resistance to flow; the lower the viscosity of a fluid, the more easily it flows. Like density, viscosity is affected by temperature. As temperature decreases, viscosity increases. Viscosity is a very important property of oils because 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.

Viscosity is the measure of the flow properties of the oil/material (Cormack, 1999). Low viscosity implies a mobile liquid and high viscosity denotes the materials that are resistant to flow, such as heavy fuel oils (Cormack, 1999). Most of the crude oils and refined products have viscosities from approximately 5 to 25000 centistokes at 15°C (Nordvik et al., 1996).

There are several ASTM Standard Methods for measuring the viscosity of oils. Of these, only Methods D 445 - Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity) and D 4486 - Standard Test Method for Kinematic Viscosity of Volatile and Reactive Liquids, will yield absolute viscosity measurements (ASTM, 1996a). Both of these methods make use of glass capillary kinematic viscometers and will produce absolute measurements in units of centistokes (cSt) only for oils that exhibit Newtonian flow behaviour (viscosity independent of the rate of shear).

## Hydrocarbon groups

The behaviour of crude oils at sea is dominated by their chemistry. The main constituents of crude oils can be grouped into several broad classes of compounds: saturates (including waxes), aromatics, resins, and asphaltenes.

Saturates are alkanes with structures of  $C_nH_{2n+2}$  (aliphatics) or  $C_nH_{2n}$  in the case of cyclic saturates (alicyclics). Small saturates ( $<C_{18}$ ) are the most dispersible components of oils. Large saturates (waxes) can produce anomalous evaporation, dispersion, emulsification, and flow behaviours.

Aromatics are compounds that have at least one benzene ring as part of their chemical structure. The small aromatics (one and two rings) are fairly soluble in water, but also evaporate rapidly from spilled crude oil. Larger aromatics show neither of these behaviours to any extent.

Resins and asphaltenes are similar in many ways. Asphaltenes can be thought of as large resins. Both groups are thought to be composed of condensed aromatic nuclei which may carry alkyl and alicyclic systems containing heteroatoms such as nitrogen, sulphur, and oxygen. Metals such as nickel, vanadium, and iron are also associated with asphaltenes. Both groups do not appreciably evaporate, disperse or degrade, and both groups stabilize water-in-oil emulsions when they are present in quantities greater than 3% (Fingas, 1994).

Waxes are predominantly straight-chain saturates with melting points above 20 °C. The preceding definitions may be overly simplistic given the complex chemical composition



of petroleum. A greater appreciation of oil chemistry and of how petroleum can be chemically fractionated can be obtained from more detailed texts such as the one by Speight (Speight, 1991).

Saturate, aromatic, and polar contents can be determined using various techniques such as open column chromatography, high pressure liquid chromatography (HPLC), or thin layer chromatography with flame ionization detection (TLC/FID, also known by the trade name Iatroscan). TLC/FID is usually restricted to determinations on weathered oils, as significant losses of low boiling component are likely with fresh oils. It should be noted that each technique will likely yield different results.

Prior to 1989, hexane was used for the precipitation of asphaltenes. Since then, n-pentane has been used as the precipitation medium. Since 1994, hydrocarbon groups in fresh and evaporated crude oils have been determined by using a combination of old and new methods. Asphaltenes are precipitated from n-pentane. Waxes can then be precipitated from a mixture of methyl ethyl ketone and dichloromethane at  $-32^{\circ}\text{C}$ . To separate saturates, aromatics, and resins, deasphalted oil (maltenes) is placed on an open silica column, and eluted sequentially with solvents of increasing polarity. If the oil used has an initial boiling point (IBP) above  $250^{\circ}\text{C}$  (determined by simulated distillation), a good mass balance can be obtained ( $>95\%$ ). However, most fresh crude oils will have an IBP well below  $250^{\circ}\text{C}$ , and the loss of light ends during solvent recovery results in a poor mass balance. Fortunately, by making the reasonable assumptions that a) resin and asphaltene contents are not affected by evaporative losses, and b) the aromatic portion of the lost light ends can be equated to the benzene, toluene, ethylbenzene, and xylenes



(BTEX) plus C<sub>3</sub>-benzenes content, it is possible to calculate the distribution of hydrocarbon groups.

### **Adhesion**

It has long been recognized that different oils tend to adhere to surfaces to a greater or lesser degree. A test was developed, using a standard surface, that gives a semi-quantitative measure of this adhesive property.

For the purposes of this test, oil adhesion is defined as the mass of oil per unit area that will remain on a standard test surface, after 'dunking and draining' for 30 minutes, under prescribed conditions. The standard procedure was developed using both fresh and evaporated oils with a wide range of viscosities. Test parameters that were evaluated included temperature, oil viscosity, time, and test-surface area. A recent study has also determined that the relative adhesiveness of different oils is independent of the type of surface material used (Jokuty et al., 1996).

### **Volatile organic compounds**

Benzene, toluene, ethylbenzene, and xylenes (BTEX), and substituted benzenes are the most common aromatic compounds in petroleum, making up to a few percent of the total mass of some crude oils. They are the most soluble and mobile fraction of crude oil and many petroleum products, and as such, frequently enter soil, sediments, and ground water because of accidental spills, leakage of petroleum fuels from storage tanks and pipelines, and improper oil waste disposal practices. BTEX are hazardous carcinogenic and

neurotoxic compounds and are classified as priority pollutants regulated by the Canada Environment and the US Environmental Protection Agency.

A rapid, reliable, and effective method for direct determination of BTEX plus C<sub>3</sub>-substituted benzenes has been developed using gas chromatography with mass spectrometric detection (GC/MS). Details of the method are given in a paper by Wang (Wang et al. 1995).

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### Surface tension and interfacial tension

Interfacial tension is the force of attraction between the molecules at the interface of two fluids. At the air/liquid interface, this force is often referred to as surface tension. The SI units for interfacial tension are millinewtons per metre (mN/m). These are equivalent to the former units of dynes per centimetre (dyne/cm).

The surface tension of an oil, together with its viscosity, affects the rate at which an oil spill spreads. Air/oil and oil/water interfacial tensions can be used to calculate a spreading coefficient which gives an indication of the tendency for the oil to spread. It is defined as:

$$\text{Spreading Coefficient} = S_{WA} - S_{OA} - S_{WO}$$

where  $S_{WA}$  is water/air interfacial tension,  $S_{OA}$  is oil/air interfacial tension, and  $S_{WO}$  is water/oil interfacial tension. Spreading to a thin slick is likely if the spreading coefficient of oil is greater than zero, and the higher the spreading coefficient, the faster the spreading will occur (Twardus, 1980).

Unlike density and viscosity, which show systematic variations with temperature and degree of evaporation, interfacial tensions of crude oils and oil products show no such correlations. Nor is there any correlation to viscosity (Jokuty *et al*, 1995).

A single ASTM method, D 971 - Standard Test Method for Interfacial Tension of Oil Against Water by the Ring Method (ASTM, 1996a), is applicable to the measurement of oil/water interfacial tensions. Measurements were taken using a Fisher Surface Tensiometer Model 21. Interfacial and surface tension measurements have been determined using a Kruss Digital Tensiometer K10ST. This instrument uses the Du Nouy principle for measuring interfacial tension, as recommended in the ASTM method. Unlike manually operated ring tensiometers, the maximum deformation of the lamella is detected electronically, and occurs before the ring pulls completely through the interface. This results in interfacial tensions that are slightly lower than those measured manually. Repeatability is +/-2% of the mean. (Jokuty *et al*, 2008)

### **Boiling point distributions**

In the oil refining industry, boiling range distribution data are used to evaluate new crude oil, to confirm crude quality before purchase, to monitor crude quality during transportation, and to provide information for the optimization of refinery processes. From the point of view of oil analysis for environmental purposes, boiling range distributions provide an indication of volatility and component distribution. In addition, this data can be used as input to some oil spill modeling programs. Boiling range distribution data may also prove to be useful in the development of equations for predicting evaporative loss.

Traditionally, boiling range distributions have been determined by distillation. 'Yield on crude' data are still widely reported in the oil assay literature, providing information on the yield of specific fractions obtained from a crude oil. Although by no means universal, atmospheric and vacuum distillation techniques have largely been replaced by 'simulated' distillation methods. These methods use low resolution gas chromatography and correlate retention times to hydrocarbon boiling points. ASTM methods D 2887 - Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography and D 3710 - Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography use external standards composed of n-alkanes (ASTM, 1996a). ASTM method D 5307 - Standard Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography is very similar to D 2887, but requires two runs to be made with each sample, one of which uses an internal standard (ASTM, 1996a). The amount of material boiling above 538 °C (reported as residue) is calculated from the differences between the two runs.

Boiling point distributions are determined by simulated distillation with an AC Analytical Controls SIMDIS analyzer, comprised of a Hewlett Packard 5290 Series II gas chromatograph with an Analytical Controls Programmable Temperature Vaporizer (PTV) injector. The system uses a special high-temperature column and is capable of determining boiling point distributions between 35 °C and 750 °C. (Jokuty, *et al*, 2008)

## **Metal content**

Metal content in crude oils can provide valuable information about the origin of those oils, potentially aiding in identifying the source of oil spills. Crude oil assays often include nickel and vanadium contents due to the detrimental effects of these metals on catalysts used in cracking and desulphurization processes. In lubricating oils, metal contents can provide information on both the types of additives used in the oil and on the wear history of the equipment being lubricated. ASTM method D 5185 - Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES), (ASTM, 1996a) can be used to determine over 20 different metals in a variety of petroleum products (Fingas et al., 1995). For Nickel, vanadium and iron in crude oil, these test methods cover, in single procedures, the determination of Ni, V, and Fe in crude oils and residual oils. These test methods complement test method D1538, which covers only the determination of vanadium.

When fuels are combusted, vanadium present in the fuel can form corrosive compounds. The value of crude oils can be determined, in part, by the concentrations of nickel, vanadium, and iron. Nickel and vanadium, present at trace levels in petroleum fractions, can deactivate catalysts during processing. These test methods provide a means of determining the concentrations of Nickel, vanadium and iron.

## **Sulphur**

The sulphur content of a crude oil is important for a number of reasons. Downstream processes such as catalytic cracking and refining will be adversely affected by high sulphur contents. During an oil spill, the sulphur content becomes a health and safety concern for cleanup personnel. In addition, if high sulphur oils are burning, they can produce dangerous levels of sulphur dioxide.

The total sulphur content of oil can be determined by numerous standard techniques. ASTM method D 129 - Standard Test Method for Sulfur in Petroleum Products (General Bomb Method) (ASTM, 1996a) is applicable to petroleum products of low volatility and containing at least 0.1 mass percent sulphur (ASTM, 1996a). In accordance with ASTM method D 4294 - Standard Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy (ASTM, 1996a). This method is applicable to both volatile and non-volatile petroleum products with sulphur concentrations ranging from 0.05 to 5 mass percent. (Jokuty *et al*, 2008)

## **Sediment and water content**

A high value of sediment and water in crude oil will make the crude oil sink when spilled on water. It does not influence the spreading rate of crude oil on water. However a knowledge of the sediment and water content of crude oil is important to operation of the refinery and sales. Water can cause corrosion of equipment and problems in processing. A determination of water and sediment content is required to measure accurately net volumes of actual oil in sales, taxation, exchange and custody transfers.



### **Ash content**

The small amount of non-combustible metallic material found in almost all petroleum products is commonly called ash. Ash content should not exceed 0.02 mass percent.

The ash content of crude oil petroleum does not influence the spreading rate of crude oil on water as burning is not a process in the spreading rate of crude oil.

Knowledge of the amount of ash forming material present in petroleum product can provide information as to whether or not the product is suitable for use in a given application. Ash can result from oil or water-soluble metallic compound or from extraneous solid such as dirt and rust.

### **Total acid number (TAN)**

The total acid number of crude oil petroleum does not affect the spreading rate of crude oil on water. Hydrochloric acid, from the hydrolysis of calcium and magnesium chlorides in crude oil is the principal strong acid responsible for corrosion of refinery equipment. Neutralizers and corrosion inhibitors will be injected to resist the corrosion reactions.

New and used petroleum product may contain acidic constituents that are present as additives or as degradation products formed during service, such as oxidation product, the relative amount of these materials can be determined by titrating with bases. The acid number is a measure of this amount of acidic substance, in the oil always under the conditions of the test. The acid number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degrading in service. Any condemning limits must be empirically established.

Since a variety of oxidation product contribute to the acid number and the organic acids vary widely in corrosion properties, the test cannot be used to predict corrosion



properties, the test method can be used to predict corrosiveness of an oil under service conditions. No general correlation is known between acid number and the corrosive tendency of oils towards metals.

### **Pour point**

Pour point is an index of the lowest temperature of its utility for certain application. Pour point and cloud point are method by which the quantity of paraffin wax with a crude oil can be measured. The lower the pour point of crude oil the faster the oil will flow. The temperature of water will affect the pour point of the crude oil whenever the oil spill on water. This is because there is interaction between the crude oil properties and the property of the water (temperature and salinity). These tests are empirical and useful for specifying the behavior of oils at low temperatures, and are determined by allowing samples of oil to cool in a standard apparatus. The temperature at which turbidity is observed is the cloud point, while the temperature at which the oil will not flow in definite manner is the pour point. Both these temperatures are determined by the precipitation of paraffin wax. The rate of cooling is important, and hence the need for standard conditions. Oils which are completely wax free such as some naphthenic oils, will show no cloud point, but will have a pour point.

### **Organic chloride content of crude oil**

This property of crude oil will increase the salinity property of the water as organic chlorides are soluble in water. Whenever the oil spill on the sea the quantity of dissolved organic chloride can be neglected since the volume of the sea water is a large ratio as compared to the oil spill so this may not affect the spreading rate. But if the crude oil spill on a small volume of water say of equal ration and a measurable quantity of the chloride

is dissolved into the water, the salinity of the water is altered and so the spreading rate of the crude oil will be affected. Organic chloride species are potentially damaging to refinery processes. Hydrochloric acid can be produced in hydrotreating or reforming reactors and the acid accumulates in condensing regions of the refinery. Unexpected concentrations of organic chloride cannot be effectively neutralized and damage can result. Organic chlorides are not known to be naturally present in crude oils and usually result from cleaning operations at producing sites, pipelines, or tanks. It is important for the oil industry to have common methods available for the determination of organic chlorides in crude oil, particularly when transfer of custody is involved.

### **Nitrogen in petroleum**

The nitrogen in crude oil petroleum does not influence the spreading rate of crude oil on water as the spreading rate of crude oil is independent of the nitrogen. Many nitrogen compounds can contaminate refinery catalysts. They tend to be the most difficult class of compounds to hydrogenate, so the nitrogen content remaining in the product of a hydrotreater is a measure of the effectiveness of the hydrotreating process. In lubricating oils the concentration of nitrogen is a measure of the presence of nitrogen containing additives. This test method is intended for use in plant control and in research.

### **Aqueous solubility**

The solubility of oil in water can be determined by bringing to equilibrium a volume of oil and water, and then analyzing the water phase. This analysis can be done by purging and trapping the dissolved hydrocarbons or, alternatively, directly analyzing the headspace above the water. (Jokuty, *et al*, 2008)

Since oil is a complex mixture of components and each component has a different solubility in water, an oil's aqueous solubility is expressed as the cumulative concentration of the individually dissolved components. The composition and concentration of the solubilized mixture will depend upon conditions used during equilibration. The term 'solubility' as applied to oils is being replaced by the technically more precise term 'water-soluble fraction'. The values have been reported in catalogues where an excess of oil was used (oil-to-water volume ratios of at least 1:20) and where the processes of evaporation and oil-in-water emulsification were prevented by Jokuty and company (Jokuty, *et al*, 2008)

## **2.6 Experimental Design**

Data for statistical studies are obtained by conducting either experiments or surveys. Experimental design is the branch of statistics that deals with the design and analysis of experiments. In an experimental study, variables of interest are identified. One or more of these variables, referred to as the factors of the study are controlled so that data may be obtained about how the factors influence another variable referred to as the response variable, or simply the response.

Factorial experiments are designed to draw conclusions about more than one factor, or variable. The term factorial is used to indicate that all possible combinations of the factors are considered. For instance, if there are two factors with  $a$  levels for factor 1 and  $b$  levels for factor 2, the experiment will involve collecting data on  $ab$  treatment combinations. The factorial design can be extended to experiments involving more than two factors and experiments involving partial factorial designs. (David, 2008)

- **Analysis of variance and significance testing**

A computational procedure frequently used to analyze the data from an experimental study employs a statistical procedure known as the analysis of variance. For a single-factor experiment, this procedure uses a hypothesis test concerning equality of treatment means to determine if the factor has a statistically significant effect on the response variable. For experimental designs involving multiple factors, a test for the significance of each individual factor as well as interaction effects caused by one or more factors acting jointly can be made. Further discussion of the analysis of variance procedure is provided by David. (David, 2008)

- **Regression and correlation analysis**

Regression analysis involves identifying the relationship between a dependent variable and one or more independent variables. A model of the relationship is hypothesized, and estimates of the parameter values are used to develop an estimated regression equation. Various tests are then employed to determine if the model is satisfactory. If the model is deemed satisfactory, the estimated regression equation can be used to predict the value of the dependent variable given values for the independent variables. (Encyclopaedia Britannica, 2008)

- **Regression model**

In simple linear regression, the model used to describe the relationship between a single dependent variable  $y$  and a single independent variable  $x$  is  $y = \beta_0 + \beta_1x + \varepsilon$ .  $\beta_0$  and  $\beta_1$  are referred to as the model parameters, and  $\varepsilon$  is a probabilistic error term that accounts for

the variability in  $y$  that cannot be explained by the linear relationship with  $x$ . If the error term were not present, the model would be deterministic; in that case, knowledge of the value of  $x$  would be sufficient to determine the value of  $y$ . (Encyclopaedia Britannica, 2008)

- **Least squares method**

Either a simple or multiple regression model is initially posed as a hypothesis concerning the relationship among the dependent and independent variables. The least squares method is the most widely used procedure for developing estimates of the model parameters. For simple linear regression, the least squares estimates of the model parameters  $\beta_0$  and  $\beta_1$  are denoted  $b_0$  and  $b_1$ . Using these estimates, an estimated regression equation is constructed:  $\hat{y} = b_0 + b_1x$ . The graph of the estimated regression equation for simple linear regression is a straight line approximation to the relationship between  $y$  and  $x$ . (David, 2008)

In multiple regression analysis, the model for simple linear regression is extended to account for the relationship between the dependent variable  $y$  and the independent variables  $p$  ranging from  $x_1, x_2, \dots, x_p$ . The general form of the multiple regression model is  $y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \dots + \beta_px_p + \varepsilon$ . The parameters of the model are the  $\beta_0, \beta_1, \dots, \beta_p$ , and  $\varepsilon$  is the error term.

- **Analysis of variance and goodness of fit**

A commonly used measure of the goodness of fit provided by the estimated regression equation is the coefficient of determination. Computation of this coefficient is based on

the analysis of variance procedure that partitions the total variation in the dependent variable, denoted by SST, into two parts: the part explained by the estimated regression equation, denoted by SSR, and the part that remains unexplained, denoted by SSE. (David, 2008)

- **Significance testing**

In a regression study, hypothesis tests are usually conducted to assess the statistical significance of the overall relationship represented by the regression model and to test for the statistical significance of the individual parameters. The statistical tests used are based on the following assumptions concerning the error term: (1)  $\epsilon$  is a random variable with an expected value of 0, (2) the variance of  $\epsilon$  is the same for all values of  $x$ , (3) the values of  $\epsilon$  are independent, and (4)  $\epsilon$  is a normally distributed random variable. (David, 2008)

- **Residual analysis**

The analysis of residuals plays an important role in validating the regression model. If the error term in the regression model satisfies the four assumptions noted earlier, then the model is considered valid. Since the statistical tests for significance are also based on these assumptions, the conclusions resulting from these significance tests are called into question if the assumptions regarding  $\epsilon$  are not satisfied. (David, *et al*, 2008)

As noted above, quantitative variables measure how much or how many; qualitative variables represent types or categories of regression model. For instance, suppose it is of interest to predict sales of an iced tea that is available in either bottles or cans. Clearly,



the independent variable “container type” could influence the dependent variable “sales.” Container type is a qualitative variable, however, and must be assigned numerical values if it is to be used in a regression study. The So-called dummy variables are used to represent qualitative variables in regression analysis. For example, the dummy variable  $x$  could be used to represent container type by setting  $x = 0$  if the iced tea is packaged in a bottle and  $x = 1$  if the iced tea is in a can. If the beverage could be placed in glass bottles, plastic bottles, or cans, it would require two dummy variables to properly represent the qualitative variable container type. In general,  $k - 1$  dummy variables are needed to model the effect of a qualitative variable that may assume  $k$  values.

The general linear model  $y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \dots + \beta_px_p + \varepsilon$  can be used to model a wide variety of curvilinear relationships between dependent and independent variables. For instance, each of the independent variables could be a nonlinear function of other variables. Also, statisticians sometimes find it necessary to transform the dependent variable in order to build a satisfactory model. A logarithmic transformation is one of the more common types. (David, *et al*, 2008)

### **The $2^k$ Factorial Design**

The full factorial experimental design (FFED) is the most efficient design for obtaining the response of variables for experiments involving the study of the effects of two or more factors.



are widely used in research work especially in experiments involving several factors where it is necessary to study the combined effects of the factors on a response. In factorial designs all possible non-repeatable combinations of the levels of factors are considered. Each complete trial or replication of the experiment allows all possible combinations of the levels of the factors to be investigated.

In this study, the  $2^k$  full factorial design provides the time frame and order of experimental runs in which the factors can be studied. With a  $2^k$  design, it is easy to write down the experimental runs in standard order at the onset and the effects of the factors and/or their interactions can easily be estimated. The statistical model for a  $2^k$  design includes  $k$  – main factors,  ${}^kC_2$  two – factor interactions,  ${}^kC_3$  three – factor interactions and one  $k$  – factor interaction. That is, for a  $2^k$  design the complete model contains  $(2^k - 1)$  effects (Chukwu, 2005). A  $2^k$  full factorial experiment (FFE) provides the basis for designing the crude petroleum multi-factor experiments (David, *et al.* 2008)

**The assumptions that are normally made include:**

- i. The values of the independent/regressor variables (the  $X_i$ ) are known in advance from the screening test data. The regressor variables are temperature, surface tension, viscosity, and specific gravity when the rate of spread of crude (R) is the dependent variable.
- ii. From related and relevant literatures, a first-order multiple linear relationships provide an acceptable approximation to the true functional relationship between the regressor variables and the dependent variable (R).

- ii. From related and relevant literatures, a first-order multiple linear relationships provide an acceptable approximation to the true functional relationship between the regressor variables and the dependent variable (R).
- iii. The design is completely randomized and the usual normality assumptions are satisfied. For every fixed value of  $X_i$ , the  $e$ 's (error term) are random quantities independently distributed with mean, 0, and common variance,  $\sigma^2$  (Chukwu, 2005).

In the  $2^4$  full factorial experiment, the low and high levels of the factors were coded as '-' and '+' respectively. The levels of the four factors are listed in standard order in the columns  $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$  in the table. To obtain the design matrix, start the column  $X_1$  ought to be started with one minus sign and subsequently alternate the signs until you reach row (run)  $2^k$ ; the column  $X_2$  will start with two minus signs and it will be alternated in signs in blocks of 2 until row  $2^k$  is reached; and column  $X_3$  will start with  $2^2 = 4$  minus signs and the signs will be alternated in blocks of 8. The sequence of + and - signs in the columns indicates how to combine the observations to get the main effects and the interactions. For example, the first run puts all four factors at their low levels; the second run sets factor  $X_1$  at high level and factors  $X_2$ ,  $X_3$ , and  $X_4$  at low levels; etc. Column  $X_0$ , having only plus signs, represents the total or average of the entire experiment. Columns  $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$  are the main effects while columns  $X_{12}$  through  $X_{1234}$  are the interactions. Experimental designs that have this property for fitting a regression model are called orthogonal designs (Chukwu, 2005). Orthogonal designs minimize the variance of the regression coefficients and provide equal precision of estimation in all directions.

A 4-variable, 2-level factorial design has the calculation matrix shown in Equation {3.1} and would be used to analyze the rate of spread of crude being modeled. The  $2^4$  factorial design was used to estimate the fifteen (15) effects indicated in the linear model. That is, with 4 variables coded as  $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$ ; a 16-run experiment permits unique solutions for the coefficients (parameters) of the equation or linear model (Chukwu, 2005).

$$R = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_{12} + b_{13}X_{13} + b_{14}X_{14} + b_{23}X_{23} + b_{24}X_{24} + b_{34}X_{34} + b_{123}X_{123} + b_{124}X_{124} + b_{134}X_{134} + b_{234}X_{234} + b_{1234}X_{1234} + e_i$$

Equation (2.1)

where:  $R$  = rate of spreading of crude oil that is being modeled;  $b$ 's = regression coefficients of the model;  $X$ 's = coded variables;  $e_i$  = random error with zero mean and constant variance. It measures the discrepancy in the functional relationship between the response and regressor variables.

The solution to Equation (2.1) is readily obtained, either in total its by computer or one parameter at a time on a desk calculator. The model describes a hyper-plane in  $k$ -dimensional space of the regressor variables ( $X_i$ ). When more than three variables are involved in a regression analysis, we cannot make use of graphs/diagrams to illustrate a plane of regression. With more than three variables, not only does the density function become "hyper-surface", but the planes of regression become "hyper-planes" (Chukwu, 2005).

The mean, dispersion, sum of the dispersion, and maximum dispersion are calculated using Equations 2.2, 2.3, 2.4, and 2.5 respectively (Chukwu, 2005). The assumed

functional relationship between the dependent variable  $R_i$  and the independent variables,  $X_i$  ( $i = 1, 2, 3, 4$ ) is formulated as a linear model Equations (2.1) (Chukwu, 2005).

(i) The mean,  $\bar{Y}_u = \frac{1}{r} \sum_{v=1}^r Y_{uv}$  Equation (2.2)

(ii) The dispersion,  $S_u^2 = \frac{1}{r-1} \sum_{v=1}^r (Y_{uv} - \bar{Y}_u)^2$  Equation (2.3)

(iii) The sum of the dispersion =  $\sum_{u=1}^N S_{uv}^2$  Equation (2.4)

(iv) The maximum dispersion =  $S_{u \max}^2$  Equation (2.5)

### Model development

The development of the model involves two key elements – the G-criteria and statistical analysis.

#### The G- criteria (G-test)

The G-test (Cochran G-criteria) is used to ascertain the possibility of carrying out regression analysis. It is used to check if the output factors of the replication have maximum accuracy of the replication. The test verifies the homogeneity of dispersion of the replicated experiments. The

calculated G-value is given as:  $G_{cal} = \frac{S_{u \max}^2}{\sum_{u=1}^N S_u^2}$  Equation (2.6)

The calculated G-value is compared with the appropriate table value. The condition of homogeneity is given as:  $G_{cal} < G_{[\alpha, N(r-1)]}$  Equation (2.7)

If the above condition is satisfied then we can proceed with regression analysis (Chukwu, 2005).

$N$  = number of experimental runs;  $r$  = number of replication;  $\alpha$  = level of significance.

## 2.7 Statistical analysis and model simulation

Statistical analyses are carried out on the experimental data and based on the results; a model will be developed, tested for adequacy and validated.

### (a) Determination of dispersion and experimental error

The dispersion (mean-squared-error) is given as Equation (2.8). It estimates the average sample variance. The experimental error is given as Equation (2.9).

$$S_y^2 = \frac{1}{N} \sum_{u=1}^N S_u^2 \quad \text{Equation (2.8)}$$

$$S_y = \sqrt{S_y^2} \quad \text{Equation (2.9)}$$

### (b) Calculation of model regression coefficients

We can estimate a mean effect, four main effects, six two-factor interactions, four three-factor interactions and one four-factor interaction for the 16 replicated runs in the  $2^4$  factorial experiments. To estimate an effect or to compute the sum of squares of an effect, we must first determine the contrast associated with that effect. This can be done using the design matrix to determine the contrast associated with that effect. This can be done using the design matrix (Table 3.1). The calculation of the regression coefficients (factorial effects) can be done by multiplying the signs in the appropriate column of the table by the corresponding experimental mean ( $R_u$ ) and adding together. Once the contrasts for the effects have been determined, we can proceed to estimate the effects and compute the sums of squares for the effects.

The mean effect ( $b_o$ ) is estimated by:  $b_o = \frac{1}{N} \sum_{u=1}^N (X_o \bar{R}_u)$  Equation (2.10)

$u = 1, 2, \dots, 16$ ;  $X_o$  = coded signs in the  $X_o$  column of the design matrix.

The four main effects ( $b_i$ ) are estimated by:  $b_i = \frac{1}{N} \sum_{u=1}^N (X_i \bar{R}_u)$  Equation (2.11)

$i = 1, 2, 3, 4$ ;  $u = 1, 2, \dots, 16$ ;  $X_i$  = coded signs in the  $X_i$  columns of the design matrix.

The six two-factor interactions are estimated by:

$b_{ij} = \frac{1}{N} \sum_{u=1}^N (X_{ij} \bar{R}_u)$  Equation (2.12)

$i \neq j$ ;  $u = 1, 2, \dots, 16$ ;  $X_{ij}$  = coded signs in the  $X_{ij}$  columns of the design matrix.

The four three-factor interactions are estimated by:

$b_{ijk} = \frac{1}{N} \sum_{u=1}^N (X_{ijk} \bar{R}_u)$  Equation (2.13)

$i \neq j \neq k$ ;  $u = 1, 2, \dots, 16$ ;  $X_{ijk}$  = coded signs in the  $X_{ijk}$  columns of the design matrix.

The one four-factor interaction is estimated by:

$b_{ijkl} = \frac{1}{N} \sum_{u=1}^N (X_{ijkl} \bar{R}_u)$  Equation (2.14)

$i \neq j \neq k \neq l$ ;  $u = 1, 2, \dots, 16$ ;  $X_{ijkl}$  = coded signs in the  $X_{ijkl}$  columns of the design

matrix. In Equations {3.10} through {3.14}, the quantities in brackets represent contrasts in the treatment combinations. A contrast is the total effect of a factor.

(c) **Testing statistical significance of the regression coefficients**

To test the statistical significance of an individual regression coefficient in a regression model, we must construct confidence interval (ci) and carry out test of hypothesis (Samprit and Bertram, 1991). Confidence intervals for the regression coefficients with confidence level,  $\alpha$ , are of the general form:

$$c_i = b's \pm t_{[\alpha, N(r-1)]} S_{b's} \quad \text{Equation (2.15)}$$

$$\Rightarrow c_i = b's \pm \Delta b's \quad \text{Equation (2.16)}$$

$S_b$ 's = the estimated standard error in the regression coefficients (the b's)

$t_{[\alpha, N(r-1)]}$  = an appropriate tabulated t-criteria with  $N(r-1)$  degrees of freedom. In this study, we will be content with a level of significance of 5% (i.e.  $\alpha = 0.05$ ).

For full factorial experiments, error in each regression coefficient is the same and is

$$\text{determined by: } S_{bo} = S_{bi} = S_{bijkl} = \frac{S_y}{\sqrt{N.r}} \quad \text{Equation (2.17).}$$

$S_y$  is the experimental error.

The statistical significance of the regression coefficients are tested by:

$$t_o = \frac{b_o}{S_{bo}}; t_i = \frac{b_i}{S_{bi}}; t_{ij} = \frac{b_{ij}}{S_{bij}}; \dots, t_{ijkl} = \frac{b_{ijkl}}{S_{bijkl}} \quad \text{Equation (2.18).}$$

To carry out the test, compare the calculated t-values with the appropriate critical table value. A regression coefficient is statistically significant if:

$$t_{cal} > t_{[\alpha, N(r-1)]} \quad \text{Equation (2.19)}$$



Table 2.1: Design Matrix for a  $2^4$  Full Factorial Experiment (FFE)

Run	$X_0$	$X_1$	$X_2$	$X_3$	$X_4$	$X_{12}$	$X_{13}$	$X_{14}$	$X_{23}$	$X_{24}$	$X_{34}$	$X_{123}$	$X_{124}$	$X_{134}$	$X_{234}$	$X_{1234}$
No.	$b_0$	$b_1$	$b_2$	$b_3$	$b_4$	$b_{12}$	$b_{13}$	$b_{14}$	$b_{23}$	$b_{24}$	$b_{34}$	$b_{123}$	$b_{124}$	$b_{134}$	$b_{234}$	$b_{1234}$
1	+	-	-	-	-	+	+	+	+	+	+	-	-	-	-	+
2	+	+	-	-	-	-	-	-	+	+	+	+	+	+	-	-
3	+	-	+	-	-	-	+	+	-	-	+	+	+	-	+	-
4	+	+	+	-	-	+	-	-	-	-	+	-	-	+	+	+
5	+	-	-	+	-	+	-	+	-	+	-	+	-	+	+	-
6	+	+	-	+	-	-	+	-	-	+	-	-	+	-	+	+
7	+	-	+	+	-	-	-	+	+	-	-	-	+	+	-	+
8	+	+	+	+	-	+	+	-	+	-	-	+	-	-	-	-
9	+	-	-	-	+	+	+	-	+	-	-	-	+	+	+	-
10	+	+	-	-	+	-	-	+	+	-	-	+	-	-	+	+
11	+	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+
12	+	+	+	-	+	+	-	+	-	+	-	-	+	-	-	-
13	+	-	-	+	+	+	-	-	-	-	+	+	+	-	-	+
14	+	+	-	+	+	-	+	+	-	-	+	-	-	+	-	-
15	+	-	+	+	+	-	-	-	+	+	+	-	-	-	+	-
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

**Decision Rule:** If:  $t_{cal} < t_{tab}$ , the coefficient is statistically insignificant and is left out of the regression model (Montgomery, 1991; Chukwu, 2005). It has to be stated at this point that insignificance of an effect does not necessarily mean that the particular factor or interaction is not important. It only implies that response is unaffected if the factor is varied over the range considered (i.e. from -1 to +1 in coded units). For example, it could be that the factor or interaction is very important but that a change over the range considered has no effect on the response. Using only the statistically significant regression coefficients, we can then define the fitted or predictive model in the form of equation (3.20):

$$R = [b_0 \pm \dots \pm \dots \pm \dots] \quad \text{Equation (2.20)}$$

The predictive model relates the response to the factors and it can be used for predicting the response at factor levels. This means that the model can be used to forecast values of R for a given set of independent variables. However, the model is valid only for values of the independent variables that fall within the intervals of values used in developing the model. Any user who applies the model to values outside the interval will be guilty of extrapolation.

The calculation of the above expression at the levels  $X_1, \dots, \dots, X_{in}$  of the independent variables provides the fitted or predicted values. The respective differences between the mean experimental observations  $\bar{R}_1, \bar{R}_2, \bar{R}_3, \dots, \bar{R}_N$  and the fitted or predicted values

$$\hat{R}_1, \hat{R}_2, \hat{R}_3, \dots, \hat{R}_N \text{ are the Residuals given by: } e_u = \bar{R}_u - \hat{R}_u \quad \text{Equation (2.21).}$$

In this way, the model can be used to generate the predicted values in the range of the observations studied (i.e. over the range of the factor levels chosen). The residuals are useful in examining the adequacy of the least squares fit. The residuals are the deviations of the measured values ( $\bar{R}_u$ ) from their predicted values ( $\hat{R}_u$ ).

**(d) Determination of model adequacy**

The adequacy of a regression model can be determined by carrying out a test of hypothesis on the individual regression coefficients. Such a test would be useful in confirming the magnitude of the estimated effects. For instance, the model might be more effective if one or more of the variables already in the model is/are deleted.

To confirm the magnitude or significance of the effects, we have to carry out an analysis of variance (ANOVA). The ANOVA involves: determining the sum of squares for each component in the model, the number of degrees of freedom associated with each sum of squares, the expected mean squares and then carrying out appropriate test statistics. The sums of squares for the effects are easily computed from the contrasts used in estimating the effects. In the  $2^k$  factorial design with replicates, the regression sum of square for any effect is calculated using equation (3.22). It has a single degree of freedom.

$$SS_R = \frac{r}{N} (\text{Contrast})^2 \quad \text{Equation (2.22).}$$

For the main effects:  $SS_{bi} = \frac{r}{N} \sum_{u=1}^N (X_i \bar{R}_u)^2$  Equation (2.23).

For the two-factor interactions:  $SS_{bij} = \frac{r}{N} \sum_{u=1}^N (X_{ij} \bar{R}_u)^2$  Equation (2.24).

For the three-factor interactions:  $SS_{bijk} = \frac{r}{N} \sum_{u=1}^N (X_{ijk} \bar{R}_u)^2$  Equation (2.25).

For the four-factor interactions:  $SS_{ijkl} = \frac{r}{N} \sum_{u=1}^N \left( X_{ijkl} \bar{R}_u \right)^2$  Equation (2.26).

If all possible interactions between k factors exist, then there are  ${}^k C_2$  two-factor interactions,  ${}^k C_3$  three-factor interactions... 1 k-factor interactions.

The total sum of squares  $SS_T$  is given as:

$$SS_T = \sum_{u=1}^{N,r} R_{uv}^2 - \frac{\left( \sum_{u=1}^{N,r} R_{uv} \right)^2}{N,r}$$
 Equation(2.27).

The error sum of squares ( $SS_E$ ) is given as:  $SS_E = SS_T - \sum SS_R$  Equation (2.28)

Equation (3.28) can also be written as:

$$SS_E = SS_T - SS_{bi} + SS_{bj} + \dots + SS_{bijkl}$$
 Equation (2.29)

In multiple linear regressions, testing the significance or contribution of individual coefficients is accomplished by testing the null hypothesis:

$$H_o : b_i = 0$$
 Equation (2.30)

The appropriate test statistic is the F-test given as:

$$F_{cal} = \frac{MS_R}{MS_E} = \frac{SS_R}{df_R}$$
 Equation (2.31)

$$\text{If: } F_{cal} > F_{[\alpha, dfR, N(r-1)]}$$
 Equation (2.32);

the null hypothesis is rejected. We then conclude that the coefficient contributes significantly to the regression (Chukwu, 2005). The ANOVA is usually summarized as shown in Table 2.2.

The adequacy of a regression model can further be checked by calculating the Coefficient of Determination (COD) represented by  $R^2$  ( $0 < R^2 \leq 1$ ). This is given by Equation (3.33).  $R^2$  refers to the proportion of variability in the data explained or accounted for by the regression model. The nearer  $R^2$  is to unity the better the goodness of fit.

$$R^2 = \frac{\sum SS_R}{\sum SS_T} \quad \text{Equation (2.33)}$$

**(e) Validation of models**

It is important to reconcile the values predicted by a model and the actual observed values. Validation is carried out on a model, preferably against a set of data from a period with changed conditions. If significant discrepancies exist, the general model formulation is reviewed and the validation cycle repeated (UNU, 1999). In this study validation was carried out using a set of data collected for Qua Iboe light crude. The aim of doing this is to ascertain the possibility of generalizing the model to other oil wells in Nigeria.

Table 2.2: ANOVA for a Replicated  $2^4$  Factorial Experiment

Source of variation	Effect	SS	df	MS	F-ratio
Main Effects					
$b_1$		$SS_{b_1}$	1		
$b_2$		$SS_{b_2}$	1		
$b_3$		$SS_{b_3}$	1		
$b_4$		$SS_{b_4}$	1		
Two-factor interaction					
$b_{12}$		$SS_{b_{12}}$	1		
$b_{13}$		$SS_{b_{13}}$	1		
$b_{14}$		$SS_{b_{14}}$	1		
$b_{23}$		$SS_{b_{23}}$	1		
$b_{24}$		$SS_{b_{24}}$	1		
$b_{34}$		$SS_{b_{34}}$	1		
Three-factor interaction					
$b_{123}$		$SS_{b_{123}}$	1		
$b_{124}$		$SS_{b_{124}}$	1		
$b_{134}$		$SS_{b_{134}}$	1		
$b_{234}$		$SS_{b_{234}}$	1		
Four-factor interaction					
$b_{1234}$		$SS_{b_{1234}}$	1		
Error		$SS_E$	$N(r-1)$		
Total		$SS_{b_1}$	$(N-1).r$		

SS = Sum of squares; df = degrees of freedom; MS = Mean squares

F-ratios are usually calculated and obtainable on the table. Both values are compared for accurate conclusions in regression modeling.



## CHAPTER THREE

### 3.0 METHODOLOGY

The experimental procedure was divided into four stages which included collection of various crude oil samples; detailed characterization of the samples; development of models to relate the properties of the oil samples with their spreading rates on the laminar water; and finally the validation of the model using the data collected from other crude oil samples.

#### 3.1 Collection of Various Oil Samples:

The oil samples were collected from various oil fields in Nigeria, namely Kolo creek Bonny light, Nembe well Bonny light and Idu Eekpeye in Bayelsa state; Obagi well 35, Obagi well 40, and Umuchem in Rivers state; Qua iboe light Enang and Qua iboe light Upenek in Akwa Ibom state, Ogara and Forcados in Delta state Owaza well 22 and Owaza well 23 in Abia state, Oguta and Egbema Opakate in Imo state.

#### 3.2 Detailed Characterization of the Samples

The crude oils were characterized by the determination of the various properties they possess. The standard test methods provided by the American Society of Testing and Materials (ASTM) were used for the determination of the crude oil properties. The properties examined include: specific gravity/<sup>o</sup>API, viscosity, pour point, total acid number (TAN), carbon residue, salt content, basic sediment and water (BSW), Reid vapour pressure (RVP), ash content, sulphur content, metal content (nickel, vanadium,) copper in petroleum, lead in petroleum, and the hydrocarbon type.



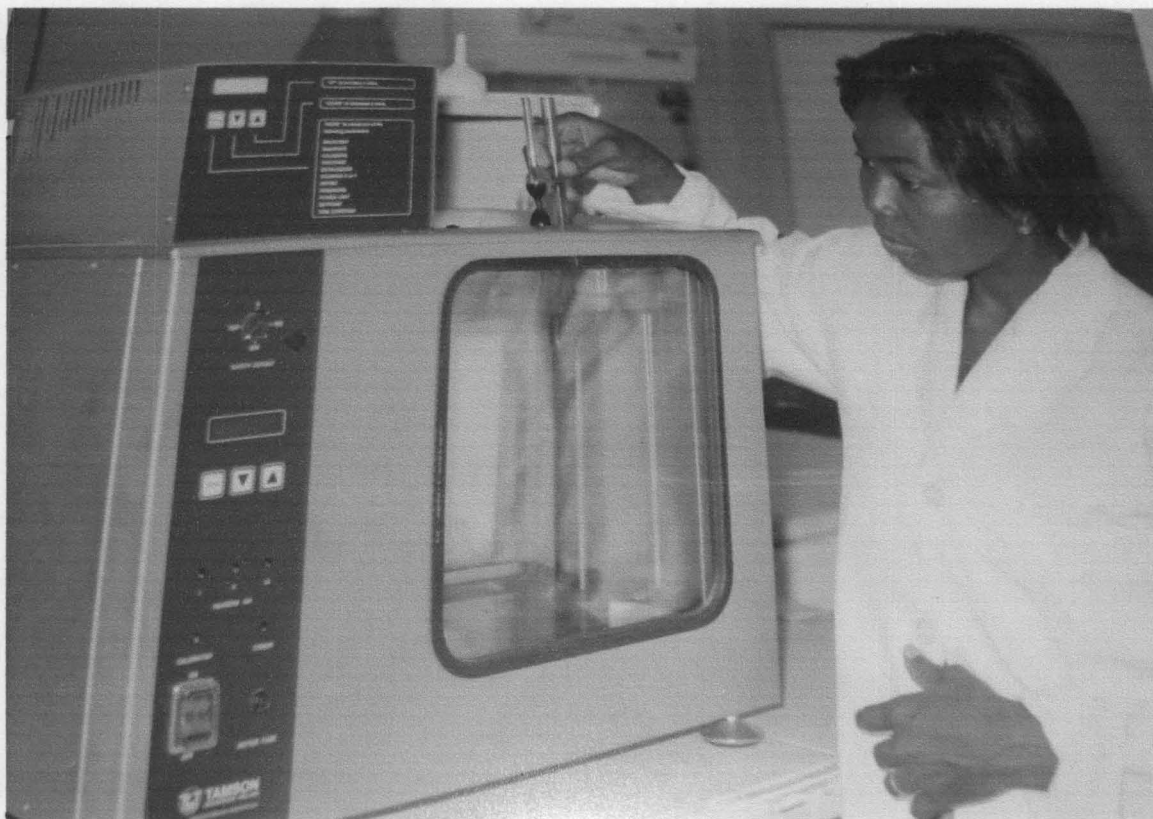
### 3.2.1 Standard test method for kinematic viscosity of crude oil (D445 – 01)

**Table 3.1: List of Equipment Used to Determine the Kinematic Viscosity**

Equipment	Description
Viscometer	calibrated glass capillary
Thermostatic controlled bath	silicon oil bath
Thermometer	range from 0-100°C
Stop watch	timing device

**Table 3.2: Materials and Chemicals Used for the Determination of Kinematic Viscosity**

Materials and chemicals	Description
Xylene and ethanol	industrial standard
Chromic acid	sample solvent
Xylene	sample solvent
Acetone	drying agent



**Figure 3.1 Silicon Bath Viscometer**

### **Procedure for the Determination of the Viscosity of Crude Oil**

The viscometer bath's control was adjusted and maintained at the required test temperature within the limits of 85°F, the thermometers were held in an upright position under the same conditions of immersion as when calibrated. In order to obtain the most reliable temperature measurement, thermometers with valid calibration certificates were used; The thermometers were viewed with a lens assembly giving approximately five times magnification to eliminate parallax errors.

A clean and dry calibrated viscometer having a range covering the estimated kinematic viscosity was selected (i.e. a wide capillary for a very viscous liquid and a narrow capillary for a more fluid liquid). Each flow time was not more than 200sec or the longer time noted. The oil sample was mixed thoroughly and charged by sucking into the viscometer to a level above the first timing mark with the sample flowing freely.

The time required was measured in second for the meniscus to pass from the first to the second timing mark. The operation was repeated until, the average of both reading were taken to obtain the dynamic viscosity. Whenever the flow time was found to be less than the specified minimum, a viscometer with a capillary of smaller diameter was selected.

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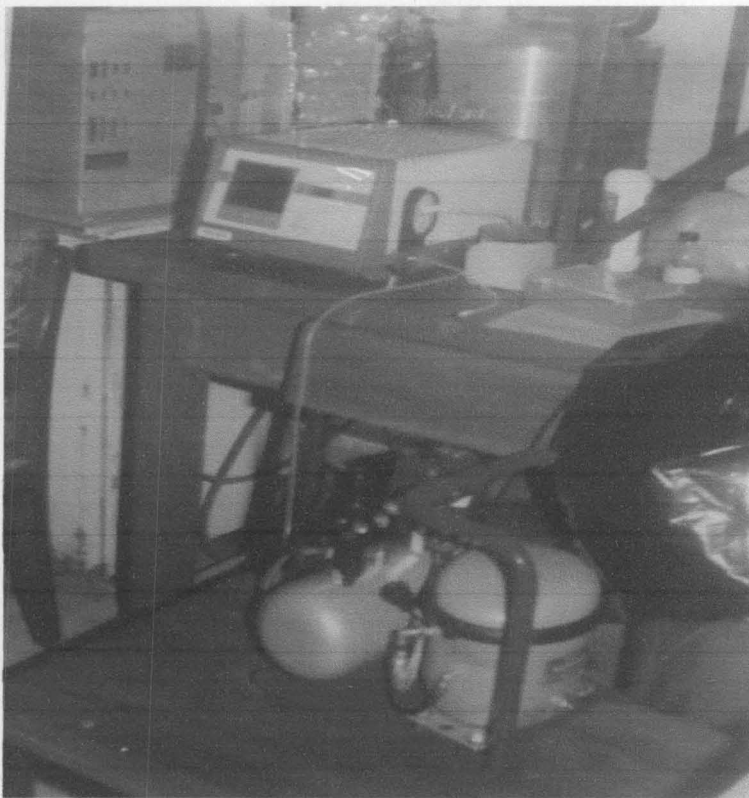
**3.2.2 Standard test method for density, relative density (or specific gravity) or API gravity of crude oil (petroleum). (D1298-99)**

**Table 3.3: List of Equipment Used for the Determination of Specific Gravity**

<b>Equipment</b>	<b>Description</b>
Density meter	density/API meter
Hydrometers	graduated in $^{\circ}$ API
Thermometer	graduated in $^{\circ}$ C
Hydrometer cylinder	25mm inside diameter
Clinical syringe	15ml

**Table 3.4: Materials and Chemicals Used for the Determination of Specific Gravity**

<b>Materials and chemicals</b>	<b>Description</b>
Hot air	heater fitted to the meter
Ultra pure water	industrial grade
Xylene and ethanol	cleaning agent



**Figure 3.2. Density Meter**

**Procedure for the determination of density, relative density (or specific gravity) or API gravity of crude oil (petroleum)**

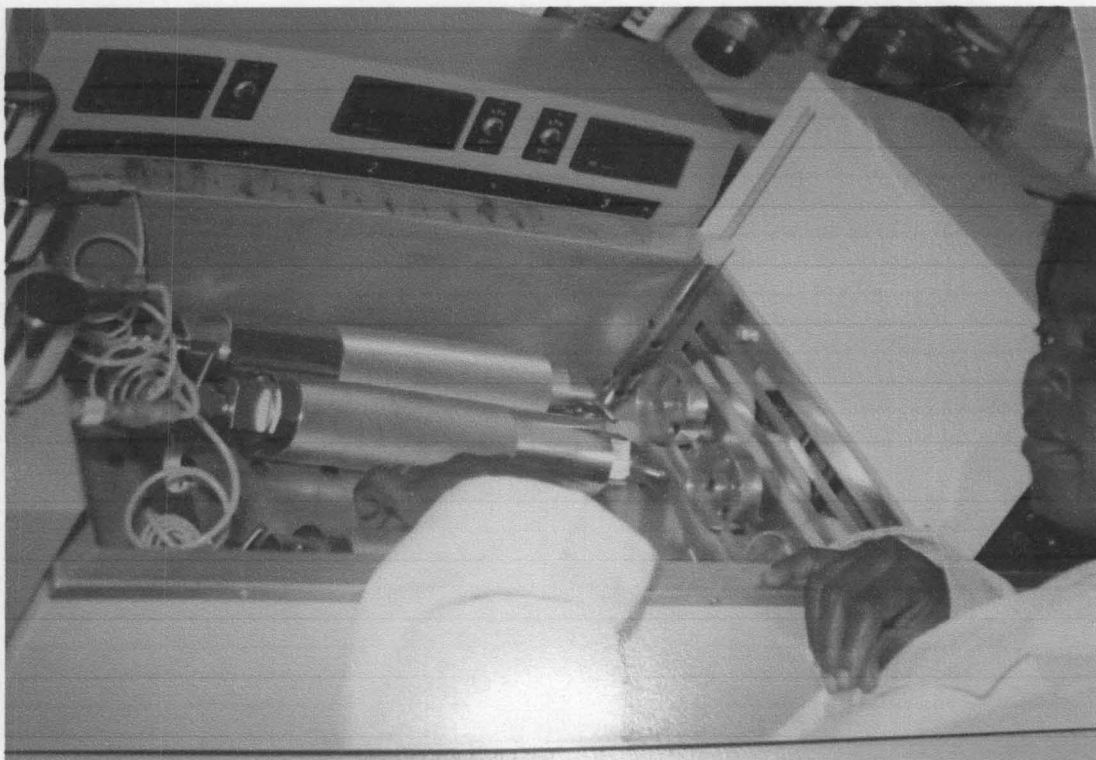
The Density meter was connected to the main and was switched on to initialize. A pump carrying hot air from the heater was attached to the density meter. The temperature of the density meter was set lower than room temperature. Condensation was observed and the pump was switched on to dry the water droplet. 15 ml clinical syringe was used to introduce the crude oil into the 1.5ml sample cell of the density meter. The capacity drain - pipe drained out any excess crude oil in the sample cell. Ultra pure water was used to set the deviation of the expected value from the observed value. The value of the specific gravity and °API was read off from the meter and printed out. The sample cell was washed with xylene and ethanol and dried. The same sample cell was used for another run of the experiment.



### 3.2.3: Standard test method for Reid vapour pressure of petroleum (Reid Method) D22-99

**Table 3.5: List of Equipment used for the Determination of Vapour Pressure**

<b>Equipment</b>	<b>Description</b>
Reid vapour pressure apparatus	measures vapour pressure automatically



**Figure 3.3 Reid Vapour Pressure Apparatus**

#### **Procedure for the determination of Reid vapour pressure of petroleum.**

The sample was removed from the cooling bath, uncapped and inserted into the chilled transfer tube. The liquid chamber was removed from the cooling bath and the chamber was placed in an inverted position over the top of the transfer tube. The entire system was rapidly inverted so that the liquid chamber is upright with the end of the transfer tube

approximately 6mm (0.25in) from the bottom of the liquid chamber. The liquid chamber was filled to overflowing.

Immediately, the vapour chamber was removed from the water bath. The spiral tubing was disconnected, at the filled liquid chamber, it was coupled to the vapour chamber as quickly as possible without spillage.

While holding the apparatus vertically, immediately the spiral tubing was reconnected. The chambers were tilted between 20-30<sup>0</sup> downward for 44.5sec to allow the sample to flow into the vapour chamber without getting into the tube extending into the vapour chamber from the gage, or pressure transducer. The assembled apparatus was placed into the water bath maintained at 37.8<sup>0</sup>C in such a way that the bottom of the liquid chamber engages the drive coupling and the other end of the apparatus rested on the support bearing. The switch was turned on and the rotation of the assembled liquid vapour chamber began. The apparatus was observed for leakage through out the test.

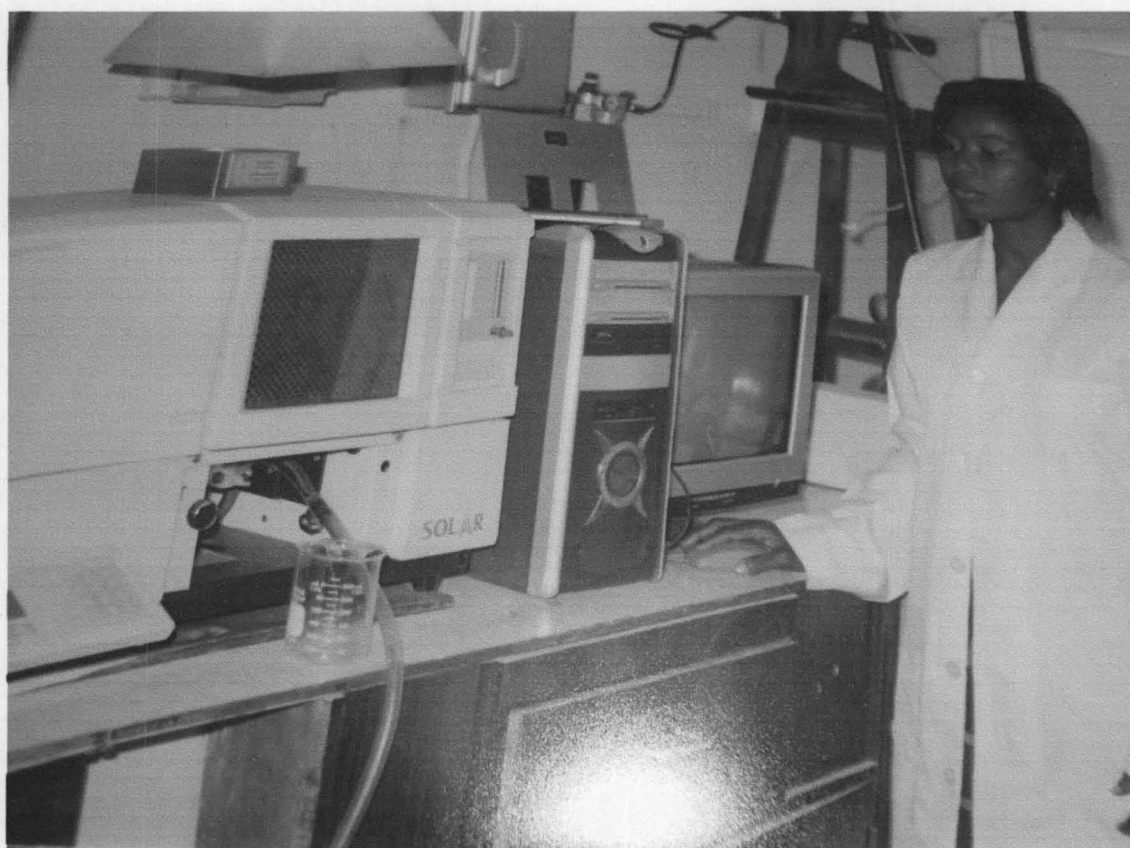
After the assembled apparatus has been in the bath for 5min the pressure-gauge was tapped lightly and the reading was observed. The tapping and reading were repeated at intervals of not less than 2min until two consecutive readings are the same.



**3.2.4: Standard test method for copper, nickel and vanadium in crude oil and residual oil fuels using atomic absorption spectrometry.**

**Table 3.6: List of Equipment Used for the Determination of Copper, Nickel and Vanadium,**

<b>Equipment</b>	<b>Description</b>
Spectrometer	atomic absorption spectrometer
Containers	specimen solution containers glass or plastic vials bottles



**Figure 3.4 Atomic Absorption Spectrometer**

**Procedure for the determination of copper, nickel and vanadium**

A two point calibration was fixed using a blank and working standard at the beginning of the analysis of each batch of specimen.

The check standard was used to ascertain if the calibration for each analyte was accurate when the result obtained on the check standard is not within  $\pm 5\%$  of the expected concentration for each analyte, corrective actions were taken and the calibration was repeated until a satisfactory result was obtained. The crude oil was fed into the specimen solution containers, the containers were fixed into the atomic absorption spectrometer and the value of nickel and vanadium content were read off.

### 3.2.5: Standard test method for basic sediments and water in crude oil by the centrifuge method (D4007-81)

**Table 3.7: List of Equipment Used for the Determination of Basic Sediments and Water**

Equipment	Description
Centrifuge	consists of centrifuge tubes and bath

**Table 3.8: Materials and Chemicals Used for the Determination of Basic Sediments and Water**

Materials and chemicals	Description
Mixed xylene, o-xylene, tetralin and mixed paraffinic blank	Dilution solvent prepared by diluting mineral oil with dilution solvent

#### **Procedure for the determination of basic sediment and water in crude oil by the centrifuge method**

Each of the two centrifuge tubes was filled up to 5.2-50mm mark with sample directly from the sample container. 50ml of toluene which has been water saturated at  $60^{\circ}\text{C}$  was added with a pipette; the oil and solvent were uniformly mixed for the viscous crude oil sample, the solvent was added to the centrifuge tube to facilitate mixing. The crude oil was not allowed to exceed the 100ml mark. The stopper was loosened slightly and the

tube was immersed, at the 100ml mark, for 15ml in the bath maintained at  $60 \pm 3^{\circ}\text{C}$ . The stopper was secured and the tubes were inverted 10times to ensure uniform mixing of the oil and solvent.

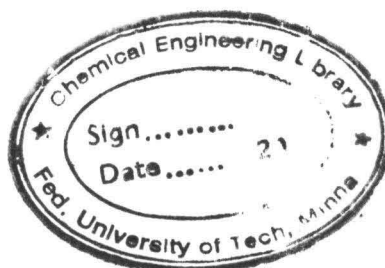
The tubes were placed in the turning on cups on the opposite sides of the centrifuge to establish a balanced condition, the corks were tightened and spins for 10minutes at a minimum relative centrifugal force of 600rpm

The combined volume of water and sediment was read and recorded (immediately after the centrifuge comes to rest following the spin.) at the bottom of each tube to the nearest 0.05ml from 0.1 to 1ml graduations. This operation was repeated until the combined volume of water and sediments remains constant for two consecutive readings. The temperature of the sample during the entire centrifuging procedure were maintained at  $60 \pm 3^{\circ}\text{C}$

### 3.2.6: Standard test method for salts in crude oil (electrometric method) (D3230-99)

**Table 3.9: List of Equipment Used for the Determination of Salts**

<b>Equipment</b>	<b>Description</b>
Control unit	capable of producing and displaying several voltage levels for applying stress to a set of electrodes
Test beaker	containing a test solution
Salt testing apparatus	apparatus capable of measuring and displaying the current (mA) conducted through the test solution between the electrodes at each voltage level.
Pipette	10ml (total delivery).
Cylinders	100ml, stopped



**Table 3.10: Materials and Chemicals Used for the Determination of Salts**

<b>Materials and chemicals</b>	<b>Description</b>
Water	pure water
Mixed Alcohol Solvent Chloride	63 volumes of 1-butanol and 37 volumes of absolute methyl alcohol (anhydrous) (CaCl <sub>2</sub> ), MgCl <sub>2</sub> and NaCl
Oil refined neutral	any refined chloride-free oil of approx 20mm <sup>2</sup> /sec (cst).
Salts	chlorides



**Figure 3.5 Salt Analyzer**

**Procedure for the determination of salts in crude oil (electrometric method)**

15ml of xylene was poured into a 100ml graduated, glass-stopped cylinder, 10ml of the crude oil sample was pipetted into cylinder then the mixture was made up to 50ml with

xylene the cylinder was vigorously shaken for approximately 60sec. It was diluted to 100ml with mixed alcohol solvent and mixed vigorously for approximately 30sec. The solution was allowed to stand for 5min and transferred into the dry test beaker.

The electrodes were placed into the solution in the beaker, ensuring that the upper edge of the electrode plates were below the surface of the solution. The indicated electrode voltage was adjusted to a series of values at 25, 50, 125, 200 and 250V. At each voltage, the current and voltage displayed were recorded. The salt content was determined by measuring the conductivity of the solution of crude oil in the polar solvent (that is the xylene and alcohol) which was subjected to the alternating electrical current. Salt content was obtained by reading of the resulting conductance on a calibration curve of conductivity versus salt content of known mixtures.

### 3.2.7: Standard test method for Conradson carbon residue and ash content of petroleum (D189-01)

**Table 3.11: List of Equipment Used for the Determination of Carbon Residue**

<b>Equipment</b>	<b>Description</b>
Iron crucible	Skid more iron crucible, flanged and ringed 65-82ml capacity, 53-57mm inside and 60-67mm outside diameter of flange, 37-39mm in height.
Iron crucible	Spun sheet iron crucibles with cover.
Wire Support	Triangle of bare Nichrome wire.
Hood	Circular sheet iron hood from 120-130mm in diameter.
Insulator	Asbestos block, refractory ring or hollow sheet-metal boot.
Burner	meeker type, having an orifice approximately 24mm in diameter





**Figure 3.6 Apparatus for Conradson Carbon Residue.**

**Procedure for the determination of Conradson carbon residue of petroleum**

The crude oil sample was mixed thoroughly. The temperature of the sample was raised to 50°C by heating for 30 minutes to reduce its viscosity. The test portion was filtered through a 100-mesh screen immediately a 10g sample of the oil was weighed. It was free of moisture and other suspended matter into a tarred porcelain or silica crucible containing glass beads about 2.5mm diameter. The bare nichrome wire triangle was placed on a suitable stand and on it the insulator. The whole set - up was covered with the sheet, iron hood, in order to distribute the heat uniformly during the heating process.

The sample was subjected to heating with a high, strong flame from the meker-type gas burner, so that the pre-ignition period will be 10min. The burner was moved immediate and 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 heat was removed temporarily, and

the screwing down the pinch-cock on the gas tubing was adjusted before replacing so that the ignited vapour burn uniformly with the flame above the chimney not above the wire bridge. When the vapour cease to burn and no further blue smoke was observed, the burner was readjusted. The burner was removed and the apparatus was allowed to cool until no smoke appears, the crucible was removed with heated tongs, it was placed in the desiccators cooled and weighed. The percentage of carbon residue on the original sample was calculated. The ash content is obtained by a complete combustion of the carbon residue using the ashing apparatus.

### **3.2.8: Standard test method for sulfur in petroleum by energy dispersive x-ray fluorescence spectrometry (D 4294)**

**Table 3.12: Materials and Chemicals Used for the Determination of Sulfur**

<b>Equipment</b>	<b>Description</b>
Di-n-butyl sulfide (DBS)	a high purity standard (DBS) with a certified analysis for sulphur content.
Mineral oil white (MOW)	reagent grade or less than 2mg/kg S
X-ray transparent film	any film that resist attack by the sample is free of sulphur. Polypropylene was used here
Sample cells	resistance to sample attack





**Figure 3.7 Apparatus for the Determination of Sulphur**

**Procedure for the determination of sulfur in petroleum**

The sample cell was filled with the sample to be measured, before filling the cell, if the sample was viscous, the temperature was raised by heating to ease pouring into the sample cell. It was ensured that no air bubbles were present between the cell window and the liquid sample. Each sample was measured for the recommended counting times for the specific concentration ranges. With minimal delay the measurement was repeated using a freshly prepared cell, and a fresh portion of the sample. An average value was used. Or the concentration of sulphur in the sample was automatically calculated from the calibration curve when the sample placed in the beam emitted from an x-ray source. The resultant excited characteristic x radiation was measured and the accumulated amounts

were compared with count from previously prepared calibration samples to obtain the sulphur concentration in mass %.

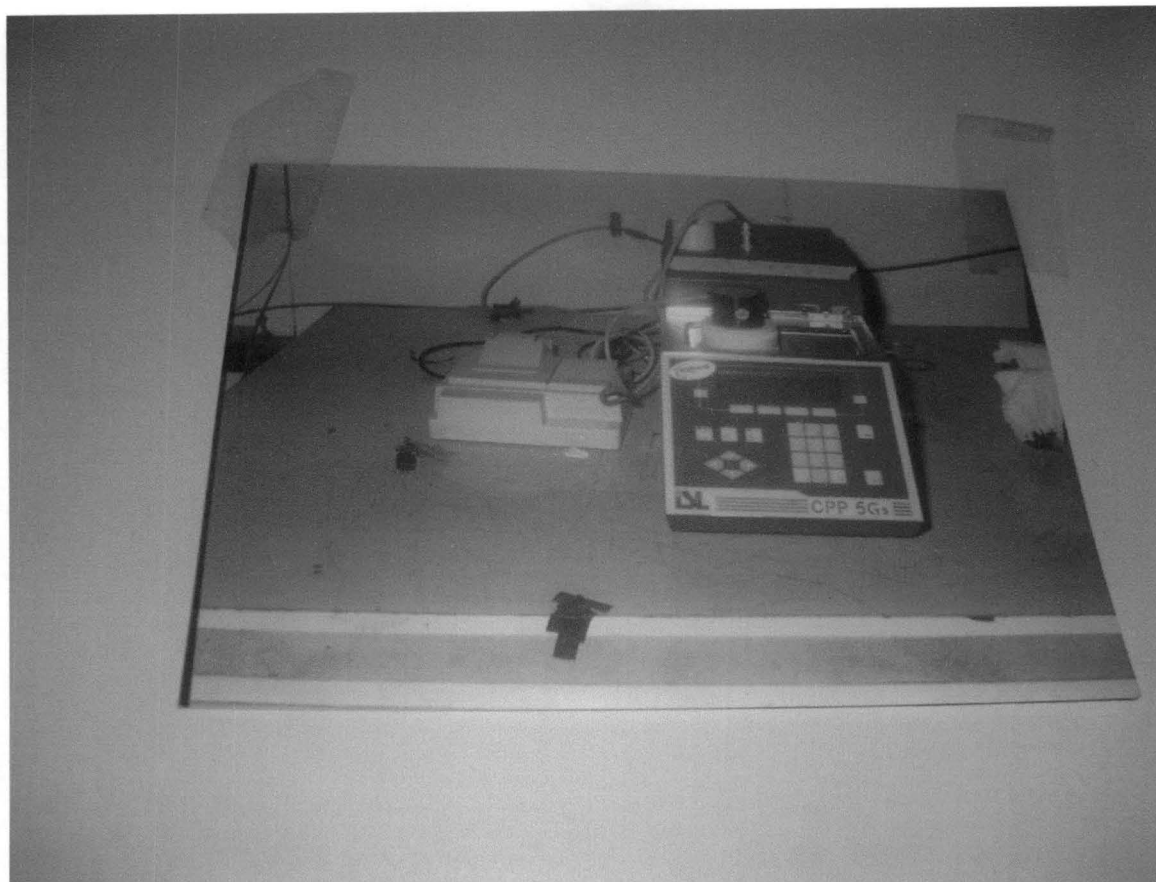
### 3.2.9: Standard test methods for the determination of pour point of crude oils.

**Table 3.13: List of Equipment Used for the Determination of pour point**

<b>Equipment</b>	<b>Description</b>
Pour point test apparatus assembly	automatic and electrically controlled
Test jar cylindrical	cylinder of clear glass, flat bottomed
Thermometers	capable of the detecting ice point temperature and used only within $\pm 1^{\circ}\text{C}$
Cork	to fit the test jar, centered bared for the test thermometer.
Jacket	watertight, cylindrical, metal flat bottomed, $115 \pm 3\text{mm}$ depth, with inside diameter of $44.2 - 45.8\text{mm}$
Disk, cork or belt	$6\text{mm}$ thick to fit loosely inside the jacket.
Cooling bath	for the required temperatures
Water bath	cavity for water
Pressure vessel	capable of withstanding a test pressure of $700\text{Kpa}$
Timing device	time in seconds and minutes

**Table 3.14: Materials and chemicals used for the experiment**

<b>Equipment</b>	<b>Description</b>
Acetone, alcohol, ethanol, methanol, Petroleum naphtha, toluene, Solid carbon-dioxide.	industrial grade



**Figure 3.8 Pour Point Apparatus**

**Procedure for the determination of pour point of crude oils.**

Since the pour point of crude oil is very sensitive to trace amount of high melting waxes, meticulous care was taken to ensure such waxes, if present were either completely melted or if volatility constraints, heating was prevented to complete melting, this was achieved by homogeneously suspending the wax in the sample. The walls of the original container were inspected to ensure that no high melting point material is left sticking to the wall.

The test sample was poured into the test jar to the level mark if it was necessary the test sample was reheated to a temperature of 20°C above the expected pour point.

The test jar was closed immediately with the cork carrying high cloud and pour thermometer.

The test jar with the specimen was maintained at room temperature between (18-24°C for at least 30min.)

The test jar was kept inside the pour point tester apparatus and the switch on; the temperature of the specimen was read off when the apparatus stops turning.

### **3.2.10: Standard test method for total acid number of petroleum by potentiometric titration method.**

**Table 3.15: Materials and Chemicals Used for the Determination of Total Acid Number**

<b>Materials and Chemicals</b>	<b>Description</b>
Hydrochloric acid, propan 2-ol, anhydrous,	industrial grade
Trimethyle pyridine , m-Nitrophenol,	
Potassium chloriade electrolyte, toluene.	

#### **Procedure for the determination total acid number of petroleum by potentiometric titration method.**

125 ml of crude oil was introduced into a 250ml beaker the beaker was placed on the titration stand and adjusted so that the electrode are about half immersed. The stirrer was started and the stirring occurs through out the experiment

The burette was filled with 0.1mol/ml alcoholic KOH solution and the burette was placed in a position on the titration assembly. It was ensured that the tip was immersed about 25mm in the liquid titration vessel.

A suitable small portion of 0.1mol/ml alcoholic KOH solution was added and a constant potential was established. The burette and meter reading was recorded,

At the start, of the titration, 0.1ml of the 0.1mol/L KOH solution was used.

The crude oil was titrated until the potential changes less than 5mV/0.1mL of KOH and the cell potential indicates that the solution was more basic than the freshly prepared nonaqueous basic buffer.

### 3.3 Development of Models of Spreading Rate of Some Nigerian Oils on Stagnant Water.

The model was developed by a stepwise increment in the properties of the water (temperature).this property interacted with the properties of the crude oil samples at every specified temperature and in turn the resultant effect is the observed value R or the changing magnitude of the spreading rate of the crude oil on water. The detailed procedure followed was for the determination of the spreading rate of crude oils on water. The experimental set up was fixed at a specified temperature for each complete trial. The temperature values specified for each complete trials runs from 2.5°C to 65°C at an interval of 2.5°C.

The sea water was sourced from Nun river in The pH of the water was 8, and the salt concentration of the sea water was 1.003g/cm<sup>3</sup>

#### 3.3.1: Determination of the spreading rate of crude oils on water

**Table 3.16: List of Equipment Used for the Determination of Spreading Rate**

<b>Equipment</b>	<b>Description</b>
Rectangular temperature controlled water bath	56cmx41cmx13cm
Tripod stand	50cm high
Video camera	non recordable
Viscometer	silicon oil based
Tensiometer	1
Temperature controlled silicon oil bath	1
Gravity meter	1

**Table 3.17: Materials and Chemicals Used for the Determination of Spreading Rate**

<b>Materials and chemicals</b>	<b>Description</b>
Ultra pure water	20ml
Pure water	1000ml
Silicon oil	500ml
Sea water pH 8	1000ml, 1.003g/cm <sup>3</sup>
Stop watch	1
Thermometer	1
Syringe	1
Plexiglass	1 sheet

**Procedure for the determination of the spreading rate of crude oils on water**

A rectangular container (56cm x 41cm x 13cm) was filled with 14 liters of sea water but the container was allowed to remain still until it equilibrated to ambient temperature (21° C). The syringe was filled with 50ml of crude oil. Subsequently, a plexiglass grid was placed on top of the container. A hole was drilled at the center of the plexiglass that is large enough for the passage of the nose of the syringe through which the oil was spilled on the water. With the aid of a tripod stand a video camera was mounted directly above the spill and focused on the spilled zone. The radius moved by the oil was visualized with the aid of the video camera and it was recorded for the first test group, test series and trial and the time taken for oil to reach the following distances 150 cm, 300 cm, 450 cm 600 cm and 750 cm was recorded. The oil was monitored and observed to spread until it had stopped spreading using the handset video camera. At the end of each round of the experiment, the spilled oil was cleaned using polypropylene pads and subsequently the pads were disposed in trash bag.

The same process was repeated at different temperatures, at an interval of 2.5 °C starting from 20 °C to 65 °C . For each 2.5° C increment in the temperature of water, the crude oil

sample used was maintained at the same experimental temperature and the viscosity, surface tension, and the specific gravity/<sup>o</sup>API of the crude oil were determined for each run.

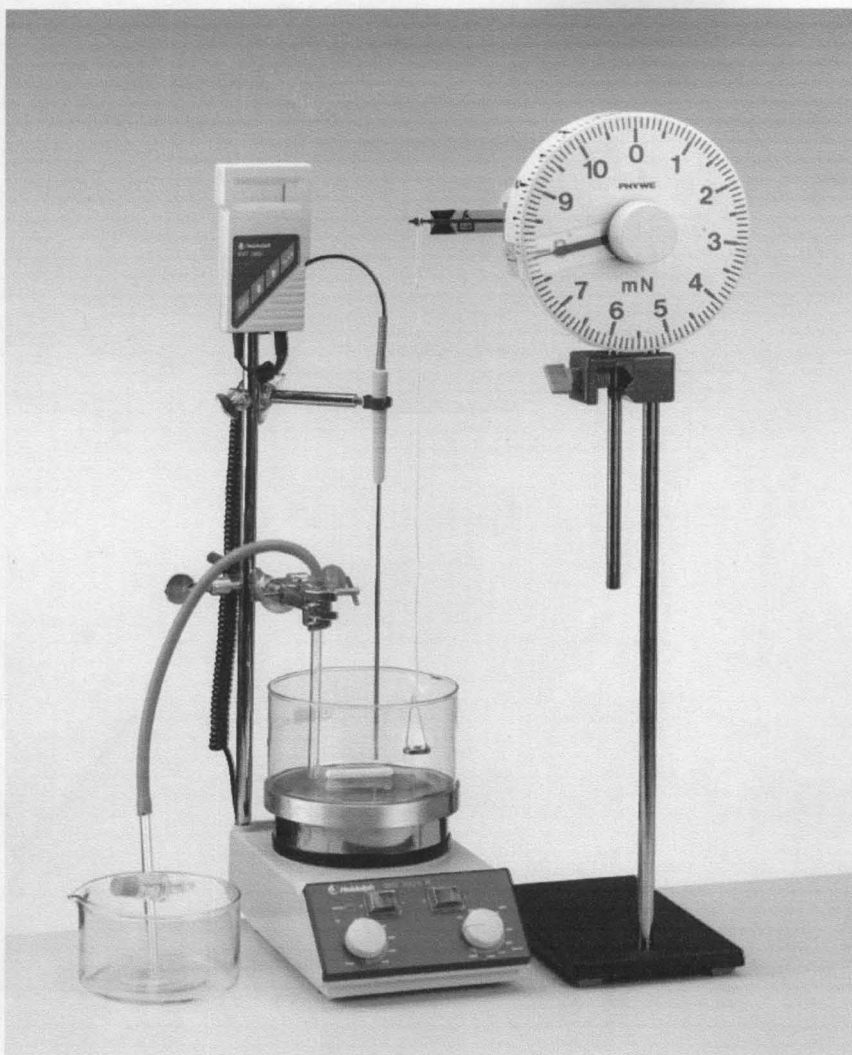
When the oil first touched the water surface the time was recorded and when the oil reached the determined point, the time was also recorded. The difference in time was determined and entered into the data table, the distances oil spreads north-south and east-west were rounded and were averaged, ratios of distance to time taken were calculated to represent the flow rate data. All the contaminated materials were disposed (polypropylene pads, syringe and plexi glass while all apparatus that have been stained were cleaned.

### 3.3.2 Standard test method for the determination of surface tension and interfacial tension of crude oil using the Ring method (DU Nouy Method) improvised

**Table 3.18: List of Equipment Used for the Determination of Surface Tension**

<b>Equipment and apparatus</b>	<b>Description</b>
Tensiometer	Du Nouy
Retort stand	500mm high
Spring balance	holder
Support rod with hole	100mm diameter
Support rod	5000mm high
Crystallizing dish	560ml





**Figure 3.9 Torsion Meter Using Ring Du Nouy**

**Procedure for the determination of surface tension and interfacial tension of crude oil.**

The measuring ring was degreased with alcohol; it was rinsed with distilled water and dried. A silk thread was used to attach the ring to the left arm of the torsion dynamometer. The indicator was set to '0' and the weight of the ring was compensated for with the rear adjusting knob so that the lever arm was in the white area between the marks. Wire frame was submerged in the crude oil and the ring was introduced into the bath. The ring was completely submerged, the torsion was switched on and the

temperature was adjusted to the required measurement temperature. When the temperature had stabilized, the torsion meter and the crude oil was allowed to come to a rest. The ring was released out of the crude oil slowly. The torsion was continuously observed while the wire frame ran out to keep the lever arm in the white area between the 2 marks.

The measurement was read off at the moment when the crude oil film tears from the ring and the last value was read off which was set on the torsion dynamometer.

The force 'F' that tears the film of the crude oil was recorded. The surface tension was calculated by dividing the force by the length of the wire used.  $\sigma = F/l$ . The experiment was repeated at an interval of 2.5°C over a temperature range of 20°C to 65°C.

### **3.3.2 The model development using a 2k factorial experimental design.**

The number of variables for crude petroleum was selected for screening based on experimental work and information available from literature. A 4-variable, 2-level factorial arrangement was used as basis. This provided a framework for designing the multi-variable (factor) experiment. The experimental design used was the design table (or calculation matrix) for the  $2^4$  full factorial experiments which is shown in Table 2.1. It indicates the mode of conducting the experiments. With four variables and two levels, a complete design leads to a total of 16 runs or observations.

### **3.3.3 Validation of the models using the data collected from other crude oil samples**

The same experimental procedure used for the determination of the spreading rate of Oguta crude oil on water was followed to obtain experimental data for the determination of spreading rate of other crude oils on water. These results were fitted into the spreading rate model developed with the Oguta crude oil.

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

The crude oil assay obtained for the 14 samples collected from various oil fields in Nigeria are presented in Tables 4.1A to 4.1B

**TABLE 4.1A: Crude Oil Analysis of 14 Samples from Various Oil Fields in Nigeria.**  
Date of Analysis: 13 – 27 th August 2007

S/N	DATE SAMPLED (MgKOH/g)	CRUDE OIL (WT%)	ASTM D1298 SPECIFIC GRAVITY	ASTM D1298 API °API	ASTM D1266 SULPHUR CONT(WT)	ASTM D445 VISCOSITY @85°F(CST)	ASTM D97 POUR	ASTM D667 TAN PT(°C)	ASTM D189-00 CAB.RES
1.	05/05/07	KOLO CREEK	0.8500	35.40 light	0.130 Sweet	5.925	-18	0.270	1.14
2.	05/05/07	NEMBE WELL	0.8756	30.10 light	0.150 Sweet	4.282	-16	0.310	1.73
3.	30/05/07	IDU EKPEYE	0.9069	24.52 medium	0.150 sweet	7.190	-23	0.270	0.05
4.	05/05/07	OBAGI WH35	0.8570	33.60 light	0.130 sweet	6.000	12	0.600	0.10
5.	20/08/07	OBAGI WH40	0.8980	26.30 medium	0.130 sweet	7.210	17	0.500	0.20
6.	06/05/07	QUA IBO UPENEK	0.8647	32.15 light	0.120 sweet	7.880	17	0.130	6.05
7.	20/08/07	QUA IBO LIGHT	0.8844	32.60 light	0.130 sweet	5.710	11	0.350	1.24

**TABLE 4.1B: Crude Oil Analysis of 14 Samples from Various Oil Fields in Nigeria.**  
Date of Analysis: 13 – 27 th August 2007

S/N	ASTM D3230 SALT CONT(lb/kb)	ASTM D96 BSW (WT)	ASTM D325 RVP (PSI)	ASTM D482-00 ASH CONT.	ASTM D863 Ni (PPM)	ASTM D863 V (PPM)	ASTM D863 Cu (PPM)	ASTM D863 Pb (PPM)	K-FACT.	AVE B.P.T.(°F)
1.	0.03	1.50	4.00	1.250	3.6	0.400	0.200	0.400	12.29 paraffinic	560
2.	0.04	3.50	1.00	2.050	3.6	0.410	0.010	0.200	10.80	435
3.	10.10	21.43	0.73	0.001	2.700	0.100	0.800	0.400	11.00 naphthenic	400
4.	0.90	28.60	1.73	0.020	3.800	0.320	0.900	0.200	10.40 naphthenic	440
5.	0.03	35.00	2.10	0.060	2.700	0.210	0.005	0.007	10.70 naphthenic	380
6.	15.00	0.74	0.97	0.210	3.660	0.500	0.700	0.900	12.00 aromatic	400
7.	12.00	0.92	0.87	0.490	4.100	0.300	0.500	0.100	11.30 naphthenic	420

**TABLE 4.1C: Crude Oil Analysis of 14 Samples from Various Oil Fields in Nigeria.**  
**Date of Analysis: 13 – 27 th August 2007**

S/N	DATE SAMPLED	CRUDE OIL	ASTM D1298 SPECIFIC GRAVITY <sup>0</sup>	ASTM D1298 API	ASTM D1266 SULPHUR CONT(WT)	ASTM D445 VISCOSITY @85 <sup>0</sup> F(CST)	ASTM D97 POUR PT( <sup>0</sup> C)	ASTM D667 TAN (MgKOH/g)	ASTM D189-00 CAB. RES (WT%)
8.	17/06/07	OGARA	0.7650	53.50 light	0.10 sweet	6.010	-1.0	0.330	1.05
9.	20/08/07	FORCADOS	0.8761	30.00 Light	0.20 sweet	6.620	-27	0.341	1.32
10.	06/08/07	OWAZA WELL22	0.8561	33.79 light	0.12 sweet	5.430	12	0.180	0.23
11.	20/08/07	OWAZA WELL23	0.8360	37.76 light	0.200 sweet	6.872	-6	0.320	0.46
12.	20/08/07	UMUCHEM	0.8490	36.00 light	0.100 sweet	6.940	-10	0.490	0.51
13.	20/08/07	OGUTA	0.8320	38.25 light	0.200 sweet	4.400	-16	0.420	1.20
14.	05/05/07	EGBEMA OPAKETE	0.9812	12.71 heavy	0.500 sour	88.300	50	0.420	0.60

**TABLE 4.1D: Crude Oil Analysis of 14 Samples from Various Oil Fields in Nigeria.**  
**Date of Analysis: 13 – 27 th August 2007**

S/N	ASTM D3230 SALT CONT(lb/Kb)	ASTM D96 BSW (WT)	ASTM D325 RVP (PSI)	ASTM D482-00 ASH CONT.	ASTM D863 Ni (PPM)	ASTM D863 V (PPM)	ASTM D863 Cu (PPM)	ASTM D863 Pb (PPM)	K-FACT.	AVE B PT.
8.	3.60	2.34	1.31	0.004	2.005	0.400	0.002	0.007	13.50 paraffinic	660
9.	3.20	10.20	0.81	0.950	3.900	1.000	0.640	0.300	10.75	380
10.	5.10	12.48	0.59	0.003	2.800	0.900	0.400	0.900	aromatic 11.50	450
11.	4.00	20.90	4.00	1.000	2.700	0.800	0.500	0.500	naphthenic 11.50	380
12.	2.00	12.50	0.98	4.200	5.200	1.400	0.400	0.050	naphthenic 11.41	450
13.	1.00	30.00	0.80	0.800	3.050	0.900	1.050	0.800	naphthenic 11.31	422
14..	3.00	2.80	0.43	0.030	2.700	0.900	1.050	0.600	naphthenic 8.83 aromatic	190

#### 4.1 Effects of Physicochemical Properties of the Crude Oils.

From Table 4.1A to 4.1D, it is obvious that crude oils possess similar physicochemical properties. They were mainly naphthenic based with characterization factor ranging from 10.4 to 13.5, the oils were all but one sweet oils with sulphur content of less than 0.3% and the oils were light having API gravity of more than 24.5. They contain very low metal content averaging 0.4wppm for vanadium and 3.0wppm for nickel. They possess low total acid number (TAN) of about 0.4mgKOH/g; their pour points averaged 15.5°C and the salt content were within the same range of 2-14lb/1000b. These oils properties are within the same range as with those obtainable from the refineries' crude oil assay. It is also obvious that though they possess similar properties each crude oil possesses its own unique properties; this agrees with the crude oil literature in Google books. However the crude oil from Egbema Opakete appears to be an exceptional crude oil, it was found to be sour, aromatic (possessing a very high sulfur content and very high specific gravity). The awkward property of this oil is probably because it was sourced from a new well and a new location and so the oil is probably not yet matured.

The main aim of analysing the properties of these Nigerian crude oils is to evaluate the potential properties responsible for spreading rate of crude oil on water. The other aim is to provide useful information to our refiners on the similarities of our crude oil so that they can utilize petroleum hydrocarbons and refining routes efficiently, (as well as characterize the petroleum-hydrocarbon if there be any differences for the utilizers to manage). Table 4.1A to 4.1D shows that the metal content in crude oil were mainly vanadium and nickel, because these crude oil contains these metals, the metals must be



removed firstly if high carbon residue are to be avoided. Since they are responsible for the carbon or ash content in the crude oil. (This metal content therefore is responsible for the carbon content obtained in the crude oil). A complete combustion of the carbon residue can be estimated as ash content by complete burning of the coke after carbon residue determination thus the same experimental procedure were used for the determination of both carbon content and ash content. From Google books literature, nickel and vanadium are said to be the principal metals in crude oil, they are said to be gotten into the crude oil by nature during formation or during storage and handling. Nickel and vanadium are responsible for the physical blockage of the pore and the destruction of active sites of catalyst used in the catalytic processing of crude oil.

The salt, basic sediment and water values obtained indicate the concentration of aqueous contamination in crude oil. They are taken up by the crude oil during formation, storage and handling. Water content below 0.5% and salt content of 20lb/1000barrel are satisfactory if the oil is to be refined. The salt content in these crude oils are therefore satisfactory. Basic sediment and water up to 0.5% are satisfactory too, these salts and basic sediment and water are also contaminants in the crude oil.

Also acid content due to the presence of inorganic constituent is not expected to be present in crude oils but organic acidity was found in these crude oils, it is composed of naphthenic acid and hydrosulfides (thiols, mercaptans, R-SH) since they were mainly naphthenic based oils. Values more than 0.5mgKOH/g are considered to be high and if the values are high the crude oil is said to be unstable. The normal and acceptable values



are between 0.1 -0.5mgKOH/g; these crude oil samples fall within is range and so they are satisfactory for processing.

The higher the pour point the more paraffinic the oil and vice versa. The pour point values of these crude oils are satisfactory. Crude oils with high pour point are said to be waxy and they enhance sludge formation during handling and storage.

The higher the API degree, the lighter the crude oil. Broad classifications of crude according to API degree vary considerably with the traditions of each market, and therefore differ from region to region and even between countries. However, Nigerian crude oils, such as those examined in this research, with 33<sup>0</sup> to 55<sup>0</sup> API are said to be very light as general broad classification states that; crude oils with grades above 30<sup>0</sup>API are generally considered light, those crude in the 22<sup>0</sup> – 30<sup>0</sup> API range are classified as medium, while those below 22<sup>0</sup> are referred to as heavy crude. Oils with low densities, and hence low specific gravities were observed to have high API gravities. The price of a crude oil is usually based on its API gravity, these Nigerian crude oils were found to be oils with high <sup>0</sup>API gravity. Therefore these oils will command higher prices. This is because they are cheaper to process and they contain valuable cuts.

The spread of petroleum pollution depends on the quantity and quality of hydrocarbon mixture and on the properties of the affected environment. At very low temperature of the environment on which the oil spill, petroleum hydrocarbon spread slowly whereas at increased water temperature, the same hydrocarbons were found to be completely spread out within a few seconds. Temperature widely determines the properties of a water environment. To determine the rate at which crude oil will spread depends largely on the

interaction between the surface tension, specific gravity and viscosity, and the properties of the polluted site mainly water temperature. This is evidently taken as evidence that these oil will spread if and only if they possess these properties responsible for spreading and these properties were found to be active in that environment.

Although, crude oil spread on water may be expected to be readily dispersed immediately it spill because of eddy activity on the sea, this occurs only after the oil has spread. The first stage of any oil spill is spreading while the dispersion follows. The dispersion may not even occur in the absence of eddy activity. These properties are therefore shown in Table 4.2 of which surface tension, viscosity and specific gravity has been found to be responsible properties for spread of crude oil on water. The same degree of expectation may be anticipated for pour point, cloud point, Reid vapour pressure, and hydrocarbon composition of crude oil. However, these properties will not affect the spreading rate of crude oil because they are properties which will not interact with the properties of water. They are rather significant in the transportation and refining of crude oil. The chemical properties of crude oil which include the carbon content, nickel, vanadium, and the copper content, the total acid number, the hydrocarbon type may also be taught to be responsible for the spreading rate of crude oil on water. in petroleum engineering handbook it was explained that the chemical properties of crude oil does not change over a range of temperature of 65°C rather they separate into cuts/fractions. Another important The action of microorganisms is another factor that may affect the properties of crude oil on water however in this experiment the action of microorganisms is assumed too slow and negligible within the experimental time frame.

Relevant information from US Emergency response programme affirm that surface tension, viscosity and specific gravity are the three properties responsible for the spreading rate of crude oil on water. This was stated thus "The rate at which an oil spill spreads will determine its effect on the environment. Most oils tend to spread horizontally into a smooth and slippery surface, called a *slick*, on top of the water. Factors which affect the ability of an oil spill to spread include *surface tension*, *specific gravity*, and *viscosity*.

Surface tension is the measure of attraction between the surface molecules of a liquid. The higher the oil's surface tension, the more likely a spill will remain in place. If the surface tension of the oil is low, the oil will spread even without help from wind and water currents. Because increased temperatures can reduce a liquid's surface tension, oil is more likely to spread in warmer waters than in very cold waters.

Specific gravity is the density of a substance compared to the density of water. Since most oils are lighter than water, they lie flat on top of it. However, the specific gravity of an oil spill can increase if the lighter substances within the oil evaporate.

Viscosity is the measure of a liquid's resistance to flow. The higher the viscosity of the oil, the greater the tendency for it to stay in one place."(U.S. ERP, 2008) ([www.epa.gov/oil spill](http://www.epa.gov/oil%20spill))

**Assumptions made in this model are:**

That the spreading rate of crude oil will be affected by the specific gravity (SG), surface tension (ST) and the viscosity (V) of the crude oil.

It was assumed that there will be interactions among these crude oil properties and there will be interaction between the crude oil properties and the properties of water (temperature).

The temperature of the water were fixed/specified for every experimental run

Wind drift current and ocean waves were assumed constant to enable accurate examination of the effect of the crude oil properties on the spreading rate of the crude oil on water.

#### **4.2 Development of the Model for Spreading Rate of Crude Petroleum and Statistical Analyses**

The spreading rate data for Oguta crude are presented in Table 4.2 .

The spreading rate dispersion values from their mean values are shown in Table 4.3.

From which, the maximum dispersion,  $S_{umax}^2 = 1.17 \times 10^{-6}$ .

Applying Equation (2.4) to spreading of oils on water surface gives  $\sum_{u=1}^{16} S_u^2 = 3.91 \times 10^{-6}$ .

To determine the possibility of carrying out regression analysis using the G-criteria, Equation (2.6) gives  $G_{cal} = 0.2992$ . This calculated G – value was compared with an appropriate table value  $G_{(0.05, 2, 16)} = 0.3222$ . Since  $G_{cal} < G_{tab}$ , the homogeneity condition Equation (2.7) is fulfilled, therefore regression analysis was carried out. Applying Equations (2.8) and (2.9), the average sample variance and the experimental error are  $2.44375 \times 10^{-7}$  and  $4.9434 \times 10^{-4}$  respectively. Since the experimental design is orthogonal, the regression coefficients were estimated using Table 2.1 and Equations (2.10) through (2.14).

After calculating the 16 effects, their statistical significance was tested. This was done by constructing confidence intervals (Equation 2.16) and testing hypothesis about each regression coefficient. Confidence intervals for the regression coefficients are of the general form given in Equation (2.16). From statistical tables,  $t_{(0.05,32)} = 1.694$ .

Applying Equation (2.17), the error in each regression coefficient is  $S_b = 0.0000714$  and  $\Delta b$ 's = 0.000121. The  $t$  - values for testing significance of each regression coefficient are estimated using equation (2.18). The summary of the estimated effects, the confidence intervals and the calculated  $t$  - values is presented in Table 4.4. Comparing each of the calculated  $t$ -values (Table 4.4) with the appropriate critical table value (1.694) shows that all the regression coefficients are statistically significant. Therefore, the model for the rate of spread of Oguta crude is:

$$R = 5.7199 + 0.3151X_1 + 0.6242X_2 + 1.2278X_3 + 2.5603X_4 + 0.0144X_{12} - 0.024X_{13} + 0.1543X_{14} - 0.0336X_{23} + 0.3256X_{24} + 0.7001X_{34} - 0.0059X_{123} + 0.004X_{124} + 0.0253X_{134} + 0.0122X_{234} - 0.0186X_{1234} \quad (4.1)$$

$X_1$  = Temperature (T), °C;  $X_2$  = Surface tension (ST), mN/m;

$X_3$  = viscosity (V), mm<sup>2</sup>/s;  $X_4$  = Specific gravity (SG); R = Spreading rate, cm/s.

The predicted values of R at the 16 points in the design were generated using equation (4.1). The mean experimental observations ( $\bar{R}$ ), the predicted values ( $\hat{R}$ ), the residuals ( $e_i$ ) and the squares of the residual ( $e_i^2$ ) are presented in Table 4.5. The residuals are the deviations of the measured values from the predicted ones.

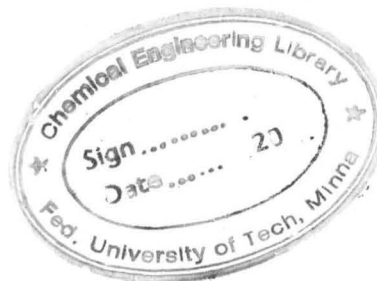


Table 4.2: Measured Data for the Study of the Effect of Crude Oil Properties on the Spreading Rate of Oguta Crude.

Run No.	Temp, °C	ST, mN/m	V, mm <sup>2</sup> /s	SG	Rate of Spread (R), cm/s			Mean R, cm/s
					I	II	III	
1	20.0	0.0594	8.13	1.2001	2.0820	2.0831	2.0839	2.0830
2	25.0	0.0481	7.02	0.9505	2.4920	2.4935	2.4941	2.4932
3	30.0	0.0409	6.43	0.9101	2.7606	2.7605	2.7610	2.7607
4	35.0	0.0378	5.23	0.8823	3.1906	3.1903	3.1910	3.1908
5	37.5	0.0363	4.99	0.8717	3.3527	3.3526	3.3531	3.3528
6	40.0	0.0348	4.75	0.8611	3.5147	3.5150	3.514	3.5148
7	42.5	0.0342	4.38	0.7860	3.7990	3.7988	3.7986	3.7988
8	45.0	0.0335	4.01	0.7109	4.0830	4.0826	4.0825	4.0827
9	47.5	0.0326	3.58	0.6905	4.9478	4.9479	4.9480	4.9479
10	50.0	0.0316	3.14	0.6701	5.8132	5.8134	5.8127	5.8131
11	52.5	0.0303	3.07	0.5601	6.8201	6.8206	6.8205	6.8204
12	55.0	0.0289	3.00	0.4501	7.8278	7.8275	7.8275	7.8277
13	57.5	0.0192	2.95	0.3636	8.7960	8.7961	8.7965	8.7962
14	60.0	0.0094	2.90	0.2771	9.7650	9.7645	9.7643	9.7646
15	62.5	0.0053	2.45	0.1956	10.6785	10.6789	10.6790	10.6788
16	65.0	0.0011	1.99	0.1141	11.5940	11.5930	11.5920	11.5930

**Legend:**

Temp -Temperature  
 ST -Surface tension  
 V -Kinematic viscosity  
 SG -Specific gravity



Table 4.3: Measured Data for the Determination of Spreading Rate Dispersion of Oguta Crude Oil.

Run No.	$R_1$	Replicates $R_2$	$R_3$	$\bar{R}$	$(R_1 - \bar{R})^2$	$(R_2 - \bar{R})^2$	$(R_3 - \bar{R})^2$	$2 \sum_{i=1}^{16} S_i^2 =$
1	2.0820	2.0831	2.0839	2.0830	$1 \times 10^{-6}$	$1 \times 10^{-8}$	$8.1 \times 10^{-7}$	$9.1 \times 10^{-7}$
2	2.4920	2.4935	2.4941	2.4932	$1.44 \times 10^{-6}$	$9 \times 10^{-8}$	$8.1 \times 10^{-7}$	$1.17 \times 10^{-6}$
3	2.7606	2.7605	2.7610	2.7607	$1 \times 10^{-8}$	$4 \times 10^{-8}$	$9 \times 10^{-8}$	$7 \times 10^{-8}$
4	3.1906	3.1903	3.1910	3.1908	$4 \times 10^{-8}$	0	$4 \times 10^{-8}$	$4 \times 10^{-8}$
5	3.3527	3.3526	3.3531	3.3528	$1 \times 10^{-8}$	$4 \times 10^{-8}$	$9 \times 10^{-8}$	$7 \times 10^{-8}$
6	3.5147	3.5150	3.514	3.5148	$1 \times 10^{-8}$	$4 \times 10^{-8}$	$1 \times 10^{-8}$	$3 \times 10^{-8}$
7	3.7990	3.7988	3.7986	3.7988	$4 \times 10^{-8}$	0	$4 \times 10^{-8}$	$4 \times 10^{-8}$
8	4.0830	4.0826	4.0825	4.0827	$9 \times 10^{-8}$	$1 \times 10^{-8}$	$4 \times 10^{-8}$	$7 \times 10^{-8}$
9	4.9478	4.9479	4.9480	4.9479	$1 \times 10^{-8}$	0	$1 \times 10^{-8}$	$1 \times 10^{-8}$
10	5.8132	5.8134	5.8127	5.8131	$1 \times 10^{-8}$	$9 \times 10^{-8}$	$1.6 \times 10^{-8}$	$1.3 \times 10^{-7}$
11	6.8201	6.8206	6.8205	6.8204	$9 \times 10^{-8}$	$4 \times 10^{-8}$	$1 \times 10^{-7}$	$7 \times 10^{-8}$
12	7.8278	7.8275	7.8275	7.8277	$1 \times 10^{-8}$	$1 \times 10^{-8}$	$4 \times 10^{-8}$	$3 \times 10^{-8}$
13	8.7960	8.7961	8.7965	8.7962	$4 \times 10^{-8}$	$1 \times 10^{-8}$	$9 \times 10^{-8}$	$7 \times 10^{-8}$
14	9.7650	9.7645	9.7643	9.7646	$1.6 \times 10^{-7}$	$1 \times 10^{-8}$	$9 \times 10^{-8}$	$1.3 \times 10^{-7}$
15	10.6785	10.6789	10.6790	10.6788	$9 \times 10^{-8}$	$1 \times 10^{-8}$	$4 \times 10^{-8}$	$7 \times 10^{-8}$
16	11.5940	11.5930	11.5920	11.5930	$1 \times 10^{-6}$	0	$1 \times 10^{-6}$	$1 \times 10^{-7}$

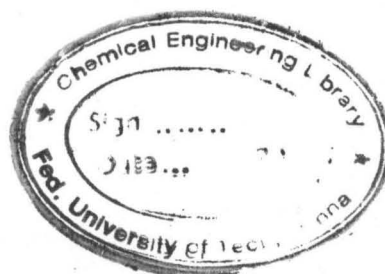




Table 4.4: The Estimated Effects, Confidence Intervals and Calculated t-values of Spreading Rate for Oguta Crude

Regression Coefficient	Estimated Effect	Confidence Interval	t-values
$b_0$	5.7199	$\pm 0.000121$	80,110.6
$b_1$	0.3151	$\pm 0.000121$	4413.17
$b_2$	0.6242	$\pm 0.000121$	8742.30
$b_3$	1.2278	$\pm 0.000121$	17196.08
$b_4$	2.5603	$\pm 0.000121$	35858.54
$b_{12}$	0.0144	$\pm 0.000121$	201.68
$b_{13}$	-0.0240	$\pm 0.000121$	336.13
$b_{14}$	0.1543	$\pm 0.000121$	2161.06
$b_{23}$	-0.0336	$\pm 0.000121$	470.59
$b_{24}$	0.3256	$\pm 0.000121$	4560.22
$b_{34}$	0.7001	$\pm 0.000121$	9805.32
$b_{123}$	-0.0059	$\pm 0.000121$	82.63
$b_{124}$	0.0040	$\pm 0.000121$	56.02
$b_{134}$	0.0253	$\pm 0.000121$	354.34
$b_{234}$	0.0122	$\pm 0.000121$	170.87
$b_{1234}$	-0.0186	$\pm 0.000121$	260.50

The predicted values of spreading rate at the 16 points in the design were generated using the regression model equation. The mean measured spreading rate for crude oil ( $\bar{R}$ ), the predicted value ( $\hat{R}$ ), the residuals ( $|e_i|$ ), and the squares of the residuals ( $e_i^2$ ) are presented in Table 4.5.

Table 4.5 Comparison of the Predicted Values with the measured the Spreading Rate of Oguta Crude.

Run No	$\bar{R}$	$\hat{R}$	$ e_i $	$e_i^2 = (\bar{R} - \hat{R})^2$
1	2.0830	2.0751	0.0079	$6.241 \times 10^{-5}$
2	2.4932	2.4999	0.0067	$4.489 \times 10^{-5}$
3	2.7607	2.7685	0.0078	$6.084 \times 10^{-5}$
4	3.1908	3.1841	0.0067	$4.489 \times 10^{-5}$
5	3.3528	3.3461	0.0067	$4.489 \times 10^{-5}$
6	3.5148	3.5229	0.0081	$6.561 \times 10^{-5}$
7	3.7988	3.8055	0.0067	$4.489 \times 10^{-5}$
8	4.0827	4.0747	0.0080	$6.400 \times 10^{-5}$
9	4.9479	4.9559	0.0080	$6.400 \times 10^{-5}$
10	5.8131	5.8063	0.0068	$4.624 \times 10^{-5}$
11	6.8204	6.8125	0.0079	$6.241 \times 10^{-5}$
12	7.8277	7.8345	0.0068	$4.624 \times 10^{-5}$
13	8.7962	8.8029	0.0067	$4.489 \times 10^{-5}$
14	9.7646	9.7565	0.0081	$6.561 \times 10^{-5}$
15	10.6788	10.6719	0.0069	$4.761 \times 10^{-5}$
16	11.5930	11.6011	0.0081	$6.561 \times 10^{-5}$

The adequacy of the spreading rate model (Equation (4.1)) was evaluated by carrying out a test of hypothesis using ANOVA on the individual regression coefficients. The sums of squares for the effects were calculated using Equations (2.23) through (2.26). The total sum of squares was found using Equation (2.27). The error sum of squares was calculated using Equation (2.28 or 2.29) and the F-ratios were calculated using Equation (2.31). The

complete ANOVA was summarized in Table 4.6. When each of the calculated F -ratio was compared with the appropriate critical table value  $F_{(0.05, 1, 32)} = 5.54$ , it was found that all the coefficients contribute significantly to the regression model. Actually all the coefficients have earlier been found statistically significant. The adequacy of the regression model was further checked by calculating the coefficient of determination (COD) represented by  $R^2$  ( $0 < R^2 \leq 1$ ). It refers to the proportion of variability in the data explained or accounted for by the regression model. For the spreading rate model and using Equation (2.33),  $R^2 = 0.9999$ . This means that 99.99% of the variability in the data was accounted for by the model. The measured and calculated curve is shown in Figure 4.1

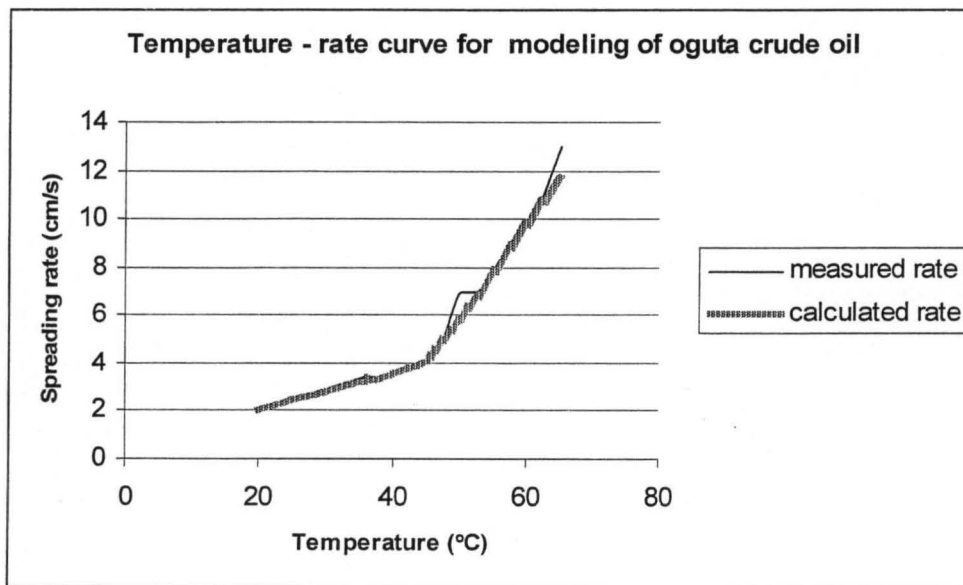


Figure 4.1: Comparison of Measured and Calculated Spreading Rate Variation with Temperature of Water for Oguta Crude Oil.

Table 4.6: ANOVA for the Replicated  $2^4$  Factorial Experiment for the Spreading Rate of Oguta Crude

Source of Variation	Effect	Sum of Squares (SS)	Degrees of Freedom (df)	Mean squares (MS)	F-ratio
b <sub>1</sub>	0.3151	4.7653	1	4.7653	101659.73
b <sub>2</sub>	0.6242	18.7024	1	18.7024	398984.53
b <sub>3</sub>	1.2278	72.3604	1	72.3604	154688.53
b <sub>4</sub>	2.5603	314.6481	1	314.6481	6712492.80
b <sub>12</sub>	0.0144	0.0099	1	0.0099	211.20
b <sub>13</sub>	-0.0240	0.0277	1	0.0277	590.93
b <sub>14</sub>	0.1543	1.429	1	1.1429	24381.87
b <sub>23</sub>	-0.0336	0.0542	1	0.0542	1156.27
b <sub>24</sub>	0.3256	5.0874	1	5.0874	108531.20
b <sub>34</sub>	0.7001	23.5288	1	23.5288	501947.73
b <sub>123</sub>	-0.0059	0.0017	1	0.0017	36.27
b <sub>124</sub>	0.0040	0.0005	1	0.0005	10.67
b <sub>134</sub>	0.0253	0.0307	1	0.0307	654.93
b <sub>234</sub>	0.0122	0.0064	1	0.0064	136.53
b <sub>1234</sub>	-0.0186	0.0167	1	0.0167	356.27
Error		0.0015	32	$4.6875 \times 10^{-5}$	
Total		440.3846	47		

### 4.3 Interpretation of the Spreading Rate Model for Crude Petroleum

Equation (4.1) is the model for predicting the spreading rate of crude petroleum. To assist in the practical interpretation of the spreading rate experiment, sensitivity analysis was carried out to determine factorial effects.

#### General Considerations

In the  $2^4$  factorial experiments for spreading rate of crude oil a total of 16 runs/observations were made. Each of the 4 factors occurred at 2 levels; a high level coded as +, and a low level coded as -, in the designed experiment.

From the 16 runs/observations in the  $2^4$  factorial experiments, at most 16 quantities were estimated; the overall mean ( $b_0$ ), the 4 main effects ( $b_1, b_2, b_3, b_4$ ), the six two factor interactions ( $b_{12}, b_{13}, b_{14}, b_{23}, b_{24}, b_{34}$ ), the four -three factor interactions ( $b_{123}, b_{124}, b_{134}, b_{234}$ ), and the one -four factor interaction ( $b_{1234}$ ).

#### Factors and interaction effects

The effect of a factor is defined to be the change in responses produced by a change in the level of the factor. The main effect of factor is the difference between the average responses at the high level of the factor. This difference is proportional to the regression coefficient  $b_1=0.3151, b_2=0.6242$ , etc mean moving 0.3151 units in the  $x_1$  direction (from its base level along the line of steepest ascent for every 0.6242 units in the  $x_2$  direction (from its base level along the line of steepest ascent).

Interactions usually exist between the various factors in an experiment. When an interaction is larger than the corresponding main effect of the interacting factors, the interaction is said to mask the significance of those main effect and has more practical importance (Montgomery, 1991).

### 4.3 Sensitivity Analysis for Spreading Rate Model

#### 4.3.1 Factorial Effects

The factorial effect is the effect of a factor when in association with other factors. It is otherwise called the simple effect of the factor. From Tables 2.1, 4.2 and 4.5, the following deductions were made on the sensitivity of the response variable (R) to changes in the levels of the regressor variables (T, ST, V, and SG). The analysis was based on the low and high levels of the factors.

1. Experiment 1 puts T (= 20°C) and other factors at their low levels and the predicted value  $\hat{R}_1 = 2.0751\text{cm/s}$ . Experiment 2 puts T (=25°C) at high level and other factors at their low levels and the predicted value  $\hat{R}_2 = 2.4999\text{cm/s}$ . This means that the factorial effect of temperature is to increase spreading rate of crude oil by 0.4248cm/s or 20.5%. This can be seen in the positive coefficient for temperature in the model. Actually, increase in temperature increases the spreading rate of crude oils as viscosity will reduce. It was concluded that an increase in temperature value by 25% led to an increase of 20.5% in spreading rate of crude.

2. Experiment 1 puts ST (= 0.0594mN/m) and other factors at their low levels and the predicted value  $\hat{R}_1 = 2.0751\text{cm/s}$ . Experiment 3 puts ST (= 0.0409mN/cm) at high level while other factors are at their low levels and the predicted value  $\hat{R}_3 = 2.7685\text{cm/s}$ . This means that the factorial effect of ST is to increase R by 0.6934cm/s or 33.4%. This can be seen in the positive coefficient for ST in the model. This is in conformity with the US "Emergency Response Program" (ERP) crude oil literature "attraction between the surface molecules of a liquid. The higher the oil's surface tension, the more likely a spill

will remain in place. If the surface tension of the oil is low, the oil will spread even without help from wind and water currents. Because increased temperatures can reduce a liquid's surface tension, oil is more likely to spread in warmer waters than in very cold waters”.

3. Experiment 1 puts  $V$  ( $= 8.13\text{mm}^2/\text{s}$ ) and other factors at their low levels and the predicted value  $\hat{R}_1 = 2.0751\text{cm/s}$ . Experiment 5 puts  $V$  ( $= 4.99\text{mm}^2/\text{s}$ ) at high level while other factors are at their low levels and the predicted value  $\hat{R}_5 = 3.3461\text{cm/s}$ . This means that the factorial effect of  $V$  is to increase  $R$  by  $1.271\text{cm/s}$  or  $61.3\%$ . This can be seen in the positive coefficient for  $V$  in the model. From theory, increase in temperature leads to decrease in viscosity and consequently increases the rate of spread of fluids such as crude petroleum. Therefore the spreading rate of crude oil was strongly and positively sensitive to changes in  $V$ . “Viscosity is the measure of a liquid's resistance to flow. The higher the viscosity of the oil, the greater the tendency for it to stay in one place.” “US (ERP) crude oil literature” invariably spilled oil will spread more at lesser viscosity.

4. Experiment 1 puts  $SG$  ( $= 1.2001$ ) and other factors at their low levels and the predicted value  $\hat{R}_1 = 2.0751\text{cm/s}$ . Experiment 9 puts  $SG$  ( $= 0.6905$ ) at high level while other factors are at their low levels and the predicted value  $\hat{R}_9 = 4.9559\text{cm/s}$ . This means that the factorial effect of  $SG$  is to increase  $R$  by  $2.8808$  or  $138.83\%$ . This is in agreement with the positive coefficient as indicated in the model. “Specific gravity is the density of a substance compared to the density of water. Since most oils are lighter than water, they lie flat on top of it. However, the specific gravity of an oil spill can increase if the lighter substances within the oil evaporate”. “US (ERP) crude oil literature”



The oil have specific gravity less than 1.00 this is in accordance with Doerffer's report. The American Petroleum Institute has developed the API gravity scale which expresses the ratio of weights of equal volumes of oil and pure water at a temperature of 16 °C and one atmosphere pressure.

### **Summary**

Based on the sensitivity analysis, it was concluded that the spreading rate of crude petroleum was strongly sensitive to T, ST, V and SG. Therefore every effort should be directed towards reducing these factors whenever there is an oil spill. However, The rate at which an oil spill spreads will determine its effect on the environment. Most oils tend to spread horizontally into a smooth and slippery surface, called a *slick*, on top of the water. Factors which affect the ability of an oil spill to spread include surface tension, specific gravity, and viscosity. "US (ERP) crude oil literature" This shows that the behaviour of the crude oil on the sea ultimately depends on the physical and chemical properties of the crude oil itself.

### **4.3.2 Main Effects**

The main effect of a factor is the difference between the average response at the low level and the average response at the high level of the factor. This difference is proportional to the regression coefficient. On the basis of the experimental results and the predictive model and for values of  $X_i$  ( $i = 1, 2, 3, 4$ ) that fall within the intervals used in developing the model, the following deductions were made.

a. The main effect of temperature is 0.3151. This means that on the average a temperature increase of 22.5°C led to a 0.3151cm/sec increase in spreading rate of crude oil. Stating

this differently, it means that a temperature increase from the low level ( $20.0^{\circ}\text{C}$ ) to the high level ( $65^{\circ}\text{C}$ ) led to a  $(2)(0.3151) = 0.6302\text{cm/sec}$  increase in spreading rate. This is explained by the positive sign against the coefficient of this factor ( $b_1 = 0.3151$ ). The implication of increased spreading rate is more damaging to the environment when there is an oil spill.

b. The main effect of ST is 0.6242. This means that on the average a ST increase of  $0.02915\text{mN/m}$  led to a  $0.6242\text{cm/sec}$  increase in spreading rate of crude oil. Stating this differently, it means that a ST increase from the low level ( $0.0011\text{mN/m}$ ) to the high level ( $0.0594\text{mN/m}$ ) led to a  $(2)(0.6242) = 1.2484\text{cm/s}$  increase in spreading rate of crude oil. This is explained by the positive sign against the coefficient of this factor ( $b_2 = 0.6242$ ).

c. The main effect of V is 1.2278. This means that on the average a viscosity increase of  $3.07\text{mm}^2/\text{s}$  led to a  $1.2278\text{cm/s}$  increase in spreading rate of crude oil. Stating this differently, it means that a V increase from the low level ( $1.99\text{mm}^2/\text{s}$ ) to the high level ( $8.13\text{mm}^2/\text{s}$ ) led to a  $(2)(1.2278) = 2.4556\text{cm/s}$  increase in spreading rate of crude oil. This is explained by the positive sign against the coefficient of this factor ( $b_3 = 1.2278$ ).

d. The main effect of SG is 2.5603. This means that on the average a SG increase of  $0.543$  led to a  $2.5603\text{cm/s}$  increase in spreading rate of crude oil. Stating this differently, it implies that a SG increase from the low level ( $0.1141$ ) to the high level ( $1.2001$ ) led to a  $(2)(2.5683) = 5.1206\text{cm/s}$ . This is explained by the positive sign against the coefficient of this factor ( $b_4 = 2.5603$ ).



### 4.3.3 Interaction Effects

#### I. Two-factor interaction

i. The interaction effect of temperature and ST is 0.0144. This means that increasing simultaneously the temperature and ST from their low levels to their high levels will increase the spreading rate crude oil by 0.0144cm/s. This is explained by the positive sign against the coefficient of the interaction between these two factors ( $b_{12} = 0.0144$ ). Each of the main effects of temperature and ST is greater than the interaction effect, indicating that there is positive synergy between the interacting factors.

ii. The interaction effect of temperature and V is -0.024. This means that increasing simultaneously the temperature and V from their low levels to their high levels will decrease slightly the spreading rate of crude oil by 0.024 cm/sec. This is explained by the negative sign against the coefficient of the interaction between these two factors ( $b_{13} = 0.024$ ). However, as the interaction is negative compared to the main effect of each of the interacting factors, we say there is negative synergism between temperature and V. This is however not surprising since increase in temperature always leads to decrease in viscosity.

iii. The interaction effect of temperature and SG is 0.1543. This means that increasing simultaneously the temperature and SG from their low levels to their high levels will increase the spreading rate of the crude oil by 0.1543cm/sec. This is explained by the positive sign against the coefficient of the interaction between these two factors ( $b_{14} = 0.1543$ ). The interaction is however positively synergistic.

iv. The interaction effect of ST and V is -0.0336. This means that increasing simultaneously the ST and V from their low levels to their high levels will decrease the

spreading rate of the crude oil by 0.0336cm/s. This is explained by the negative sign against the coefficient of the interaction between these two factors ( $b_{23} = - 0.0336$ ). The interaction is however negatively synergistic. The surface tension of an oil, together with its viscosity, affects the rate at which an oil spill spreads. Air/oil and oil/water interfacial tensions can be used to calculate a spreading coefficient which gives an indication of the tendency for the oil to spread. It is defined as:

$$\text{Spreading Coefficient} = S_{WA} - S_{OA} - S_{WO}$$

where  $S_{WA}$  is water/air interfacial tension,  $S_{OA}$  is oil/air interfacial tension, and  $S_{WO}$  is water/oil interfacial tension.

Spreading to a thin slick is likely if the spreading coefficient of an oil is greater than zero, and the higher the spreading coefficient, the faster the spreading will occur (Twardus, 1980). Unlike density and viscosity, which show systematic variations with temperature and degree of evaporation, interfacial tensions of crude oils and oil products show no such correlations. Nor is there any correlation to viscosity (Jokuty et al., 1995).

v.the interaction effect of ST and SG is 0.3256. This means that increasing simultaneously the ST and SG from their low levels to their high levels will increase the spreading rate of crude oil by 0.3256cm/s. This is explained by the positive sign against the coefficient of the interaction between these two factors ( $b_{24}=0.3256$ ) indicating positive synergism.

vi. The interaction effect of V and SG is 0.7001. This means that increasing simultaneously the V and SG from their low levels to their high levels will increase the spreading rate of crude oil by 0.7001cm/s. This is explained by the positive sign against the coefficient of the interaction of the two factors ( $b_{34} = 0.7001$ ). This means positive synergism.

## II. Three-factor interactions

a. The interaction effect of temperature, ST, and V is -0.0059. This means that increasing simultaneously the temperature, ST and V from their low levels to their high levels will decrease the R spreading rate of the crude oil by 0.0059cm/sec. This is explained by the positive sign against the coefficient of the interaction between these three factors ( $b_{123} = -0.0059$ ).

b. The interaction effect of temperature, ST and SG is 0.004. This means that increasing simultaneously the temperature, ST and V from their low levels to their high levels will increase the spreading rate of the crude oil by 0.004cm/s. This is explained by the positive sign against the coefficient of the interaction between these three factors ( $b_{124} = 0.004$ ). However, the interaction effect is small compared with the main effect of these factors.

c. The interaction effect of temperature, V and SG is 0.0253. This means that increasing simultaneously the temperature, V and SG from their low levels to their high levels will increase the spreading rate of crude oil by 0.0253cm/s. This is explained by the positive sign against the coefficient of the interaction between these three factors ( $b_{134} = 0.0253$ ). The interaction effect is however small compared to the main effects of temperature, DV and SG.

d. The interaction effect of ST, V and SG is 0.0122cm/s. This means that increasing simultaneously the ST, V and SG from their low levels to their high levels will increase the spreading rate of the crude oil by 0.0122cm/s. This is explained by the positive sign against the coefficient of the interaction between these three factors ( $b_{234} = 0.0122$ ). The interaction effect is however small compared to the main effect of the interacting factors.

### **III. Four-factor interaction**

The interaction effect of temperature, ST, V and SG is -0.0186. This means that increasing simultaneously the four factors from their low levels to their high levels will lead to a decrease in the spreading rate of the crude oil by 0.0186cm/s. This is explained by the negative sign against the coefficient of the interaction between the four factors ( $b_{1234} = -0.0186$ ). The interaction is however negatively synergistic.

### **Validation of the spreading rate model Using the Data collected for Qua Iboe light crude oil**

It was proven that the measured data for Qua Iboe light fitted well into the model obtained for Oguta crude oil. Implying that the model is adequate for predicting the spreading rate of Nigerian crude oil on sea as long as wind drift current is neglected. This is shown in figure 4.2 to figure 4.13.

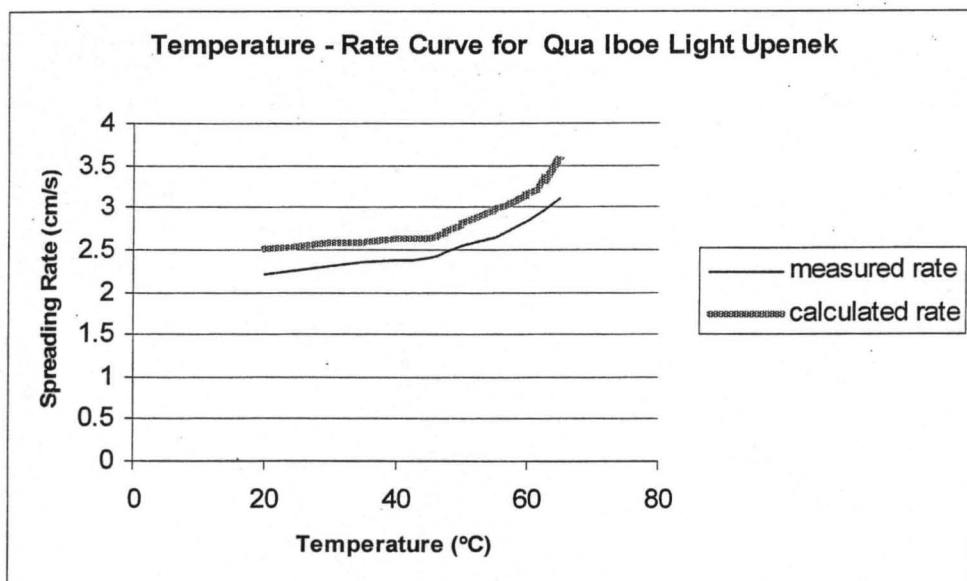


Figure 4.2: Comparison of Measured and Calculated Spreading Rate Variation with Temperature of Water for Qua Iboe Upenek Crude Oil.

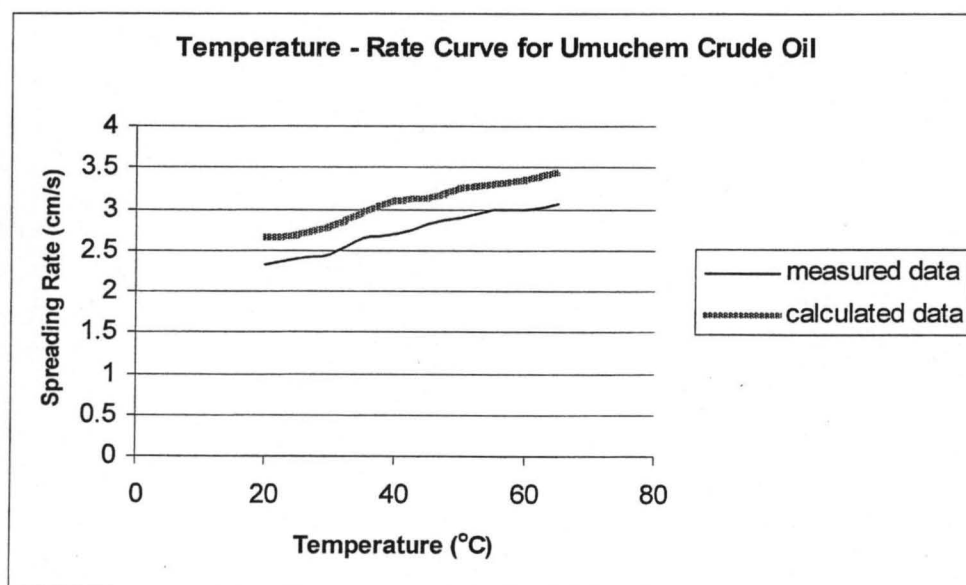


Figure 4.3: Comparison of Measured and Calculated Spreading Rate Variation with Temperature of Water for Umuchem Crude Oil.



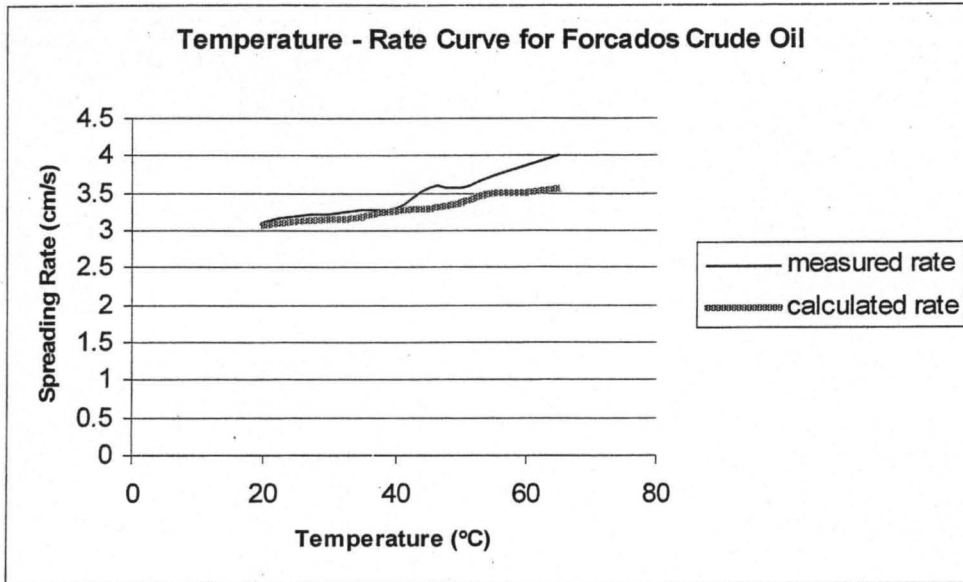


Figure 4.4: Comparison of Measured and Calculated Spreading Rate Variation with Temperature of Water for Forcados Crude Oil.

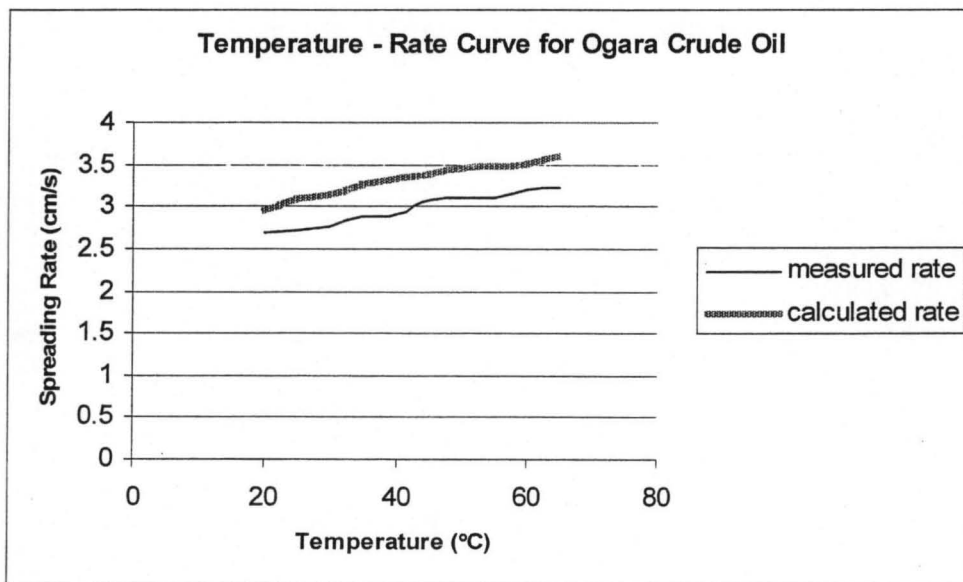


Figure 4.5: Comparison of Measured and Calculated Spreading Rate Variation with Temperature of Water for Ogara Crude Oil.

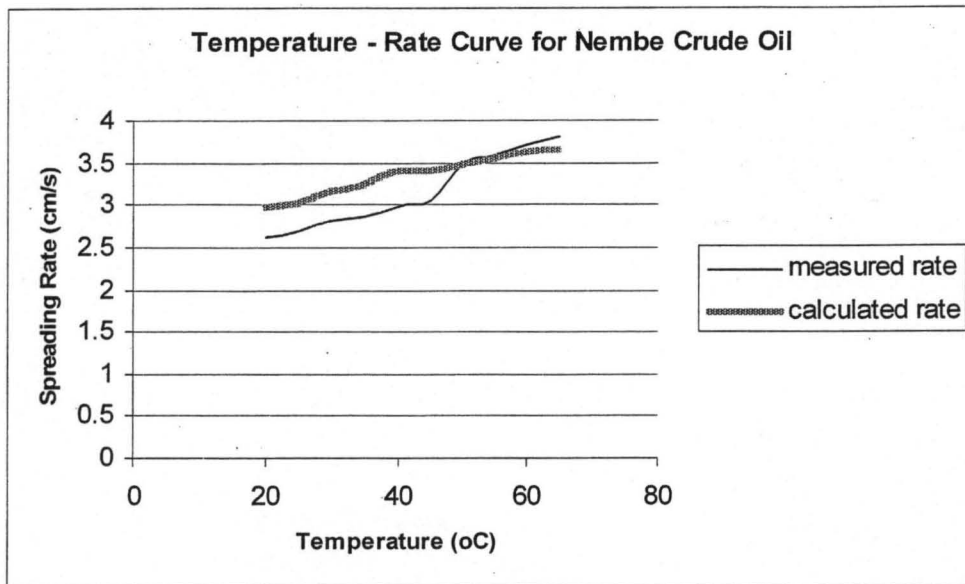


Figure 4.6: Comparison of Measured and Calculated Spreading Rate Variation with Temperature of Water for Nembe Crude Oil.

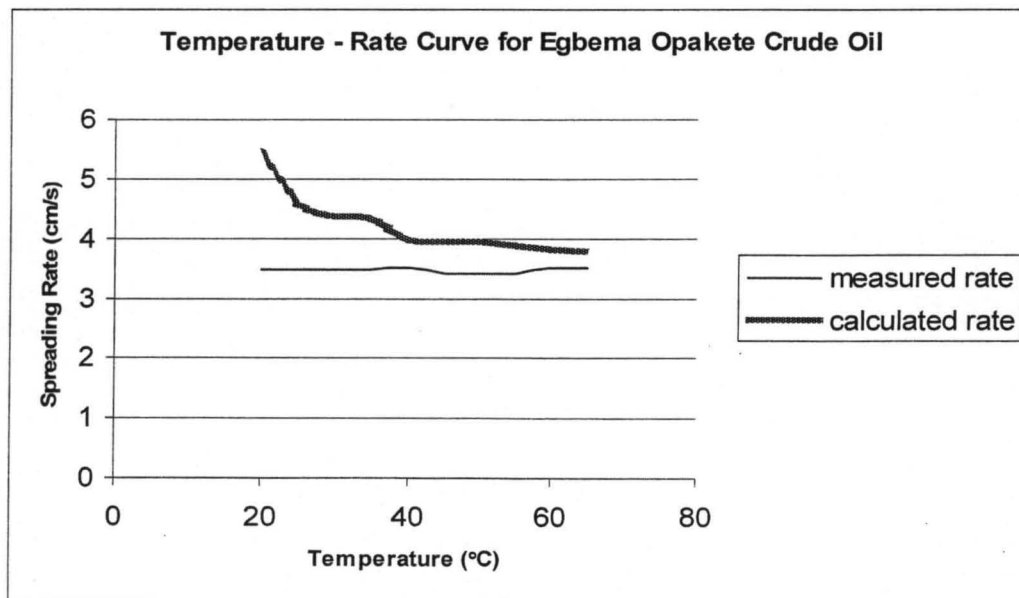


Figure 4.7 Comparison of Measured and Calculated Spreading Rate Variation with Temperature for Egbema Opakete Crude oil.

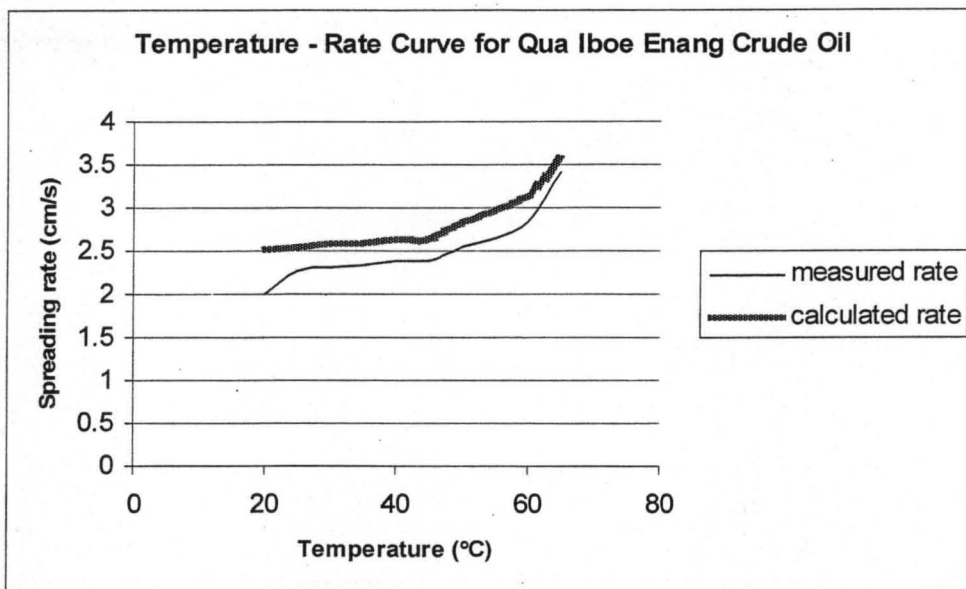


Figure 4.8 Comparison of Measured and Calculated Spreading Rate Variation with Temperature for Qua Iboe Enang Crude oil.

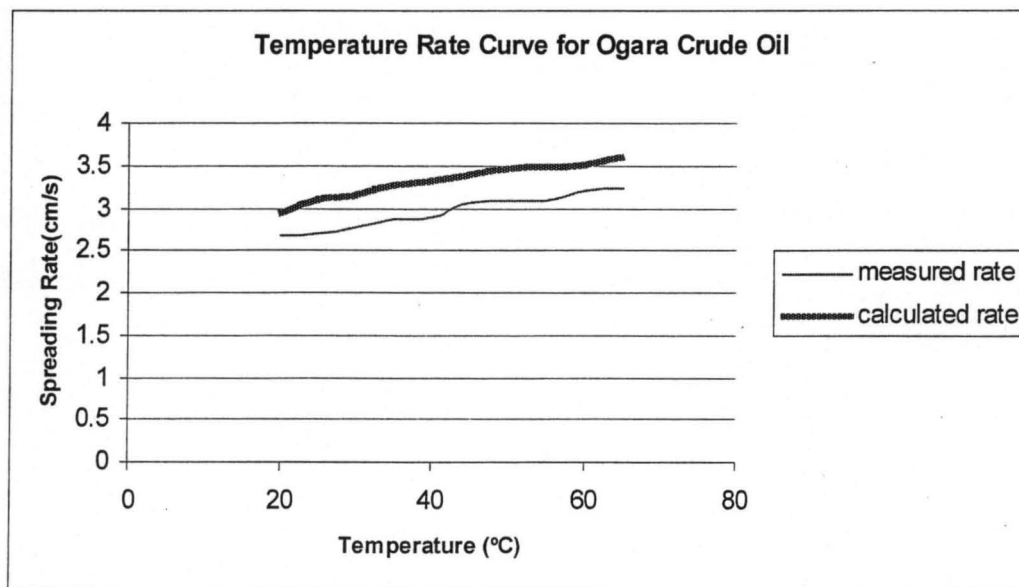


Figure 4.9 Comparison of Measured and Calculated Spreading Rate Variation with Temperature for Ogara Crude oil.

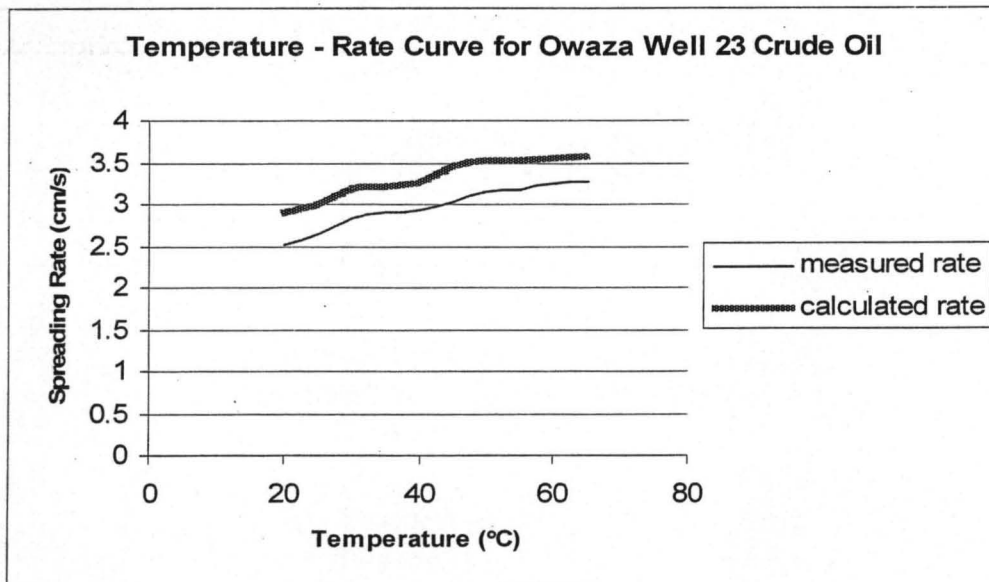


Figure 4.10 Comparison of Measured and Calculated Spreading Rate Variation with Temperature for Owaza well 23 Crude oil.

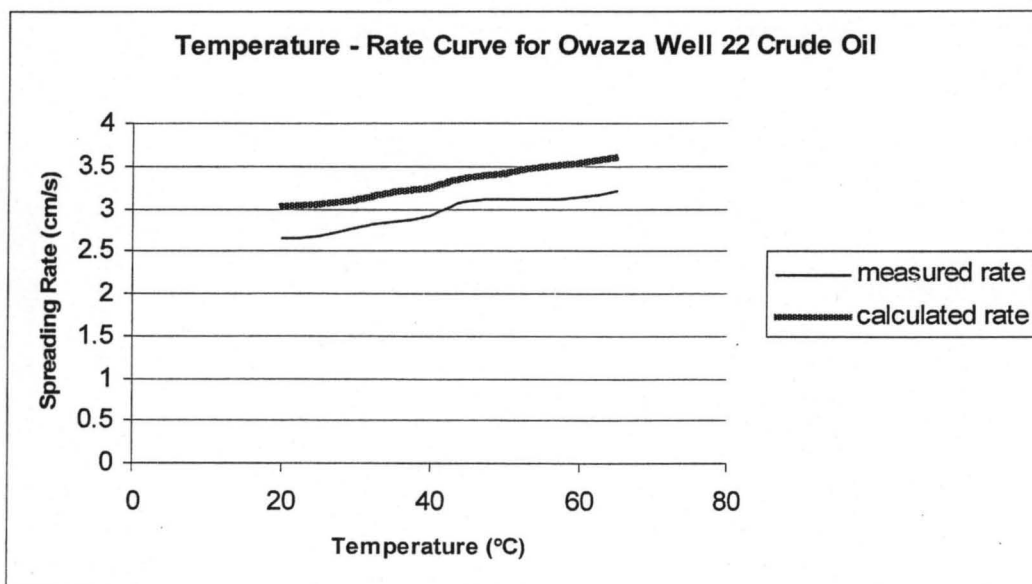


Figure 4.11 Comparison of Measured and Calculated Spreading Rate Variation with Temperature for Owaza well 22 Crude oil.

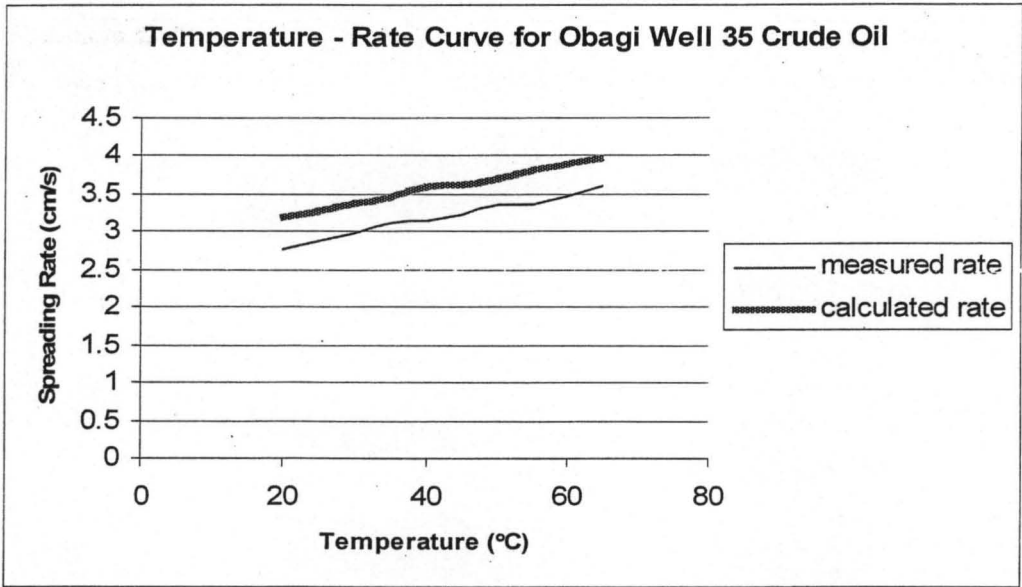


Figure 4.12 Comparison of Measured and Calculated Spreading Rate Variation with Temperature for Obagi well 35 Crude oil.

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## CHAPTER FIVE

### 5.0 CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

The crude oils possess similar physicochemical properties since they were found to be mainly naphthenic based, sweet, with low sulphur content of less than 0.3%. They were light crude oils API gravity of less than 24.5°API They contain very low metal content averaging 0.4wppm for vanadium and 3.0wppm for nickel. They contain low total acid number (TAN) of about 0.4mgKOH/g their pour point averaged 15.5°C and the salt content were within the same range of 2-4lb/1000b. however the crude oil from Egbema Opakete was an exceptional crude oil which was found to be sour, dense and aromatic. The reason for this difference was obvious from the onset as the crude oil was sourced from an oil field which is not yet producing. Therefore the immaturity of the crude oil was responsible for its awkward properties.

Each crude oil possess its own unique properties, however they were similar. This was evident from the result as no single value of any of the properties was the same.

The three properties of crude oil found to be responsible for spreading rate of crude oil on water were the surface tension, specific gravity and viscosity, since they are the only properties that interacted with the properties of water resulting to its spreadability on water.

The severity of an oil spill's impact or spreadability rate has been found to depends on these two major factors, these three physical properties of the oil and their interactions



with the property of water, (from the factorial analysis and deduction/interpretations, it can be concluded that all the main effects and interactions in the predictive model have significant impacts on the spreading rate of the crude oil. That is temperature, surface tension, viscosity, and specific gravity with main effects of 0.3151, 0.6242, 1.2278 and 2.5603 respectively. They have higher incremental influences on spreading rate of crude oil. High levels of each of these will lead to a drastic increase in the spreading rate of crude oil and the consequent devastation effect on the environment.

The interactions temperature/viscosity, surface tension/viscosity, temperature/surface tension/viscosity and temperature/surface tension/viscosity/specific gravity, with coefficients -0.024, -0.0336, -0.0059 and -0.0186 respectively all have significant influences on spreading rate of crude oil, because the spreading rate is appreciably influenced by such interactions.

When the predicted values based on the predictive model (Equation 4.1) are compared with the mean experimental values for the 16 experimental runs (Table 4.5), it was observed that experiment 1, with predicted value  $R_1 = 2.0751\text{cm/s}$ , maintains the spreading rate of the crude oil at the lowest level. Therefore it is concluded that the optimum condition that permits minimum spreading rate is that of experiment 1, that is: temperature, surface tension, viscosity and specific gravity must be at their minimum levels. Since spills occur despite efforts to prevent them. They happen on water mainly, during the day and at night, on warm days and cold, under clear skies and in the rain and snow. Quantity of oil spill vary in size, from just a few hundred gallons to the millions of gallons. Preparing a timely and coordinated transportation of such valuable resources

should be properly defined at any time it must be transported. Therefore crude oil should be transported when it is cold this will reduce the temperature of the water thus inducing a negative interaction between the properties of oil and water. This will significantly retard the spreading rate.

## **5.2 RECOMMENDATIONS**

The model equation obtained in this work is recommended to determine the spreading rate of Nigerian crude oils on Nigeria's sea. Since shore commanders cannot determine the properties of crude oil at the instant of spill. Once the temperature of the sea water is known the spreading rate can be determined.

During an oil spill all effort should be made to increase surface tension of crude oil, reduce viscosity, reduce specific gravity and reduce temperature to reduce the spreading rate of crude oil. This will no doubt reduce the negative impact on biota and terrestrial life. Therefore oil should be transported on a cool day.

Despite the nation's best efforts to prevent spills, almost 14,000 oil spills are reported each year, mobilizing thousands of specially trained emergency response personnel and challenging the best-laid contingency plans. Although many spills are contained and cleaned up by the party responsible for the spill, some spills require assistance from local and state agencies, and most urgently the immediate people living along the coast, such people living along the coast should be empowered to apply surface tension retardant to the polluted site.

Since spilled oil poses serious threats to fresh water and marine environments, affecting surface resources and a wide range of subsurface organisms that are linked in a complex food chain that includes human food resources and since spilled oil can harm the environment in several ways, including the physical damages that directly impact wildlife and their habitats (such as coating birds or mammals with a layer of oil), and the toxicity of the oil itself, which can poison exposed organisms, all effort should be made towards retarding the positive interaction between the crude oil property and the property of water.

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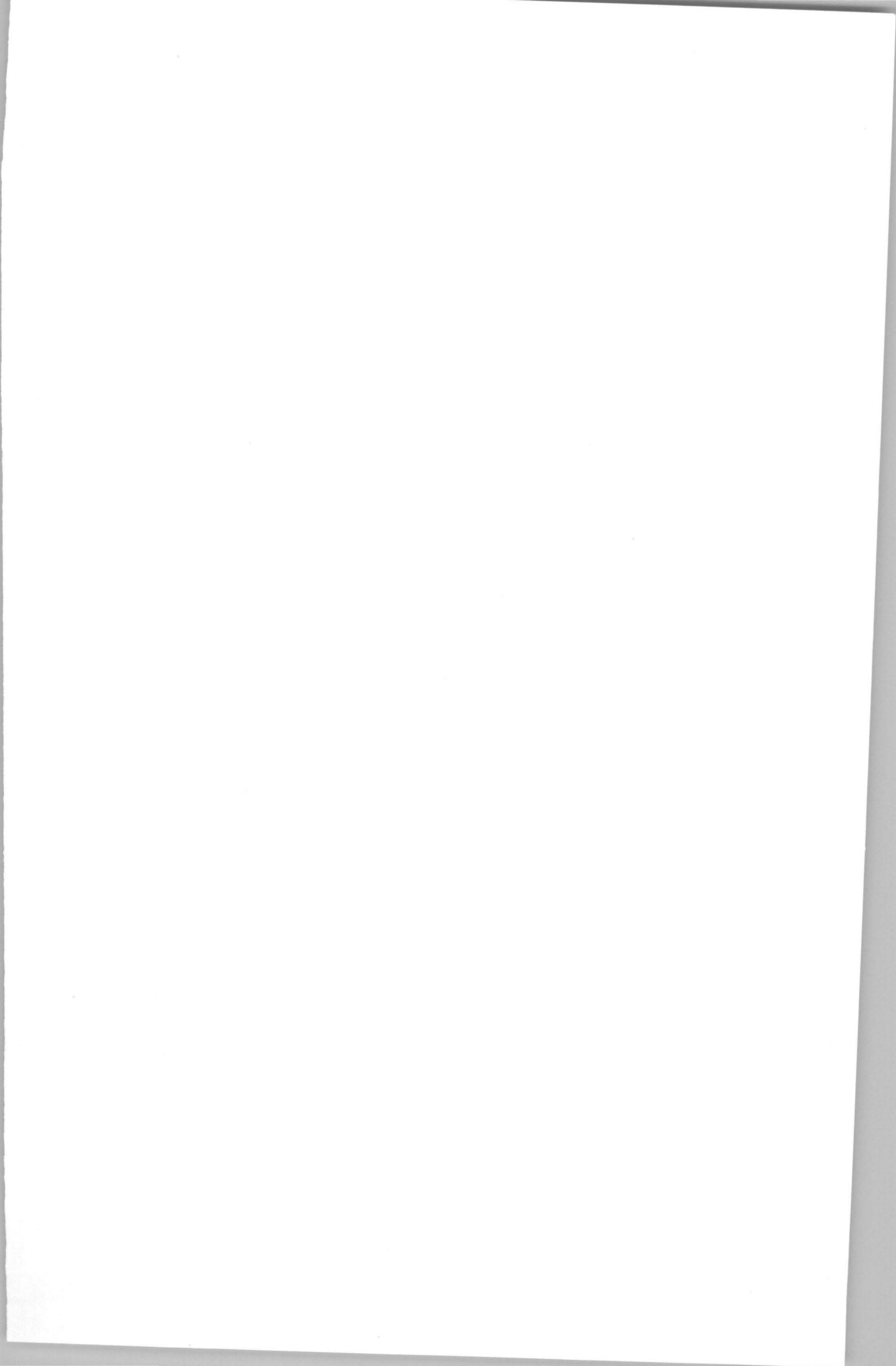
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## APPENDICES

### APPENDIX A

**Table A 4.7: Validation of the Spreading Rate Model Using the Data Collected from Other Crude Oils.**

temp (°C)	ST(mN/m)	vis(mm <sup>2</sup> /s)	sp gravity	rate(cm/s)	Simulated Rate (cm/s)	Relative error	%error
x1	x2	x3	x4	$\bar{R}$	$\hat{R}$	E	E%
Ogara well							
20	0.0834	6.13	0.9999	2.6811	2.9492	0.2681	9.99%
25	0.0771	5.86	0.9857	2.7065	3.1125	0.4060	15%
30	0.0671	5.47	0.9025	2.7616	3.1482	0.3866	13.99%
35	0.0602	5.02	0.8945	2.8758	3.2784	0.4026	13.99%
40	0.0599	4.76	0.8235	2.8998	3.3348	0.4350	15%
45	0.0484	4.12	0.7989	3.0669	3.4043	0.3374	11%
50	0.0435	3.89	0.7346	3.0939	3.4652	0.3713	12%
55	0.0387	3.25	0.6892	3.0961	3.4986	0.4025	13%
60	0.0345	2.95	0.6102	3.1963	3.5159	0.3196	9.99%
65	0.0302	2.38	0.5928	3.2318	3.6159	0.3841	11.88%
nembe							
20	0.0834	6.13	0.9999	2.6065	2.9714	0.3649	13.99%
25	0.0771	5.86	0.9857	2.7000	3.0241	0.3241	12%
30	0.0671	5.22	0.8769	2.8073	3.1722	0.2992	10.66%
35	0.0602	4.98	0.8432	2.8682	3.2411	0.3729	13.03%
40	0.0599	4.02	0.7893	2.9889	3.4074	0.4185	14%
45	0.0484	3.56	0.7011	3.0616	3.4290	0.3674	12%
50	0.0435	3.19	0.6227	3.1461	3.4922	0.3461	11%
55	0.0387	2.99	0.5378	3.1901	3.5538	0.3637	11.4%
60	0.0345	1.09	0.4777	3.2107	3.6377	0.4270	13.30%
65	0.0302	1	0.1234	3.2749	3.6515	0.3766	11.50%
kolo creek							
20	0.0496	4.93	1.9999	2.3895	2.7240	0.3345	13.99%
25	0.0459	4.19	0.9897	2.5044	2.8049	0.2609	10.42%
30	0.0448	3.61	0.8941	2.5542	2.8096	0.2554	9.99%
35	0.0368	3.14	0.8412	2.5729	2.8817	0.3088	12%
40	0.0301	2.75	0.7998	2.6129	2.9787	0.3658	13.99%
45	0.0298	2.43	0.7558	2.6783	3.0801	0.3079	11.50%
50	0.0178	2.17	0.6909	2.7217	3.1572	0.4355	16%
55	0.0018	1.96	0.6024	2.8065	3.1994	0.3929	13.99%
60	0.0014	1.77	0.5728	2.8930	3.3269	0.4339	14.99%
65	0.0011	1.61	0.5299	3.0386	3.4336	0.3950	12.99%

**Table A 4.8: Validation of the Spreading Rate Model Using the Data Collected from Other Crude Oils.**

temp (°C)	ST(mN/m)	vis(mm <sup>2</sup> /s)	sp gravity	rate(cm/s)	Simulated Rate (cm/s)	Relative error	% Error
x1	x2	x3	x4	$\bar{R}$	$\hat{R}$	E	E%
oguta							
x1	x2	x3	x4	y			
20	0.0498	5.3	0.9412	2.3493	2.7252	0.3759	16%
25	0.0496	4.8	0.9311	2.4754	2.8447	0.3693	14.92%
30	0.0363	4.4	0.921	2.5539	2.9881	0.4342	17%
35	0.0362	4	0.8679	2.6656	3.0654	0.3998	14.99%
40	0.0346	3.9	0.8598	2.8287	3.1964	0.3677	12.99%
45	0.0320	3.1	0.7999	2.8997	3.2477	0.3480	12%
50	0.0310	2.6	0.7456	2.9720	3.2990	0.3270	11%
55	0.0289	2.4	0.7112	3.0565	3.4233	0.3668	12%
60	0.0211	2.3	0.6721	3.1977	3.5494	0.3517	10.99%
65	0.0200	1.9	0.5914	3.2114	3.5646	0.3532	10.99%
umuchem							
20	0.0667	4.71	0.9899	2.3203	2.6684	0.3481	15%
25	0.0516	4.19	0.9019	2.3889	2.6995	0.3106	13%
30	0.05035	3.77	0.8879	2.4451	2.7874	0.3423	13.99%
35	0.0482	3.38	0.8797	2.6536	2.9720	0.3184	11.99%
40	0.0458	3.01	0.8587	2.6960	3.1004	0.4044	15%
45	0.0325	2.97	0.7577	2.8218	3.1322	0.3104	11%
50	0.0289	2.84	0.7174	2.8864	3.2616	0.3752	12.99%
55	0.0257	2.34	0.6451	2.9972	3.2969	0.2997	9.99%
60	0.0128	1.9	0.5864	2.9995	3.3594	0.3599	11.99%
65	0.017	1.5	0.5102	3.0611	3.4590	0.39799	12.99%
qua iboe upenek							
20	0.0742	5.25	1.0029	2.4194	2.7823	0.3629	15.25%
25	0.0687	4.62	0.9987	2.5621	2.8952	0.3331	13%
30	0.0597	4.21	0.9882	2.6915	3.0386	0.3471	12.90%
35	0.0536	4.01	0.8808	2.8039	3.1404	0.3365	12%
40	0.048	3.39	0.8618	2.9100	3.2302	0.3202	10.99%
45	0.0431	3.03	0.7904	2.9438	3.2676	0.3238	10.99%
50	0.0358	2.44	0.7101	2.9871	3.4053	0.4182	14%
55	0.0229	2.19	0.6367	3.1003	3.4724	0.3721	12%
60	0.0121	1.63	0.3451	3.1674	3.5792	0.4246	13.41%
65	0.0101	1.01	0.2222	3.3663	3.7366	0.3703	11%

**Table A 4.9: Validation of the Spreading Rate Model Using the Data Collected from Other Crude Oils.**

temp (°C)	ST(mN/m)	vis(mm <sup>2</sup> /s)	sp gravity	rate(cm/s)	Simulated rate (cm/s)	Relative error	% Error
x1	x2	x3	x4	$\bar{R}$	$\hat{R}$	E	E%
Owaza well 23							
20	0.0827	5.87	0.9999	2.5106	2.8997	0.3891	15.50%
25	0.0766	5.25	0.996	2.6226	3.0107	0.3881	14.79%
30	0.0687	5.01	0.9972	2.8211	3.2019	0.3808	13.49%
35	0.0599	4.58	0.9016	2.8935	3.2118	0.3183	11%
40	0.0535	4.01	0.8611	2.9322	3.2723	0.3401	11.60%
45	0.0481	3.89	0.8588	3.0308	3.4672	0.4364	14.36%
50	0.0431	3.48	0.8064	3.1517	3.5288	0.3771	11.96%
55	0.0401	3.11	0.7225	3.1676	3.5382	0.3706	11.70%
60	0.0385	2.76	0.6454	3.2339	3.5573	0.3234	10%
65	0.0345	2.38	0.5761	3.2594	3.5853	0.3259	9.89%
owaza well 22							
20	0.0734	6.61	0.9999	2.6393	3.0431	0.4038	15.29%
25	0.0661	5.71	0.9706	2.6844	3.0656	0.3812	11.96%
30	0.0592	5.12	0.8773	2.7802	3.1138	0.3118	11.22%
35	0.0485	4.75	0.8298	2.8382	3.2072	0.3690	13%
40	0.0467	4.35	0.8174	2.9276	3.2613	0.3337	11.40%
45	0.0371	3.98	0.7978	3.0754	3.3829	0.3075	9.99%
50	0.0329	3.47	0.7389	3.1009	3.4110	0.3101	10%
55	0.0293	3.01	0.6999	3.1134	3.4870	0.3736	11.99%
60	0.0253	2.85	0.6358	3.1381	3.5523	0.4142	13.20%
65	0.0225	2.37	0.5989	3.2093	3.6265	0.4172	12.99%
obagi well 35							
20	0.0922	7.49	0.9889	2.7629	3.1911	0.4282	15.49%
25	0.0895	7.01	0.9576	2.8696	3.2828	0.4132	14.40%
30	0.0854	6.83	0.9025	2.9945	3.3838	0.3893	13%
35	0.0819	6.25	0.8896	3.1056	3.4783	0.3727	12%
40	0.0766	5.86	0.8708	3.1536	3.5951	0.4415	13.99%
45	0.0681	5.28	0.8108	3.2203	3.6228	0.4025	12.49%
50	0.0610	4.79	0.7523	3.3518	3.7205	0.3687	11%
55	0.0570	4.34	0.7011	3.3717	3.8168	0.4451	13.20%
60	0.0523	3.93	0.6832	3.4756	3.9135	0.4379	12.59%
65	0.0492	3.37	0.6189	3.6017	3.9979	0.3962	11%

Table A 4.10 Validation of the Spreading Rate Model Using the Data Collected from Other Crude Oils.

temp (°C)	ST(mN/m)	vis(mm <sup>2</sup> /s)	sp gravity	rate(cm/s)	calculated rate (cm/s)	Relative error	% Error
x1	x2	x3	x4	$\bar{R}$	$\hat{R}$	E	E%
egbema							
20	1.1136	25.3	0.9999	4.7095	5.4159	0.7064	14.99%
25	1.1135	25.1	0.9998	4.0840	4.6215	0.2185	5.35%
30	0.9988	16.4	0.9997	3.9038	4.3722	0.4684	11.99%
35	0.9101	15	0.9876	3.7476	4.3472	0.5996	15.99%
40	0.8655	12.9	0.8686	3.4951	3.9844	0.4893	13.99%
45	0.7658	11.1	0.8434	3.4149	3.9613	0.5464	16%
50	0.6532	10.6	0.7916	3.4147	3.9611	0.5441	15.93%
55	0.2345	9.9	0.5979	3.4062	3.8831	0.4769	14%
60	0.1234	8.3	0.5358	3.3875	3.8279	0.4404	13%
65	0.0325	8.01	0.4675	3.3342	3.8011	0.4669	14%
forcados							
20	0.0553	6.73	0.9999	2.6695	3.0699	0.4004	14.99%
25	0.0527	6.01	0.9785	2.7754	3.1363	0.3609	13.52%
30	0.0488	5.53	0.9011	2.8225	3.1612	0.3387	12%
35	0.0481	5.01	0.8412	2.8798	3.1956	0.3158	10.96%
40	0.0451	4.50	0.8123	2.9000	3.2771	0.3771	13%
45	0.0414	4.0	0.7456	2.9709	3.2977	0.3268	11%
50	0.0298	3.65	0.7121	2.9776	3.3945	0.4169	14%
55	0.0198	3.15	0.6998	3.1315	3.5073	0.3758	12%
60	0.0114	3.05	0.6001	3.1635	3.5115	0.3480	11%
65	0.0111	2.85	0.5421	3.1865	3.5689	0.3824	12%
qua iboe light							
20	0.0453	5.63	0.9411	2.1977	2.5273	0.3296	14.99%
25	0.0432	5.07	0.9002	2.2534	2.5463	0.2929	12.99%
30	0.04	4.54	0.8923	2.3103	2.5876	0.2773	12%
35	0.0391	4	0.8821	2.3445	2.6024	0.2579	11%
40	0.0364	3.75	0.8632	2.3705	2.6312	0.2803	11.82%
45	0.0333	3.55	0.8001	2.3881	2.6508	0.2627	11%
50	0.0141	3.04	0.7501	2.5436	2.8234	0.2800	11%
55	0.0013	2.5	0.4811	2.6431	2.9867	0.3436	12.99%
60	0.0014	2.09	0.3441	2.8409	3.1534	0.3125	11%
65	0.0016	1	0.2211	3.1025	3.5369	0.4344	14%



Table A 4.11 Validation of the Spreading Rate Model Using the Data Collected from Other Crude Oils.

temp (°C)	ST(mN/m)	vis(mm <sup>2</sup> /s)	sp gravity	rate(cm/s)	calculated rate (cm/s)	Relativ e error  E	% Error E%
x1	x2	x3	x4	$\bar{R}$	$\hat{R}$		
				obagi well	40		
20	0.0614	6.73	0.9911	2.6813	3.0567	0.3754	14
25	0.0586	6.01	0.9906	2.7699	3.1522	0.3823	13.80
30	0.0542	5.75	0.8884	2.8212	3.1795	0.3583	12.70
35	0.0464	5.02	0.8601	2.8562	3.2275	0.3713	12.99
40	0.04	4.86	0.7937	2.9783	3.3059	0.3276	10.99
45	0.0399	4.34	0.7403	2.9814	3.3392	0.3578	12.00
50	0.0365	3.99	0.6881	3.0065	3.3974	0.3909	13.00
55	0.0299	3.58	0.6305	3.0401	3.4353	0.3943	12.97
60	0.0293	3.03	0.5901	3.0926	3.4884	0.3958	12.80
65	0.0287	2.92	0.5403	3.1639	3.5752	0.4113	12.99
				idu	ekpeye		
20	0.09291	8.87	0.9902	3.0003	3.4443	0.4413	14.71
25	0.0968	8.11	0.9901	3.1012	3.5385	0.4373	14.10
30	0.09461	7.99	0.8991	3.1500	3.5784	0.4284	13.60
35	0.9174	7.68	0.8987	3.3003	3.7393	0.4390	13.30
40	0.0896	7.25	0.8894	3.4056	3.8620	0.4564	13.40
45	0.0821	6.97	0.8795	3.5436	4.0114	0.4678	13.20
50	0.0793	6.38	0.8501	3.5637	4.0626	0.4989	13.99
55	0.0721	5.99	0.8498	3.7097	4.2142	0.5045	13.59
60	0.0699	5.48	0.8036	3.8166	4.2364	0.4198	10.99
65	0.0625	5.03	0.7894	3.9524	4.3476	0.3952	9.99

## APPENDIX B

### PROGRAM FOR THE PREDICTION OF THE SPREADING RATE OF NIGERIAN CRUDE OILS ON SEA WATER.

Dim x1

Dim x2

Dim x3

Dim x4

Dim R

Dim E

Dim R\_exp

Dim E\_per

Private Sub Check1\_Click()

Text5.Enabled = True

Text5.BackColor = RGB(255, 255, 255)

End Sub

Private Sub Command1\_Click()

End

End Sub

Private Sub Command2\_Click()

R = Round((5.7199 + 0.3151 \* x1 + 0.6242 \* x2 + 1.2278 \* x3 + 2.5603 \* x4 + 0.0144 \* x1 \* x2 - 0.024 \* x1 \* x3 + 0.1543 \* x1 \* x4 - 0.0336 \* x2 \* x3 + 0.3256 \* x2 \* x4 + 0.7001 \* x3 \* x4 - 0.0059 \* x1 \* x2 \* x3 + 0.004 \* x1 \* x2 \* x4 + 0.0253 \* x1 \* x3 \* x4 + 0.0122 \* x2 \* x3 \* x4 - 0.0186 \* x1 \* x2 \* x3 \* x4 + E) / 10, 4)

E = Round(Abs(R\_exp - R), 4)

E\_per = Round(E \* 100 / R, 2)

Label5.Caption = " R = " & R & " cm/s"

Label7.Caption = " Relative Error " & E

Label8.Caption = "% Error " & E\_per & "% "

End Sub

Private Sub Form\_Load()

E = 0

End Sub

Private Sub Text1\_LostFocus()

x1 = Val(Text1)

End Sub

Private Sub Text2\_LostFocus()

x2 = Val(Text2)

End Sub

Private Sub Text3\_LostFocus()

x3 = Val(Text3)

End Sub

Private Sub Text4\_LostFocus()

x4 = Val(Text4)

End Sub

Private Sub Text5\_LostFocus()

R\_exp = Val(Text5)

End Sub