NUCLEAR MAGNETIC RESONANCE STUDIES OF SOME NIGERIAN PETROLEUM PRODUCTS - A COMPARISON OF NMR AND CHROMATOGRAPHIC RESULTS

By

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TO

MY FAMILY, with gratitude for their never-ending patience and support during the seemingly interminable duration of this course.

D E C L A R A T I O N

I declare that this thesis is my work and has not been submitted in any form for another degree or diploma at any other University or Institution. Information derived from the published or unpublished work of others has been acknowledge in the text.

OLUFEMI S. LADEJI

Date:.....

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A B S T R A C T

Hydrocarbon-Type composition analyses by Nuclear Magnetic Resonance (NMR) technique were carried out on some Nigerian Petroleum Produces - Heavy-Naphtha, Aviation Turbine Kerosine (ATX) and straight-run kerosine.

The results were compared and correlated with corresponding results obtained from the PONA Analyser and FIA techniques (these results were obtained from the Nigerian National Petroleum Corporation Refinery, Kaduna) using a computer Regression subprogram.

Analysis of the regression output showed that there is a good fit between the NMR and the FIA data for the ATK fractions, while the fit between the NMR and PONA analyser for Heavy-Naphtha were not as good. A number of prediction equations were given based on the regression output.

The NMR technique compares favourably with the established methods and coupled with faster times of analysis, (an average of 30 to 40 minutes per sample compared to an average of 2 to 3 hours per sample for FIA technique), lower cost in terms of instrumentation and man-power. The NMR technique can be standardized

and used for hydrocarbon-type composition analysis. With consideration being given to the construction of a completely automated NMR for performing these tests, the NMR technique is on its way to being an important supplemental technique for hydrocarbon - type analysis.

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CHAPTER ONE

I N T R O D U C T I O N

SCOPE OF PROJECT

The extraction and utilization of crude petroleum has an enormous impact on the quality of life experienced by most of the citizens of the modern world. Over the years, there have been extensive studies directed towards the identification and measurement of the general classes of compounds and individual components found in crude petroleum. Detailed compositional characterization of petroleum fraction is extremely important, but has proved both difficult and time consuming. No two crude oils are identical, and therefore each oil must be evaluated for its own characteristic properties before it can be processed in the refinery. Each type of crude oil contains a large variety of compounds and it sometimes becomes difficult to classify an oil. For this reason, a number of tests or criteria are employed in classifying crudes. These analyses are very important in the refining and utilization of petroleum and petroleum products. The analytical methods for petroleum meterials are among the most standardized and well documented in analytical chemistry and are widely used throughout the world.

Inspite of all these achievements, investigations in petroleum chemistry have traditionally sought to develop new methods which give more, accurate, precise, sensitive selective, meaningful and timely results at a lower unit cost. In processing and refining, improved analytical data lead to more efficient utilization of valuable resources and lower operating cost.

Apart from its physical characteristics and effects of additives such as gum inhibitors and antiknock compounds, the quality of petroleum products depend on their chemical composition, but because petroleum products consist of a very large number of different hydrocarbons, their composition is usually expressed in terms of hydrocarbon types (saturates, Olefins and Aromatics) rather than in terms of individual hydrocarbons. Several procedures have been devised for the determination of hydrocarbon types, and of those which are standardized, the method based on Fluorescent indicator Adsorption (FIA) is the most widely employed.

The assessment of the quality of petroleum is of major concern not only to the refiner and marketer but also to the user who may be a direct consumer on a

manufacturer whose products incorporate petroleum products. Products, specifications, and consumer requirements can change. As consumers requirements change, it becomes necessary to devise more useful tests. An efficient and sound specification should embody those facts which, apart from controlling product quality, also measure independent properties with suitable precision and economy of man-power and equipment. Earlier test methods were largely empirical in nature, but with the increase in the uses to which petroleum could be put, the trend has moved towards chemical and physical analysis.

The analysis of hydrocarbon mixtues has in recent years progressed to a stage, whereby instrumental methods such as infra-red, ultra-violet mass spectrometry and nuclear magnetic resonance spectroscopy can, with their superior sensitivity, satisfy modern requirements of speed and accuracy. There are many established but unstandardized methods of analysis involving all forms of spectroscopy in which results can be recorded for immediate use or transmitted as electrical impulses for automatic control of refirery plant and product quality.

The purpose of this project was to analyse some Nigerian Petroleum Products for their hydrocarbon-type composition using the Nuclear Magnetic Resonance (NMR) spectrometric methods and, as far as possible, to describe the products in terms of a hypothetical average molecule.

Although performance tests are the ultimate criteria of quality, they are too costly, time consuming and inprecise for use as quality control tests, thus other properties must be found which can be established simply and precisely by laboratory tests and which correlate with performance. One of such method is the NMR method. The NMR method is based on calculating, from the NMR integral trace, the relative number of hydrogen and carbon atoms classified as aromatic, paraffinic or olefinic in a petroleum sample. The precision of the method of integrated intensifies of NMR signals has been satisfically assessed, and is sufficietly informative. For example, in a collaborative study in which six different Laboratories assayed identical sealed samples, a standard deviation of approximately 0.15-0.5% was found for the major constituents (1). Reports

of studies on a single instrument and on inter-laboratory studies generally indicate that a standard deviation of the mean of 0.5% is obtainable for several repetitive runs. In one study the percent of total hydrogen in chemically different sites of over twenty compounds were determined with an absolute error between theoretical and found values no greater than 0.5% (2). This example illustrates the accuracy that may be obtained with NMR spectrometric analysis. The cost of the equipment and materials in the long run are acceptable and the man-power involved in carrying out the analysis and the elapsed time of the analysis are minima.

P E T R O L E U M

1. THE OCCURRENCE AND ORIGIN OF PETROLEUM

Petroleum, etymologically, means rock oil or mineral oil, but in modern technical usage it has a wider meaning which includes, natural gas, mineral wax and bitumen in addition to crude oil. In many contexts, oil and petroleum are used interchangably. Thus to most people the oil industry and the petroleum industry are synonymous.

The origin of petroleum is not merely a matter of academic interest. The greater the advancement towards a full understanding of this complex problem, the more intenlligently and effectively can the search for new oil field be carried out.

Crude oils range widely in their physical and chemical properties. Its natural colour is most often green, brown and black although there are rare examples of white or straw coloured oils. In terms of elements, crude oils are composed principally of carbon and hydrogen, with sulphur, oxygen and nitrogen present in relatively small amounts. A wide range of metallic elements are also present in trace amounts.

Crude oil is not a uniform substance. Its appearance and characteristics vary widely from oilfie'd to oilfield and even from well to well in the same oilfield. It may not even be a homogeneous substance. One authority defines crude petroleum as follows:

"A naturally occuring mixture, consisting predominantly of hydrocarbons and/or sulphur nitrogen and/or oxygen derivatives of hydrocarbon which is removed from the earth in liquid state or is capable of being removed.

Crude petroleum is commonly accompanied by varying quantities of extraneous substances such as water, inorganic matters and gas. The removal of such extrameous substances alone thus not change the status of the mixture as crude petroleum. If such removal appreciably affects the composition of the oil mixture, then the resulting product is no longer crude petroleum." (3).

2. THE NATURE OF OIL AND GAS ACCUMULATIONS

At an early date it was recognized that hydrocarbon accumulations require the existence of a reservoir rock to store the fluids and a cap rock, to prevent their escape (4). In addition to these readily appreciated

requirements, the idea developed that there must be a source rock in which oil and gas were formed. The rocks acting as the reservoir and cap are obvious for any accumulation, the source rock for a given oil and gas accumulation is a matter of debate.

3. THE FORMATION OF OIL ACCUMULATIONS

The problem of the mode of oil accumulations has attracted attention for many years. The earlier hypothesis on the origin of petroleum postulated its generation from inorganic materials such as the action of water on metallic carbides or water and carbon dioxide interacting with alkali or alkaline earth metals. The detection of hydrocarbon materials in some meteorites and atmospheres of certain planets also leads to the suggestion that the hydrocarbons present in the premaeval earth gave rise to oil accumulations. These ideas, find few, it any supporters now. The same is true of the hypothesis that petroleum is one of the products of volcanism. This hypothesis required some improbable materials or associations and could be expected, if correct, to lead to a general pattern of oil and gas accumulations differing from that observed.

A more widely accepted hypothesis on the formation of petroleum takes as a starting point, organic matter which was converted in part to oil and gas. There are arguments about the nature of the source material, whether it was animal or vegetable or both, and about the nature of the transforming agent. Heat, bacteria, radioactivity and low temperature catalysis have all been proposed as the means of transformation.

The gas in many fields is mainly methane with small amounts of higher homologs. When oil is present, the proportion of these and other light hydrocarbons in the vapour phase rise considerably, especially when the hydrocarbon accumulation is under high pressure and relatively high temperature. Commonly, there are appreciable amounts of non-hydrocarbon gases such as nitrogen, carbon dioxide and hydrogen sulphide.

The main types of hydrocarbons present in crude oils are paraffins, naphthenes, aromatics and hybrids involving combinations of these types. Naphthenic acids, complex nitrogen compounds and mercaptans account for some of the oxygen, nitrogen and sulphur present in the crude.

Chlorophylls and porphyring have been found in small amounts in many crudes (4) These compounds indicate a contribution from plant sources, a comparatively low-temperature history and probably a reducing environment. Isoprenoid hydrocarbons have also been detected. These compounds have structures typical of substances formed bologically.

In recent years extremely sensitive analytical techniques have become available and experiments on various types of materials have shown the formation of some hydrocarbons which occur in petroleum. For example, Toluene was produced from β - carotene at the sequence of temperature 188°, 150° and 119°C. Comparable results were obtained when carotenoids were thermally degraded in mud. Behenic acid heated under pressure (200 °C) in the presence of liquid water and clay was decarboxylated to give paraffin hydrocarbons as the main products. These and many others has been helpful supports for the biological origin of petroleum.

Animal and vegetable matters contain several main types of compounds; fats, proteins and carbohydrates. Fats are the nearest in composition to hydrocarbons; and

there has been a tendency to consider them to be of prime importance in oil formation. Proteins are more easily attacked by bacteria and the same is true of carbohydrates.

Laboratory and other observations made on the effects of bacteria on various organic substances does not support a direct bacteria formation of petroleum, although certain considerations suggest that anaerobic conditions would probably exist in rocks thought to be involved in the formation of oil and gas.

On the basis of laboratory studies, experiments employing radioactive materials on organic compounds have produced methane, carbon dioxide, hydrogen and other gaseous products. Nonetheless, hydrogen is conspiquously absent in gases associated with petroleum. Studies on the rates of production of hydrocarbons in some shale containing organic matter indicated that long geological periods were necessary for the formation of appreciable amounts of hydrocarbons. In view of the apparent requirements that oil should be available early in the history of the sediments, it is unlikely that radioactivity contributed significantly to oil formation.

The use of mineral catalyst, some of them of clay type, have led to suggestions that such catalyst play a part in oil formation. Investigations have shown that the presence of clay minerals and water affects reactions involving crude oils or their possible antecedents. Should all of these observations be generally applicable, it is reasonable to infer that some changes did took place in the sediments in the course of deep burial. Circumstantial and experimental evidences suggest that the modest increases in temperature played the principal role in causing the changes .

Hydrocarbons in commercially significant quantities are found in sedimentary rocks with a few exceptions. This is supported by factual data from over 100 years of exploration activities throughout the world. The negative information that oil and gas are not found in significant quantities in igneous or metamorphic rocks not contiquous with sedimentary rocks also confirms the sedimentary origin of the hydrocarbons in which the oil industry is interested. Experience and theoretical reasoning suggest that oil formation in commercial qualities require some minimum thickness of overlying rock to provide the source material,

temperature and pressure necessary for oil formation. Many of the details of the processes of oil formation still remain matters of speculation.

4. CONSTITUENTS OF CRUDE OILS

The main constituent of crude oils are the hydrocarbons, and theyaccount for over 75% of the composition. The other elements present, (sulphur, nitrogen and oxygen) appear in the form of organic compounds which, in some cases, form complexes with metals as in the case of the metal porphyrins. Metals can also appear as salts of organic acids. Inorganic sulphur can be present as elemental sulphur or as hydrogen sulphide dissolved in the oil.

The proportion of the main types of hydrocarbons vary from one crude oil to another and this property have been used as a basis for broad classification of crude oils into paraffin base, mixed base and Asphalt base. Many members of each type are present, and crude oils are complex by reason of the number and variety of the compounds the contain.

The table below shows the elements present in crude oils (3).

TABLE 1

ULTIMATE (ELEMENTAL) ANALYSIS OF CRUDE OILS

ELEMENTS	PERCENTAGE (Wt)
Carbon	83.90 - 86.80
Hydrogen	11.40 - 14.00
Sulphur	0.06 - 8.00
Nitrogen	0.11 - 1.70
Oxygen	0.50
Metals (Fe,V,Ni etc)	0.03

A look at the above table shows that the elements present in crude oils vary only between narrow limits. This seems to contradict the earlier assertion that crude oils vary widely in composition. This apparent contradiction was explained by C.F. Mabery who proposed that "crude oils are mainly composed of hydrocarbons belonging to a few homologous series, with individual members of each type being quite numerous." (3). In this way the differences between crude oils could be explained by the relative amounts of the series present in a given oil,

and the extent to which individual members of the series appear in the crude. This proposal has been verified by modern studies.

HYDROCARBONS: The hydrocarbons present in crude oils range from methane up to molecules containing 60 or more carbon atoms i.e. a range of molecular weights from 16 up to 850 or more. They are members of the homologous series of even hydrogen numbers.

$C_nH_{2n + 2}$

C_nH_{2n}

$C_nH_{2n - 2}$

.....

.....

$C_nH_{2n - 30}$

or lower in hydrogen content.

The homologous series are grouped into main classes, defined as follows.

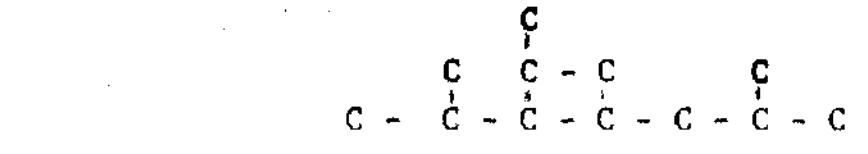
i. Normal or straight Chain Paraffins (n-Alkanes): These are saturated hydrocarbons with open-chain-carbon skeleton.

C - C - C - C - C - C

i. Normal Paraffin.

The presence of members of this series from C_1 to C_{42} has been established and most have been isolated. They are important constituents of light crudes (paraffin crudes) particularly in low boiling fractions. Their concentration decreases progressively with increasing molecular weight of the fraction.

ii. Branched - Chain Paraffins (iso paraffins, iso-alkanes) saturated hydrocarbons with one or more alkyl side chains.

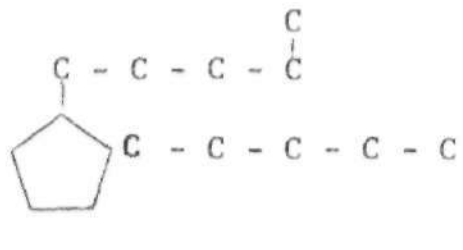


ii Isoparaffin

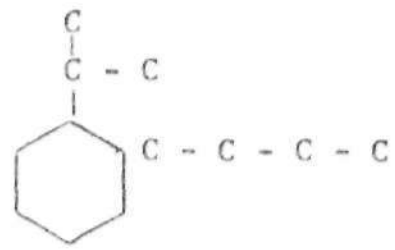
The predominant members of this class are those with slight degree of branching particularly the 2-methyl (iso-compounds) and 3-methyl (ante-iso-compounds) types. In refined products, particularly, gasolines, iso-paraffins with high degree of branching are very important constituent.

iii. Naphtheness (cycloparaffins, cycloalkanes): These are molecules with one or more saturated rings, and possibly alkyl side chains. The cyclopentanes (iii) and cyclohexanes

(iv) are predominant.



iii Alkylcyclopentane

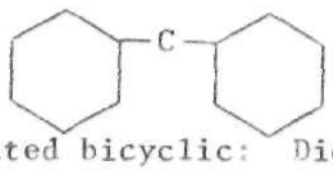


iv Alkylcyclohexane

Traces of cycloheptane derivatives have also been detected.

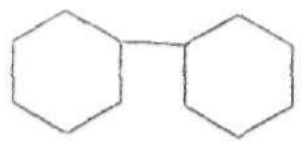
Different types of compounds can exists with two or more naphthenic rings in the molecule, depending on the way in which the rings are linked.

(a) Isolated rings: The naphthenic rings are separated by paraffin chains.



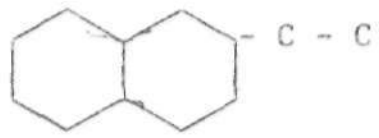
v. Isolated bicyclic: Dicyclohexyl alkane.

(b) Conjugated rings: Rings link by a bond between a carbon atom on one ring and a carbon atom on another ring.



vi. Conjugated bicyclic: Alkyldicyclohexyl

(c) Condensed Rings: Two or more rings with at least two vicinal carbon atoms in common.

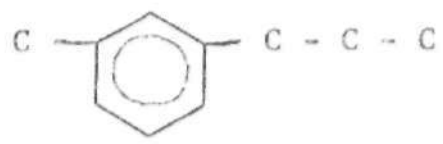


vii. Condensed bicyclic: Alkyldecalin

Bicyclic naphthenes are important constituents of kerosine and gas-oil fractions. Tetracyclic and pentacyclic naphthenes have been identified and isolated from lubricating oils and there is analytical evidence that in such fractions compounds of up to ten condensed rings do exist.

The general formula for the naphthenes is $C_nH_{2n+2-2R_N}$ where R_N is the number of naphthenic rings in the molecule.

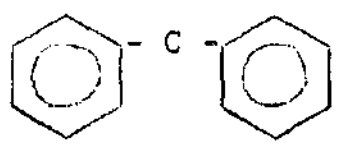
iv. Aromatics (Arenes): hydrocarbons with at least one benzene ring in the molecule



viii Monocyclic Aromatic: Alkyl benzene

For molecules containing more than one benzene ring the same considerations as indicated for poly nuclear naphthenes apply. i.e.:

isolated rings as in poly phemyl alkanes

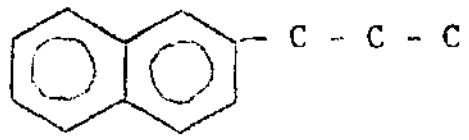


ix isolated bicyclic: Diphenyl alkane.

Conjugated rings as in alkyldiphenyls.



x. Conjugated bicyclic: Alkyl diphenyl or condensed aromatic rings as in naphthalenes



xi. Condensed bicyclic : Alkyl naphthalene.

The condensation can be ortho - in which the two benene rings share two vicinal carbon atoms as in naphthalene, anthracene etc or ortho- and peri-condensations in which one carbon atom of a ring is shared by

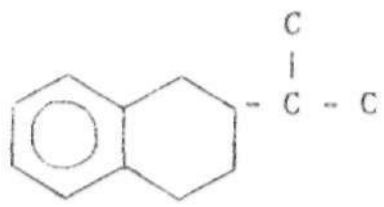
more than two rings e.g. Pyrene.

The general formula of ortho- condensed aromatic molecule is

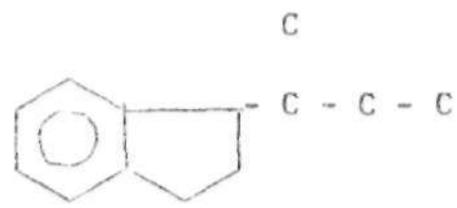
$$C_nH_{2n+2-6R_A-2R_{AS}}$$

where R_A is the number of aromatic rings and R_{AS} is the number of "substantial aromatic ring" i.e. the first benzene ring in an ortho- condensed group.

v. Mixed Naphtheno-aromatics: These are compounds containing naphthanic and aromatic rings and alkyl side chains in the same molecule. As a class these appear in the kerosine fractions, increasing in concentrations in the higher boiling fractions and residue. In kerosine and light gas oils, tetralin, indane, and their homologs have been separated and identified.



xii. Alkyl tetralin



xiii. Alkyl indane.

NON-HYDROCARBONS: Crude oils contains appreciable amounts of organic non-hydrocarbon constituents, mainly sulphur, nitrogen and oxygen - containing compounds and in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension.

Although their concentrations may be quite small, their influence is important. For example, in refining operation, the deposition of inorganic salts present in the crude can cause serious breakdowns; thermal decomposition of deposited inorganic chlorides with evolution of free hydrochloric acid can give rise to serious corrosion problems in the distillation equipment. Acidic organic components (mercaptans and acids) can also promote metallic corrosion. Deposition of traces of metals can cause passivation and/or poisoning of cracking catalysts. In finished products the presence of traces of non-hydrocarbons may impart objectionable characteristics: discolouration, lack of stability on storage, etc.

It is obvious that a more extensive knowledge of these compounds and of their characteristics would result in improved refining methods and finished products of better quality.

5. PETROLEUM REFINERY PROCESSES

The flow diagram below gives a simplified overview of Petroleum refinery operations.

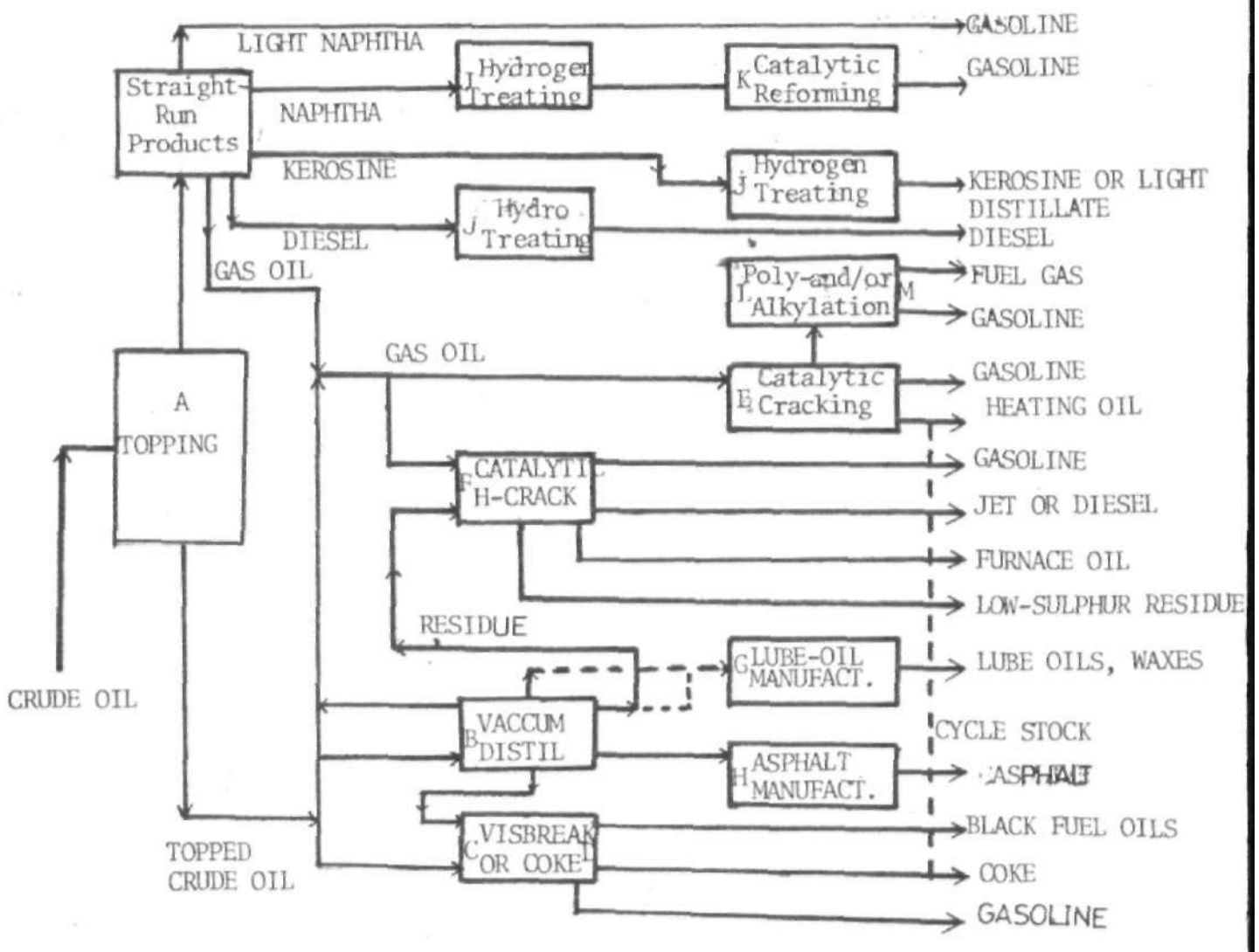


Fig.1 BASIC REFINERY OPERATIONS

Essentially all crude oils are subjected first to a distillation at near at atmospheric pressure known as topping or crude distillation. The residue or topped crude oil is further reduced or processed in five main ways:

(1) Viscosity breaking (C) or coking (D) or vacuum distillation (B) followed by

(2) Catalytic cracking (E),

(3) hydrocracking (f)

(4) Lubricating oil manufacture (G) and

(5) ashphalt manufacture (H).

Possibly significant amout of residue will soon be directly hydrocracked (F) for the production of low sulphur residual fuel oil.

The lowest - boiling straight-run product of topping (A) known as light naphtha usually goes directly into gasoline. The other straight run products (diesel fuel and kerosine or light distillate) are usually desulphurized or treated with hydrogen (J) and the heavy naphtha must be catalytically reformed (K) to improve its octane number.

The highest-boiling straight run product - gas oil (both from topping and vacuum flashing) constitute the feed stock to catalytic cracking (E) or hydrocracking (F).

Olefin gases are assemble from all decomposition (C, D & E) for pdymerization (L) or more often alkylation (M) into the boiling range of gasoline and in the case of alkylation the isobutane is also assembled from operations F and K as well as C, D and E.

Finally about 2% of lubricating oils and wax (G) are produced.

6. CRUDE OIL PROCESSING SCHEME OF NNPC REFINERY KADUNA

The Kaduna Refinery is designed to process two types of crude oils: The Nigerian Light Crude and imported heavy crude. The Nigerian Light crude which is basically naphthenic, is reserved for the manufacture of fuel products; the imported heavy crude which is paraffinic is on the other hand used mainly for the production of lubricating oils, waxes and asphalt. Consequently the refinery has two process sections - the Fuel Section and the Lubricating oil, Wax and Asphalt Section.

The flow diagram below gives a schematic outline of the crude oil processing scheme of NNPC Refinery Kaduna.

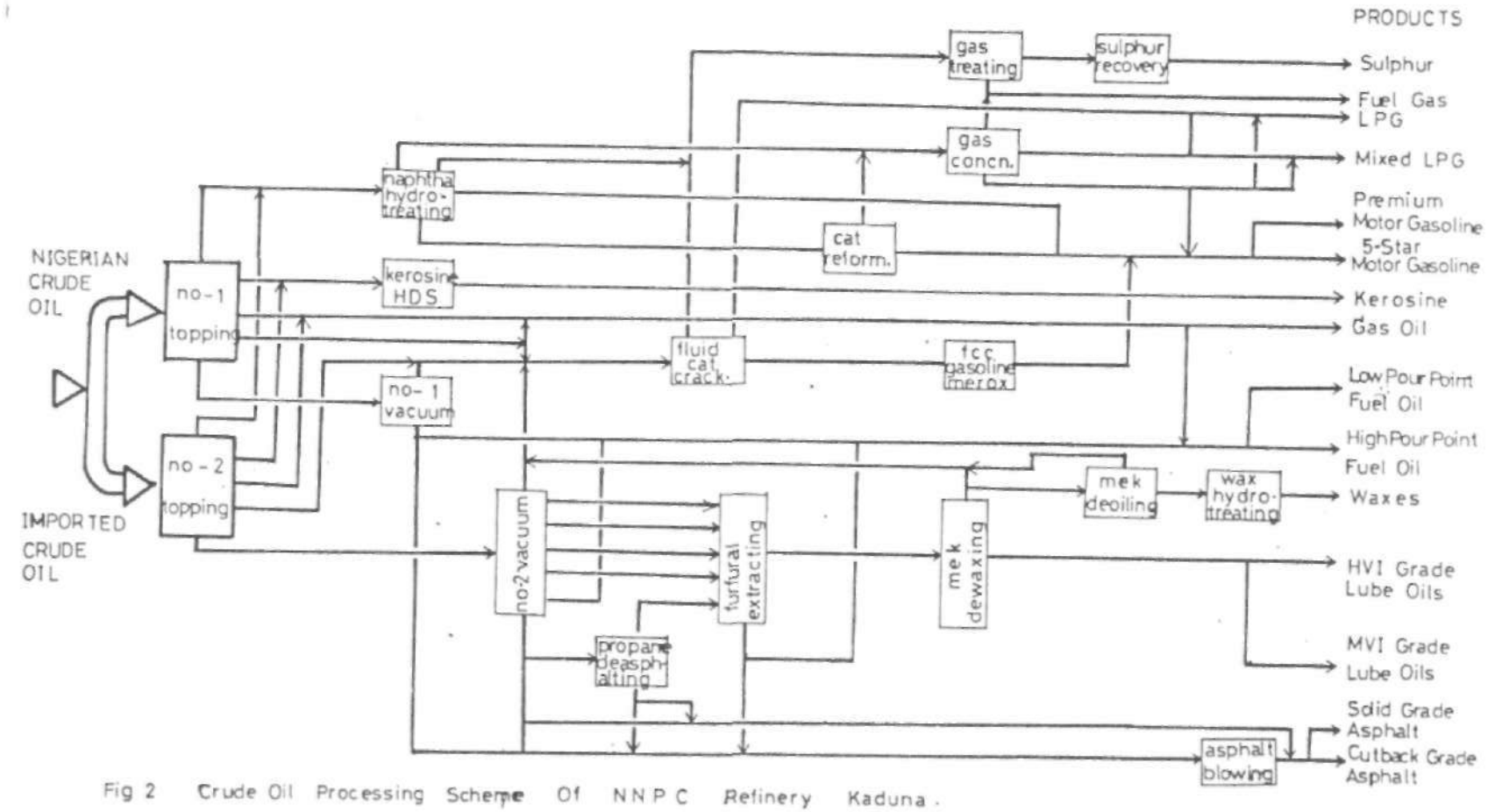


Fig 2 Crude Oil Processing Scheme Of NNPC Refinery Kaduna.

FUEL SECTION: The fuel section of the Kaduna Refinery is designed to process Nigerian crudes in the Crude Atmospheric and Vacuum distillation Units while the rest of the Fuel section is designed to process a mixture of fractions from the domestic crude as well as from the imported crude used in the Lube section.

The fuel section incorporates the following process units.

Crude Distillation Unit No 1	Vacuum Distillation Unit No 1
Naphtha Hydrotreating Unit	Fluid Catalytic Cruding Unit
Catalytic Reforming Unit	Gas Treating Unit
Kerosene Hydrodesulphurisation Unit.	FCC Gasoline Merox Unit
Gas concentration Unit	Sulphur Recovery Unit.

The Crude is preheated in a heat exchange or train. The pre-heated crude is fed to the desalter to remove salts and water after which it is partially vaporized in a furnace before being fed to the distillation column where separation into various intermediate products take place. The intermediate products include whole naphtla, kerosene, Ligh and Heavy gas oils and reduced crude.

The reduced crude from CDU - 1 is processed further in the vacuum Distillation Unit No 1 (VDU - 1) which separates it into vacuum gas oil, which is the main feed to the Fluid catalytic cracking unit. The vacuum residue is used either as fuel oil blend or for the production of asphalt.

The combined whole naphtha from the two crude distillation units (CDU-1 and CDU-2) are routed to the Naphtha Hydrotreating Unit (NHU) where the naphtha is hydrotreated to eliminate substances which would deactivate and poison the reformer catalyst. The stabilized whole naphtha is split into light and Heavy Naphtha. The Light naphtha is sent to gasoline blending to be used directly as a component for gasoline production while the heavy naphtha is the reformer feed.

The catalytic Reforming Unit (CRU) restructures the hydrocarbons in the heavy napttha and converts the naphtha into Reformate, which by virtue of its very high aromatic and isoparaffinic content has an octane number of nearly 100 and is an important component of super and 5-star gasolines.

The Fluid catalytic cracking Unit (FCC) upgrades heavier distillates into more valuable lighter products

mainly gasoline and LPG and a substantial amount of fuel gas. The FCC Gasoline Merox Unit is to treat the cracked naphtha from the FCC before the former is routed to Gasoline blending.

LUBE OIL. WAX AND ASPHALT SECTION:

The Lube Oil, Wax and Asphalt section consist basically of the following Units:

Crude Distillation Unit No. 2	MEK Deoiling Unit
Vacuum Distillation Unit No 2	Wax Hydrotreating Unit
Propane Deasphalting Unit	Hot oil system.
Furfural Extraction Unit	Sour water stripper
MEK Dewaxing Unit	Asphalt Blowing Unit

The Imported Crude oil first undergoes processing in the Crude Distillation Unit No. 2. The naphtha Kerosene Light gas oil and heavy gas oil are steam stripped to produce more stable products and then charged to the fuel section of the refinery for further processing.

The reduced crude oil from CDU - 2 is then fed into the VDU-2 which consist of two vacuum fractionating columns arranged in series. Three product streams are obtained. They are: Light Spindle Oil (LSPO). Heavy Spindle Oil (HSPO) and Light Machine Oil (LMO). The products are

stabilized by steam stripping and then pumped into intermediate tankage.

The Lubricating oils are further treated in the MEK Dewaxing Unit (MDU) to removed paraffinic hydrocarbons while makes the product usually waxy and of high pour point. The process of achieving this utilizes Methyl-Ethyl-ketone as solvent hence the name MEK Dewaxing.

The production of base waxes of various melting-point specifications is done by removing almost all the oil left in the wax to acceptable limits in the MEK Deoiling Unit.

PRODUCTS: Based on 50,000 barrel per stream day (BPSD) of Nigerian Crude Oil and 50,000 BPSD of imported Crude Oil, the following products in tons per annum will be manufactured:

LPG - Propane/Butane Mixture	10,000
Gasoline - Super and 5 star	1,211,000
Kerosene - Dual purpose	614,000
Gas oil	888,000
Fuel Oil - Low and High pour Point	415,000
Lubricating Oil (Base Oils)	250,000
Wax (Basic)	24,000
Asphalt - Solid and Cut back	690,000
Sulphur	2,200

7. PETROLEUM PRODUCTS

Approximately, 2500 products are currently produced wholly or in part from petroleum, in addition to 3000 petrochemicals. In the early days of petroleum refining, it was simple to pinpoint the major markets of the petroleum industry - illuminants and lubricants. Now petroleum products supply power for a vast transportation network, factories and farms; the heat for homes and large buildings; the lubricants for many industries; the material for highway, road and street networks; and feedstock for many industries.

Under the petroleum refinery processes, the major petroleum products are shown as they are formed in the course of refining operations - distillation, cracking solvent refining and chemical treatments. To the consumer, however, this information is insufficient; it must be supplemented by data on those critical properties that make product suitable or unsuitable for a given end use.

Because of the multiplicity of market requirements, a refinery will primarily produce a range of blending fractions for each product range, any particular requirement being met by mixing suitable blending stocks and additives

rather than by making the product in a primary refinery operation. Many of the petroleum products of commerce are therefore blended, compounded or otherwise modified materials and not the primary stocks as they come from the petroleum refining plants. Still further complications stem from the fact that the trade names under which the customer knoens andbuy the products are not necessarily the refiners' names, and there may be more than one trade name designation of the same basic product depending upon the end use.

The exact nature and quality of each refining product is dictated by the specifications imposed upon the commercial products by reputable international bodies. The table below lists some of the more important specifications for a typical petroleum product (Aviation Turbine Fuels) given by the American Society for Testing and Materials (5). These specifications give an idea of the nature of the commercial petroleum products.

TABLE II

SPECIFICATIONS OF AVIATION TURBINE FUELS

(ASTM D-566)

	TYPES[a]		
PROPERTIES	JET A	JET A-1	JET B
gravity °API	51-39	51-39	57-45
distillation, °F			
10% evaporated, max	400	400	

PROPERTIES	TYPES[a] JET A	JET A-1	JET B
20%, evaporated, max			290
50% evaporated, max	450	450	370
90% evaporated, max			470
Final boiling point, max	550	550	
Vapour pressure, max, psi			3
Flash point, °F	110-150	110-150	
Freezing point, max °F	-36	-54	-56
Viscosity, kinematic, max, CS at -30°F	15	15	
net heat of combustion, min, Btu/16	.....	18,400	.....
Sulphur, max, wt%	.....	0.3	.....
water tolerance, max, ml	.....	± 1	.....
gum, existent, max, mg/100 ml	.....	7	.....
Aromatics, max, vol %	.....	20	.....

[a] Jet A is a kerosine fuel of high flash point (for somewhat greater safely against fire) Jet A-1 is similar to Jet A but it has a lower freezing point for use at lower temperature. Jet B is a wide boiling - range, volatile distillate containing both gasoline-range and kerosine-range fractions with a very low freezing point.

The petroleum products of interest in this study are Heavy naphtha, Aviation Turbine Kerosine and straight run kerosine, all products of the Nigerian National Petroleum Corporation Refinery in Kaduna.

The section on the petroleum refinery process gave a simplified overview of the refinery process and the various products. This section aims at providing a brief description of these products..

HEAVY NAPTHA: Naphtha is one of the products (straight run products) of crude distillation. Other products include light gasoline, diesel fuel, kerosin and gas oil.

The naphtha is of very low octane number about 40 compared with a market demand, by which process octane numbers of 95 to 105 canbe obtained. The "reformate" is blended with the more volatile light gasoline to give gasoline of correct volatility and high octane number.

AVIATION TURBINE KEROSINE - TURBO - FUELS

The original development of the jet engine was carried out using illuminating kerosine as fuel. This was done to reduce the fire hazards in high pressure fuel systems, to conserve gasoline stocks in war time and, of course, because of its ready availability.

There are three main categories of aviation turbo-fuels, ranging from low-flash point wide-cut distillation products to high - flash point narrow cut kerosine-type materials. (see table).

Properties: A prime characteristic of a turbo fuel is that it shall be stable, clean-burning and non-corrosive to materials of construction of the aircraft engine and airframe.

An approximate distribution of the hydrocarbon types in turbo-fuels is as follows (6).

Paraffins	33 - 61% Vol.
Olefins	0.5 - 5
Naphthenes	10 - 45
Total Aromatics	12 - 25

The distribution of these hydrocarbon types vary with the crude source.

Paraffins have a high heat content on a weight basis, with nahthenes slightly less and aromatics, lowest. However, when heat of combustion is considered on volume basis, the order is changed with monocyclic aromatics having higher values than paraffins which in turn are merginally higher than naphthenes.

Aromatics have a more luminous flame than paraffins and cause smokiness, and carbon deposition. They are also better solvents and cause many elastomers present in fuel hose atimes to swell. For these reasons, an upper limit to the amount of anomatics is set in specifications. This is usually 20-25% Vol.

Olefins are limited usually to 5% vol on account of instability, - chemical reactivity and ease with which they will form gum.

The non-hydrocarbon present in turbo-fuels are compounds containing sulphur, nitrogen and oxygen. The total sulphur is limited with specifications of 0,2% wt. max. and never greater than 0.4% wt. This restricts the amount of corrosive combustion products, SO_2 or H_2SO_4 present in the combustion chamber and turbine section of the engine.

In the presence of sulphur compounds, even stable fuels are capable of absorbing oxygen when subjected to heat. This may lead to the preciptation of a solid phase insoluble in the fuel. To ensure that this does not happen, the total sulphur and mercaptan sulphur content of the fuels are strictly controlled as well as thermal stability.

Mercaptan sulphur is controlled specifically for its corrosiveness to copper and cadmium strips and for its disagreable odour. As a further protection against sulphide corrosion on silver parts, present in some fuel pumps. a similar type of test has been introduced using a silver strip. These tests are complementary.

Additives: Oxidation inhibitors are used in turbon fuels to prevent gum formation and to retard peroxide formation in hydrotreated fuels. Other additives include metal deactivators, anti-icing additives, anti-static additives, corrosion inhibitors, anti-smoke additives and fuel soluble biocides.

KEROSINE: Kerosine, or paraffin as it is commonly known was for many years the most important product of refining. Although its predominant market share has long been lost to gasoline, the demand for kerosine is now growing again with the steady development of the oil-fired heating market.

There are a number of specifications for fuel oils in the United Kingdom, fuel oils are classified as classes C_1, C_2, D, E, F, G and H. Classes C_1, C_2 and D are distillates and include the domestic fuels.

The table below gives the specifications for these fuels (7).

TABLE III

SPECIFICATIONS FOR CLASSES C AND D OIL FUELS

BRITISH STANDARD 2869 - 1970

PROPERTIES	TYPES CLASS C_1	CLASS C_2	CLASS D
Viscosity, kinematic (cst) at 37.8°C (100°F)			
Min	--	--	1.6
Max	--	--	6.0
Carbon residue, Corrodson, on 10% residue, % wt max	--	--	0.2
Distillation			
recovery at 200°C (392°F) % vol max	15	15	--
recovery at 357°C (675°F) vol min	60	--	90
final boiling point, °C, max	280	300	--
Flash point, closed Abel, °F min	110	100	--
Flash point, closed Perisky-Martens °F min	--	--	130
Water content, % vol, max	Free	Free	0.05
Sediments % wt, max	From visible water. Free from visible sediment	From visible water. Free from visible sediment	0.01

The calorific value of a fuel is the amount of heat released when a unit quantity is completely burnt.

Smoke Point: A factor of some significance in the acceptability of oil-fired domestic appliances is the absence of smoke, hence the importance fo smoke point in specifications. The smoke point of the oil is more critical, however, when it is to be burnt in the wick-type burners employed in flucless heaters. In this application the smoke point is a factor in limiting the flame height and therefore the heat output of the appliance. The tendency of iverosive to smoke is mainly dependent on their hydrocarbon-type compositon. The greater the percentage of aromatics in the oil, the greater the ease with which the oil will smoke.

The burning tests for kerosine give results in all types of applicances very much in line with what is expected.

THE NUCLEAR MAGNETIC RESONANCE ANALYTICAL METHOD

Nuclear magnetic resonance (NMR) spectroscopy has perhaps had a greater impact on a diverse variety of chemical investigations than any other single instrumental development. Provided that analytical chemistry is broadly defined as the practice of characterizing the chemical and physical properties of compounds or mixtures NMR is an important load for that practice.

The major application of NMR spectroscopy has been in structure elucidations and qualitative analysis. Other applications include the quantitative determinations of percentage composition of complex mixtures. It is in this other application that we are interested.

The topic of NMR spectroscopy has already been treated in several excellent texts. The aim of this review is not to go into the fine details of NMR theory. The approach has been to provide a brief background into the theory of NMR, and then discuss possible analytical applications with special reference to the problem at hand; i.e. hydrocarbon - type analysis of petroleum products. Emphasis is concentrated on providing a physical picture of the NMR process as applied to petroleum product analysis rather than developing the theory in rigorous mathematical detail.

1. THE ORIGIN OF THE SIGNAL

Magnetic Properties of Nuclei: Certain nuclei when placed in a magnetic field, behave as if they were spinning charged particles. Nuclei that possess this property are said to have angular momenturn designated as P.

Quantum mechanics requires that the measurement of a component of P in any direction must yield an integer or half integer or half integer multiple or $h/2\pi$ commonly denoted as $\hbar$. The maximum possible number of these units is called I, the spin quantum number. Its value can only be zero or a multiple of $\frac{1}{2}$. Thus a nucleus can have 2I + I possible states in which the component of the angular momentum will have values I, (I - 1). ... (-I + 1), -I

$$P = \sqrt{I(I+1)}\,\hbar. \qquad (1)$$

The values of I follow certain rules. It is zero for nuclei with even mass and even atomic numbers; 1, 2, 3..... for nuclei with even mass and odd atomic numbers and it is an odd multiple of $\frac{1}{2}$ for nuclei having an odd mass number regardless of the atomic number.

In a magnetic field, nuclei behave as if they were spinning charged particles. A rotating charged particle acts like a current in a loop; it generates a magnetic

moment μ which is always taken to be collinear with the vector of the angular momentum P. Because of the quantization of the angular momentum, a series of magnetic quantum numbers m can be introduced, which describe the permitted values of the vector moment, m = I,(I + 1) .... (-I + 1), -I corresponding to the possible spin states. For the case, I = $\frac{1}{2}$, this is reduced to two possibilities, +$\frac{1}{2}$ and -$\frac{1}{2}$. The easiest way to visualize this in a magnetic field is an alignment with or against the field. In the absence of a field all these states have the same energy and they are said to be degerate.

In a magnetic field, these states have different energy levels. Observations of transitions between these levels is the basis of NMR spectroscopy.

The magnetic moment μ of a nucleus is proportional to the magnitude of its spin, and is given as

$$\mu = \frac{e \cdot \hbar}{M \cdot C} \cdot I \qquad (2)$$

where e is the charge of the particle, m its mass, c, the velocity of light and I the spin.

2. THE NMR PHENOMENON: When a nucleus with a non-zero magnetic moment (say a proton, μ = $\frac{1}{2}$) is put in a magnetic

field, the nucleus takes up the allowed orientations i.e. $+\frac{1}{2}$ or $-\frac{1}{2}$.

The transition of the proton from one possible orientation to another is effected by the absorption or emission of a discreet amount of energy such that

$$\Delta E = h\nu = 2\,\mu\,B_o \qquad (3)$$

where ΔE is energy difference between different orientations, h is Black's constant, ν is frequency of radiation and B_o the applied magnetic field.

The interactions between μ and B_o result in a torque acting on μ which tend to tip it towards B_o, and since the nucleus is spinning, instead of tipping, the torque causes μ to precess about field B_o

The precessional frequency of μ about B_o is given as

$$V_o = \frac{\gamma}{2\pi} B_o \qquad (4)$$

where V_o is the precessional frequency also called the Lamour frequency. γ is the gyromagnetic ratio. Equation 4 is sometimes called the Lamour equation.

If another field B_1 is applied in the x - y plane, and rotating in the same direction as μ, interactions between B_1 and μ occur. So long as B_1 is rotating at some frequency V , other than the Lamour frequency V_o, the effect of B_1 on μ results in slight

oscillations in the angle between μ and B_o. When the frequency of oscillation of B_1 coincides with the prec ssional frequency V_o i.e. $V = V_o$, μ will experience the effect of both B_1 and B_o and will exhibit large osc llations in the angle between μ and B_o, such that the direction of μ with respect to B_o changes. Energy is absorbed and the magnetic moment is said to have "flipped" from one magnetic orientation to the other.

The absorption of energy when $V = V_o$ is the NMR phenomenon.

3. INTERACTION OF NUCLEI WITH THEIR ENVIRONMENT

The NMR spectrum of a sample that contains several chemically different types of the same nuclei, say protons, is observed to have separate signals for each type of chemically different proton. The separation between the signals for the different protons is called the chemical shift. Different chemical shifts arise from the fact that the magnetic field experienced by the nucleus depend on its environment. and is not necessarily identical with the applied field.

All nuclei of one isotope will resonate at a given frequency in a field determined by the Lamour equation.

The effective field surrounding the nucleus is however never identical with the applied field B_o since there are no bare nuclei in solution. Nuclei are surrounded by a cloud of electrons which have shielding effect directed against the applied field. The density of this cloud is a function of the chemical state of the nucleus i.e. its valency and type of atom it is bound to, and also influenced by its environment beyond its immediate neighbours.

The shielding or screening effect occurs because the electrons, being charged particles and with a spin, precess about the field direction with their Lamour frequency given by

$$\frac{e \cdot B_o}{2M.C} \qquad (5)$$

causing an induced magnetic field B^1 which is opposed to the applied field B_o.

Thus, the effective field felt by the nucleus is

$$B_{eff} = Bo - B^1 \qquad (6)$$

or, since the induced shielding field is proportional to the applied field,

$$B_{eff} = B_o \ (1 - \sigma) \qquad (7)$$

where σ is the shielding constant.

It is not possible to measure the resonance of a bare nucleus in solution, hence, all chemical shifts are given with respect to a reference compound. The chemical shifts of a compound i can be expressed as

$$\delta_{ij} = \sigma_i - \sigma_j \qquad (8)$$

where j is the refrence compound. For proton - NMR, the convention has been established to use tetramethylsilane $Si(CH_3)_4$ as reference and give it the position 0.

Resonance condition may be satisfied by varying either the frequency or the applied field. Chemical shifts may therefore be expressed in frequency units (Hz) or field units (gauss). In order to eliminate the need to specify either the megnetic field or the frequency used, a method for reporting the chemical shift in non-dimensional unit is usually employed:

For measurements made at constant frequency, the chemical shift is defined as

$$\delta = \frac{Bj - Bi}{Bj} \times 10^6 \text{ ppm.} \qquad (9)$$

Bj & Bi are the applied field for the absorptions of the reference compound and a given nucleus in the sample respectively.

At constant applied field, the frequency is varied, i.e. "Frequency sweep", the chemical shift is given as

$$\delta = \frac{Vi - Vj}{Vj} \times 10^6 \text{ ppm} \qquad (10)$$

Vi and Vj are the frequencies of absorptions of the sample nuclie and the refrence compound respectively.

4. METHODS OF QUANTITATION

Basically, there are three types of information available from an NMR spectrum: (1) the chemical shift (2) Integrated intensity and (3) coupling constant. Each of these pieces of information provides unique information for use in qualitative and quantitative analyses.

Although the most common and usually the most practical method of quantitation by high-resolution NMR is peak area measurements there are several potentially useful methods of quantitation.

(1) [illegible]: The value of the chemical shifts allow for the determination of the type of protons present in the sample i.e. protons bonded to saturated, olefinic and aromatic carbons and to carbons in functional groups such as aldehydes etc. In some cases, specific type of protons such as methyl, methylene, methine

etc can be distinguished. For a simple spectrum the number of absorptions determines the number of chemically different types of protons.

COUPLING CONSTANT: The coupling constant provides information on the geometrical relationship of the protons in the sample.

INTEGRATED INTENSITY OR AREA MEASUREMENTS: The integrated intensity provides information about the relative number of protons of each chemically different type.

The integration of the NMR resonance Line.

One of the major advantages of NMR over other forms of conventional spectroscopy is that the integrated intensity/the area of an NMR absorption signal is directly related to the number of nuclei giving rise to the signal and is not related by an absorption coefficient.

The area under the signal depends on a number of factors including the applied field B_o the radiofrequency B_1, relaxation times T_1 and T_2 the absolute temperature T, and the number and type of Nuclei giving the signal

$$A \alpha \frac{N B_1 \mu^2}{k T (1 + \gamma^2 B_1^2 T_1 T_2')^{\frac{1}{2}}} \qquad (11)$$

Measurements of the area under a signal is the most frequently used method of quantitation. This can be done by triangulation, by cutting and weighing or with all modern instruments, through electronic integration. In this case, the signal is a step in the baseline of the integral curve, which occurs at the place of the peak in the absorption spectrum. The step bright is proportional to the area under the peak. Using modern electronic integrator circuits, integrations can be performed with a precision of a few tenths of one percent.

The most common use of integration is probably the comparison of the intensities of various or all resonances of one spectrum. In a pure compound, this gives the ratio of different protons. This is a powerful tool in identification work. The characteristic chemical shifts, the spin-spin spliting pattern and the number of protons in each magnetically equivalent group can be used to determine the structure of the molecule.

In mixtures of known compounds, it allows the quantitative determination of the composition provided that all the constituent are NMR active or the inactive part can be determined. An excellent example of quantitative NMR is seen in the analysis of APC tables for the

aspirin, phenacetin and caffeine contents. (2)

5. TECHNIQUES: There are three principal methods of quantitation using the integrated intensity. First, a calibration curve technique may be used provided a pure sample of the material to be determined in unknown solution is available. In this technique, standard solutions of the compound(s) to be determined are prepared which encompass the concentration range expected in the unknowns. The area of one or more resonance lines is plotted against the concentration of each standard. The plot should be linear and least square methods may be applied to the line if desired. The concentration of the unknown sample(s) may be read directly from the curve once the area has been obtained. The primary advantage of this technique is an improvement in the statistics of measurement if many samples are to be determined at one time, it is an excellent method.

A second method which may be used if a pure sample of the unknown is available is the method of standard addition. In this method, the spectrum of the unknown is taken with and without a known amount of the pure compound. The intregrated resonance of the unknown (Ax) and mixture (Am) is given as

$$Ax = K\,Cx \qquad (12)$$

$$Am = k, \quad \frac{Vx\,Cx + Vs\,Cs}{Vx + Vs} \qquad (13)$$

where k is a porportionality constant Cx and Cs are the concentrations of the unknown and standard respectively and V and Vs are the respective volumes in the mixture. Solving for Cx

$$Cx = \frac{Ax\,Vs}{Am(Vx + Vs) - AxVx}\,Cs \qquad (14)$$

The method has the advantage that fewer samples have to be prepared than for the calibration method.

The third and the most important method of quantitation is the method of internal standard. Exploiting the intrinsic property of NMR that all nuclei of a given type give resonance areas proportional to their concentration, and independent of their chemical environment, the reference standard need not be the same compound as the unknown. Though the analyst should be alert to possible chemical effects. In the absence of any chemical effect, any suitable compound may be used as standard.

The method of internal standard is a simple and direct method ideally suited for quantitative NMR using peak area measurements. The method is based on the addition of a known amount of an inert compound to the sample. The relative area of the integrated intensities of the unknown and the standard are directly compared. The following very general equation is used for the calculation

$$Wx = \frac{Ns \cdot Mx\ Hx}{Nx\ Ms\ Hs} \qquad (15)$$

Where Wx and Ws are the weights of the unknown and standard, Nx and Ns are the number of active nuclie of unknown and standard, Mx and Ms are the molecular weights and Hx and Hs are the step heights of their integrated intensities. D.E. Leyden and R.H. Cox (2) enumerated the requirements of a good internal standard. They include solubility in the solvent used, chemical inertness to both the solvent and the sample; resonance lines which overlap those of the sample and, preferably, it should give a single line which has similar saturation characteristics as the line(s) used for the sample, moderately high molecular weight and it should be easily removed from the sample

if needed. A list of compounds which have been used as standard was given by Kaster. (1).

6. APPLICATION TO PETROLEUM ANALYSIS

The applications of NMR to problems in the petroleum and fuel industries began in the late 1950s and have been numerous. Of importance to knowledge in these fields are the chemical composition and structure of the compound in petroleum crude and refined products. In recent years NMR spectrametry has played and increasingly important role, often in conjuction with other techniques, in the characterization of crude and petroleum products.

In one of the earliest application(2), it was shown that NMR could identify two types of hydrogen in alkyl concentrates of gas oil (methyl and acyclic methylene) and three types (aromatic, alkyl alpha to an aromatic ring and other alkyl) in catalytic cycle stock and asphalt.

The applications of NMR to petroleum analysis range from detailed compositional characterization of petroleum and petroleum products to hydrocarbon-type composition. There have been many applications of NMR to hydrocarbons derived from petroleum. Examples include: the determination of structure of hydrocarbon components and fractions

from petroleum; the analysis of aromatic, and polycyclic compounds in petroleum; investigations of alkyl side chains in cyclic hydr ..s, analysis of fractions cont ing ..gen, nitrogen and sulphur, structure of ..sphalt compounds and numerous quantitative analysis. Myers et al (8) used NMR spectrometry in the determination of hydrocarbon type distribution and hydrogen carbon ratio of a wide range of gasoline samples. Their results showed an absolute standard deviation of 1.9, 3.2 and 2.4% for the aromatic, paraffin and Olefin content respectively from the traditonal FIA methods. The same workers (9) also used the NMR technique to determine gasoline octane numbers and found out that the results correlate well with those obtained from engine tests.

Several specific determinations have also been ..ported. For example, the use of double resonance to simplify spectra of complex mixtures for quantitative measurements. (10)

There has been an increase in the application of ..C-NMR to the analysis of petroleum hydrocarbons. The usually simplified interpretation of proton decoupled ..C-NMR over ^{1}H-NMR will likely find the former technique

growing in popularity. Qualitative applications are being reported with increasing frequency. A report that may prove to be useful in the determination of the structure of hydrocarbons using ^{13}C-NMR was published by Lindeman and Adams(11) They illustrated the increased potential of ^{13}C-NMR over ^{1}H-NMR with the spectra of pristane. The ^{1}H.NMR spectrum does not resolve CH and CH_2 proton types while the ^{13}C-NMR showed a resolved resonance for each of the nine different carbon atoms in the molecule.

Obviously, NMR (^{1}H and ^{13}C) has played, and will play, a significant part in the identification, characterization and quantitation of compounds in the peteroleum inudstry.

7. HYDROCARBON-TYPE COMPOSITION BY NMR

This theory of hydrocarbon type compos ion was first developed by Myers et al (8) The theory was based on calculating the relative numbers of carbon atoms classified as aromatic, paraffinic or Olefinic in a gasoline sample from the ^{1}H - NMR spectrum.

The ^{1}H-NMR methods separates hydrogen by the type of carbon to which it is bonded (aromatic, Olefinic, paraffinic etc) and also by the environment in which it is located. The type and number of carbon atoms can therefore be calculated by proper correlation between the NMR active hydrogen and the skeletal carbon atoms using the integral trace and the characteristic chemical shifts of the chemically different types of hydrogen in a molecule.

To a first approximation, the hydrocarbon - type composition is given by

$$\text{Aromatics, vol. \%} \simeq \frac{Ca}{Ca + Cp + Co} \times 100 \qquad (16)$$

$$\text{Paraffin, vol \%} \simeq \frac{Cp}{Ca + Cp + Co} \times 100 \qquad (17)$$

$$\text{Olefin, Vol \%} \simeq \frac{Co}{Ca + Cp + Co} \times 100 \qquad (18)$$

where Ca, Cp and Co are the total number of aromatic, paraffinic and Olefinic carbons, respectively.

HYDROCARBON TYPE AND NMR REGIONS

Table IV indicates the varous organic functional groups commonly found in petroleum fractions, the spectra region in which their protons resonate, the letters designating the integrals of the regions and the corresponding total number of carbons of the type indicated in terms of the integnal heights.

TABLE IV

NMR SPECTRAL REGIONS OF ORGANIC FUNCTIONAL GROUPS COMMONLY FOUND IN PETROLEUM FRACTIONS.

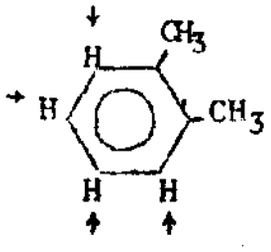
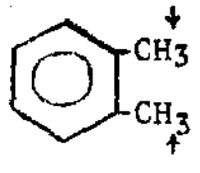
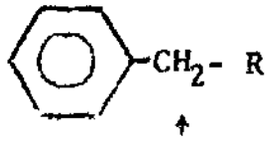
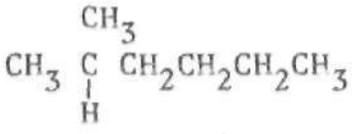
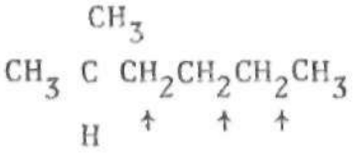
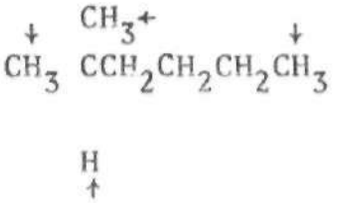
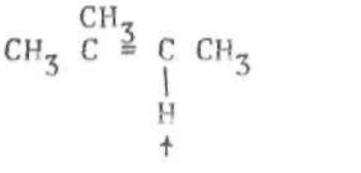
PROTION TYPE	SPECTRAL REGIONS, ppm from TMS	INTEGRAL DESIGNATION	TOTAL NO OF CARBONS (OF TYPE INDICATED)
	AROMATICS		
	6.6 - 8.0	A	KA
	2.0 - 3.0	C	R [C/3]
			

Table IV Contd.

PARAFFINS

	1.5 - 2.0	D	KD
	1.0 - 1.5	E	$K\{^{E}/2\}$
	0.6 - 1.0	F	$K\{^{F}/3\}$

OLEFINS

	4.5 - 6.0	B	KB

Some carbon atoms go "uncounted" because they are completely substituted and give no NMR signal. Other carbons are eronously counted as belonging to different hydrocarbon classes because their protons resonate in the region of the NMR spectrum where other hydrocarbon types normally appear. From the consideration in table 1, the following uncorrected, expressions for Ca, Cp and Co are obtained.

$$Ca \simeq k\,(A + C/3) \tag{19}$$

$$Cp \simeq k\,(D + E/2 + F/3) \text{ and} \tag{20}$$

$$Co \simeq k\,B \tag{21}$$

where k is an instrumental constant. With these explicit expressions for Ca, Cp and Co, equations to becomes

$$\text{Aromatic, Vol \%} = \frac{(A + C/3)}{(A + C/3) + (D + E/2 + F/3) + B} \times 100 \tag{22}$$

$$\text{Paraffin, Vol \%} = \frac{(D + E/2 + F/3)}{(A + C/3) + (D + E/2 + F/3) + B} \times 100 \tag{23}$$

$$\text{Olefin, vol \%} = \frac{B}{(A + C/3) + (D + E/2 + F/3) + B} \times 100 \tag{24}$$

However, Myers and his colleageues proposed a series of corrections to these basic equations.

DENSITY AND CARBON COUNTS: The densities of light paraffin and aromatics are significantly different and since these affect the carbon count, they must be corrected for. The densities of both the aromatics and olefinic components are normalized to that of the paraffin

i. Corrections for Aromatics: 1. Density correction: The densities of aromatic hyrocarbons are significantly greater than those of light paraffins. Equation (22) gives a high estimate of the volume percent of the aromatic content. The aromatic term $(A + C/3)$ needs to be multiplied by a constant term to correct for this density difference.

The weighted average density defined as

$$\text{weighted average density} = \sum_i \frac{\{\text{vol \% (i)}\}\{\text{density(i)}\}}{\sum_i \{\text{vol \% (i)}\}} \qquad (25)$$

for the aromatic and paraffinic components present in typical petroleum fractions are 0.8732 and 0.6612 g/ml respectively. The aromatic term must therefore be multiplied by ratio of the weighted average densities i.e. 0.6612/0.8732 = 0.7572 to correct for the density difference.

2. Uncounted Carbons: Not all the aromatic carbons are counted. The ring carbons to which the alkyl groups are attached have no remaining hydrogen atoms and hence give no NMR signal.

The examination of aromatic compound present in typical petroelum fractions shows that a ratio of carbon atoms counted to those actually present can be calculated. And with the volume precent of the different compounds, a weighted average ratio defined as

$$\text{weighted average ratio (carbon counted/carbon present)} = \sum_i \frac{\{\text{vol. \%}\}(i)\ \frac{\text{no of carbons counted (i)}}{\text{no of carbons present (i)}}}{\sum_i \{\text{vol \% (i)}\}} \quad (26)$$

A value of 0.7835 was obtained. The aromatic term $\{A + C/3\}$ must therefore be multiplied by $\frac{1}{0.7835} = 1.2763$ to correct for the uncounted carbon atoms.

The overall correction terms for the aromatic term is therefore 0.97 (0.7572 x 1.2763).

ii Corrections for Paraffins: No density corrections are necessary for the paraffin components as both the densities of aromatics and naphthenes are normalized to that of the paraffins.

Uncounted Carbons: The weighted average ratio of carbons counted to carbons actually present is calculated to be 0.9831. The paraffic term will therefore have to be multiplied by $^{1}/0.9831 = 1.02$.

iii Corrections For Olefins: The weighted average density for the olefin is 0.6808g/ml. The weighted average ratio (carbon counted/carbon present) is calculated to be 0.2917. The overall correction, term for the, olefinic term is 3.33 (0.6808 x 0.2917).

iv Cross Correction Terms: The alkyl parts of the olefin molecules produce signals in the D, E and F regions of the NMR spectrum. These signals introduce errors in the determination of the paraffin content. The most significant of the errors is that caused by signals due to methyl and methylene groups α to C = C, These signals add to the paraffin methine region D. To correct for this, a quantity 2B is subtracted from region D so that the paraffinic term becomes $(D-2B + {}^{E}/2 + {}^{F}/3)\ 1.02$. There are other numerous corrections but these can be neglected as they introduce only insignificant errors.

Taking into account all the correction terms, the hydrocarbon- type compositions will be given by the following equations:

$$\text{Aromatics, Vo. \%} = \frac{(A + C/3)\ 0.97 \times 100}{(A+C/3)0.97 + (D-2B+E/2+F/3)1.02 + 3.33B} \quad (27)$$

$$\text{Paraffin, Vol \%} = \frac{(D - 2B + E/2 + F/3)1.02 \times 100}{(A + C/3)0.97 + (D-2B+E/2+F/3)1.02+3.33B} \quad (28)$$

$$\text{Olefin, Vol \%} = \frac{3.33B \times 100}{(A + C/3)0.97 + (D-2B+E/2+F/3)1.02+3.33B} \quad (29)$$

These equations were used in the experimental work for determining the hydrocarbon type distribution

8. DETERMINATION OF HYDROGEN/CARBON RATIOS

The total number of carbon atoms per unit sample volume can be determined from the denominator in equations (27) through (29). In this case the density correction terms will have to be removed and the resulting terms multiplied by the instrumental constant k. The total number of carbon atoms is therefore given by:

$$\Sigma(\text{all carbon atoms}) = k\{(A+C/3)1.28+(D-2B+E/2+F/3)1.02+3.42B\} \quad (30)$$

The total hydrogen content per unit sample volume is given by:

$$\Sigma \text{ (all hydrogen atoms)} = (A + B + C + D + E + F) \quad (31)$$

Thus the expression for the hydrogen/carbon ratio is:

$$\text{Hydrogen/Carbon ratio} = \frac{A + B + C + D + E + F}{(A+C/3)1.28 + (D-2B+E/2+F/3)1.02 + 3.42B} \quad (32)$$

CHAPTER TWO

E X P E R I M E N T A L

E X P E R I M E N T A L

1. SAMPLES: Samples of Heavy naphtha, Aviation turbine kerosine and straight run kerosine, products of the Nigerian National Petroleum Corporation (NNPC) Refinery Kaduna were collected over a period of eight months (April to November 1981). To a large extent the samples were representative of the production streams of the refinery.

2. SAMPLE PREPARATION: The petroleum sample and the standard, ethylene glycol, were directly weighted into the NMR sample tube. The sample size was approximately 0.1400 to 0.3732g. The mixture was diluted to about 1.0ml with carbon tetrachloride containing 1% tetramethysilane (TMS) as a chemical shift reference and for field locking.

3. INSTRUMENTAL CONDITIONS: The spectra were obtained on a Varian T60 internal Lock Nuclear Magnetic Resonance Spectrometer operating at 60 MHz.

The absorption and integral spectra were obtained in separate scans from 0 to 8 ppm from TMS at room temperature. The spectrometer was operated in the field sweep mode to obtain the most accurate integrals.

Sweep times of 250 and 50 seconds were used for the absorption and integral scans, respectively. A sweep width of $500H_2$ was used and the RF power level was set at 0.1

No apparent saturation effects were observed on the absorption spectra and the much faster integral sweep ensures that such effects are absent from the integral spectrum.

4. ANALYSIS TIME: On the average the time for each analysis ranged between 30 to 40 minutes.

5. POSSIBLE SOURCES OF ERROS: Inhomogeneity might cause standard and unknown to be exposed to different field strengths inside the porbe. It was discovered Later in the experimental work that in some cases the standard and the sample were not totally miscible. In such instances the standard seperates as a top layer in the sample tube. This inhomogeneity may help explain the inconsistencies in the integral step heights of the standard which does not show any definite pattern where compared with the weights of standard used.

CHAPTER THREE

RESULTS AND DISCUSSION

High resolution ^{1}H-NMR spectra of typical Heavy-Naphtha, Aviation Turbine kerosine (ATK) and straight - run kerosine fractions are shown in figures 3,4 and 5 respectively. The six spectral regions (A, B, C, D, E and F) and the type of protons they represent are also indicated.

The integral value for the various spectral regions were obtained from the spectra and the results are shwon in tables V, VI and VII. Applying equations (27) through (33) to determine the hydrocarbon - type compositions, the results obtain on 44 samples of heavy - naphtha, 13 samples of ATK and 15 samples of straight run kerosine are given in tables VIII IX and respectively. The tables also include data on the Hydrogen/carbon ratio calculated according to equation (32) and molecular weights calculated using equation (35).

CORRELATION WITH FIA DATA ON HYDROCARBON-TYPE COMPOSITION

FIA data on hydrocarbon-type composition for a number of samples representative of the total number of samples worked on were collected from the NNPC Refinery in Kaduna. Tables XI and XII show the hydrocabon - type composition calculated from the NMR data and the corresponding FIA values for the heavy - naphtha and ATK fractions respectively.

A computer program - subprogram Regression from the statistical Package for the social sciences (SPSS) Program library was used to process the data. The statistic obtained for the bivariate regression of hydrocarbon - type composition from the two methods are given in the tables XIII and XIV for heavy-naphtha and ATK respectively.

An examination of table XIII shows that there is generally a weak correlation between the hydrocabon-type composition values computed by the two methods for the heavy-naphtha fraction: 0.2656 for N-Aromatics (Aromatic vol % by NMR with F-Aromatics (Aromatics Vol % by FIA) and 0.2553 for N-Paraffins with F-Paraffins. There is a stronger linear relationship in the ATK values (Table XIV) where the correlation coefficient for N-Aromatic with F-Aromatic is -0.9261, 0.7382 for N-Olefin with F-Olefin and -0.5732 for N-Paraffin with F-Paraffin. The signs on the coefficients show the direction of the relationship. A negative correlation coefficient R does not mean a bad fit, rather it denotes an inverse relationship.

The poor correlation between the NMR values and the corresponding FIA values for heavy naphtha seems to collaborate the findings of other workers. For example Ozubko

et al (12) returned a verdict of poor agreement among the results obtained for a given sample using different techniques.

The poor agreement between the NMR and FIA techniques for the heavy-naphtha fraction may be attributed to two main reasons.

(1) the basic difference in the fundamental basis of the methods of analyses and

(2) correction factors used in the NMR analysis.

1. Difference in Fundamental basis of Analysis.

The FIA method is a chromatographic technique which acts at a molecular level i.e. there is a molecular separation followed by detection and analysis of molecules. The NMR method on the other hand, observes the carbon or hydrogen on an atom by atom basis. i.e. atomic analysis. Thus while it is possible for the NMR to classify parts of a single molecule with more than one functional group into the different groups, the best the FIA method can achieve is to separate it into a group depending on the molecular weight and the retention characteristics, therefore on incomplete separation. Incomplete separation

of hydorcarbon groups by the FIA method has been confirmed by mass spectrometric investigation of separated hydrocarbons (12). This may help to explain the relatively high values for the aromatic vol. % by the FIA method.

Thus for a fair comparison, one must make sure that the comparisons are made on the same basis.

2. Incorrect "Correction Factors":

The number and types of hydrocarbons in petroleum fractions depend on the crude. The correction factors used to compute the NMR hydrocarbon-type composition values were those derived by Myers et al (8) for US - gasoline samples. Thus there was an implicit assumption that the relative amounts of the various individual components in gasoline are approximately the same as those in the sample worked on.

The correlation coefficients show that even if this is true for ATK, it is certainly not true for heavy-naphtha. The inconsistencies are not necessarily overwhelming since Myers et al (8) emphasized that the correction factors apply only to full boiling range gasoline and would probably not give the hydrocarbon-type distribution accurately for other petroleum products and fractions.

To get a "good fit", there are two options open: either (a) correct the "incorrect correction factors" or (b) get a new set of correction factors. The two options available were exploited. To get a"new" set of correction factors, the hydrocarbon-type compositions were computed from the "raw data" (Uncorrected integrals of the different spectral regions.) The values with the corresponding FIA values are shows in table XV and XVI.

ALTERNATIVE (a): Table XIII shows selected statistics from multiple regression generated by the SPSS subprogram regression.

Multiple regression is a general statistical technique through which one can analyse the relationship between a dependent variables and a set of independent variables. The output may be used either as an inferential tool by which the relationship in the population are evaluated from the examination of sample data, or as a discriptive tool by which linear dependence of one variable on others is summarized and decomposed.

Multipe regression was used both as a discriptive and inferential tools to find the best linear prediction equations and evaluate the prediction accuracies. The FIA data were set as the dependent variables while the NMR dat: are the independent variables. This order is justified by the fact that the FIA method is the standard method with which the NMR method is to be compared and evaluated.

In simple regression analysis, values of the dependent variables are predicted from a linear function of the form (13).

$$Y^1 = A + \beta_1 X_1 + \beta_2 X_2 + \ldots\ldots + BnXn \qquad (33)$$

where Y^1 is the estimated value of the dependent variable Y, the βi are constants by which all values of the independent variable X are to be multiplied - Regression coefficients, and A is a constant which is added to each case.

When standardized regression coefficients (Beta weights) are used, the regression equation becomes

$$Y^1 = \beta_1 X_1 + \beta_2 X_2 + \ldots\ldots\ldots + \beta_n X_n \qquad (34)$$

where β are the standardized regression coefficients Beta weights.

From tables XI 1 and 2, the regression equations for aromatics and paraffin vol% for the Heavy - naphtha fractions are given as:

For Aromatics

$$Y_A^1 = 17.8724 + 0.2197X_1 + 0.32X_2 + 0.7826X_3 \qquad (35)$$

For Paraffins.

$$Y_P^1 = 6.7800 + 0.4418X_1 + 0.4933X_2 + 0.2592X_3 \qquad (36)$$

Y_A^1 and Y_B^1 are the predicted values for the aromatic and paraffin vol %. X_1, X_2 and X_3 are the aromatic, Olefin and Paraffin vol % respectively calculated by the NMR method.

There is no corresponding prediction equation for the Olefin as the FIA data show a zero vol% for olefins.

The R^2 statistics (coefficient of determination) evaluates the prediction equation and indicates the proportion of the variations explained by the different variables.

R^2 for the predicted aromatic equation is 0.3179, this is interpreted to mean that 31.79% of the variations in the predicted values are accounted for by, variations

in the components of the prediction equation i.e. variations in the aromatic, olefin and paraffin vol% calculated by the NMR. The standard error of estimate or the standard deviation of the predicted values Y^1 from the actual values of Y is 1.0391 and the coefficient of variability is 7.4%. The strength and direction of the relationship is given by the multiple regression coefficient R. The direction of the relationship is positive while the absolute value of R gives the strength as 0.5639.

For the paraffin prediction equation, 10,05% of the variations will be explained by variations in the different variables with an error of prediction of 1.3535 and coefficient of varibility of 1.6%. The strength of the correlation is given as 0.3171 in a possitive direction.

ALTERNATIVE (b): To get a "new" set of correction factors independent of the basic assumption that the correction factors of Myers et al are applicable, the raw NMR data and the corresponding FIA values were processed with the multiple regression subprogram. It was not possible to use the Myers' approach as information on the

compositional nature of the samples was not available. Thus the method of generating prediction equations from the regression output was used.

The selected statistics from the multiple regression output are shown in tables XVII and XVIII . Using these statisties a number of prediction equations were arrived at.

The prediction equations are:

For Heavy - Naphtha.

$$Y_A^1 = -175.5057 + 2.1116X_1 + 3.6789X_2 + 1.8660X_3 \quad (37)$$

$$Y_P^1 = 719.6288 - 7.2727X_1 - 8.2530X_2 - 6.2289X_3 \quad (38)$$

For ATK

$$Y_A^1 = 434.2470 - 4.6326X_1 - 4.4951X_2 - 4.1044X_3 \quad (39)$$

$$Y_O^1 = -43.8393 + 0.3945X_1 + 0.6274X_2 + 0.4537X_3 \quad (40)$$

$$Y_P^1 = -290.4077 + 4.2382X_1 + 3.867\,X_2 + 3.6508X_3 \quad (41)$$

Table XIX lists the values of the overall R^2 and Partial R^2 statistics of independent variables in equations [illegible] through [illegible]. A close examination of the table shows that there is a better correlation/fit with the ATK data. For example only about 31.65% of the variations in predicted

Aromatic Vol % in ATK (equation [illegible]) is attributable to variations in the independent varibles.

Comparison of tables XIII and XVII, XIV and XVII show that there is little difference in the strength of the relationship ie.g the R values. Thus it can be cancluded that the error introduced by the "incorrect" correction factor is minimal.

METHOD OF STANDARD ADDITION: The method of standard addition was attempted and the calculations based on this were carried out. Results of the calculations do not allow a clear-cut pattern. There is a wide variation in the values (see table VIII, IX and X). This leads to the conclusion that this method of analysis will not be of much help in this type of samples.

This conclusion is justified on the basis of the complexity of petroleum products. When one compares the petroleum products under study with other compounds to which the method has been successfully applied (1, 4 , one can then appreciate the role

played by the complexity of the sample under consideration. These other compounds are basically single compounds with impurities which are either NMR inactive or absorb in regions other than those of interest. Petroleum and petroleum products on the other hand are complex mixtures: in the words of C.F. Mabery ".....mixtures consisting mainly of hydrocarbons belonging to a few homologous series with individual members of each type quite numerous" (3).

Thus while it is true that the total NMR intensity of the sample is quantitative, relevant information about the relative proportions of the different components is lacking.

CHAPTER FOUR

C O N C L U S I O N

C O N C L U S I O N

On the basis of the foregoing discussions, which is basically a direct comparison of the NMR and the FIA data, it becomes quite difficult to make unambiguous conclusions about the relative merits of this technique over others.

From tables XIII, XIV, XVII and XVIII it has been concluded that the error introduced by assuming the applicability of the Myers et al correction factors is minimal, one is therefore left with only one alternative: the differences in the fundamental basis of analysis are reponsible for the different values.

If one attempts a recalculation of the NMR results from an atomic to a molecular basis, or vice versa (the FIA from molecular to atomic), a large number of assumptions will be involved thus giving a result of doubtful integrity.

Earlier in this report it has been asserted that, for a fair and just comparison, the comparison should as far as possible be on the same basis. Thus in fairness to the two methods of analysis, the comparison should have been on the same basis, either at an atomic level or molecular level. As this will introduced a number of

assumptions which may not necessarily, be true, it is better to consider the two methods on their individual merits.

On this basis, the NMR technique compares favourably with the established methods and couple with faster times of analysis (an average of 30 to 40 minutes per sample compared to an average of 2 to 3 hours per sample for the FIA technique) and lower cost in terms of instrumentation and man-power, the NMR technique can be standardized and used for hydrocarbon - type composition analysis.

Thus more energy should be spent on standardizing the technique rather than on comparative studies; and with consideration being given to the construction of a completely automated NMR for performing these tests, the NMR is on its way to being an important supplemental technique for hydrocarbon type analyses.

APPENDIX

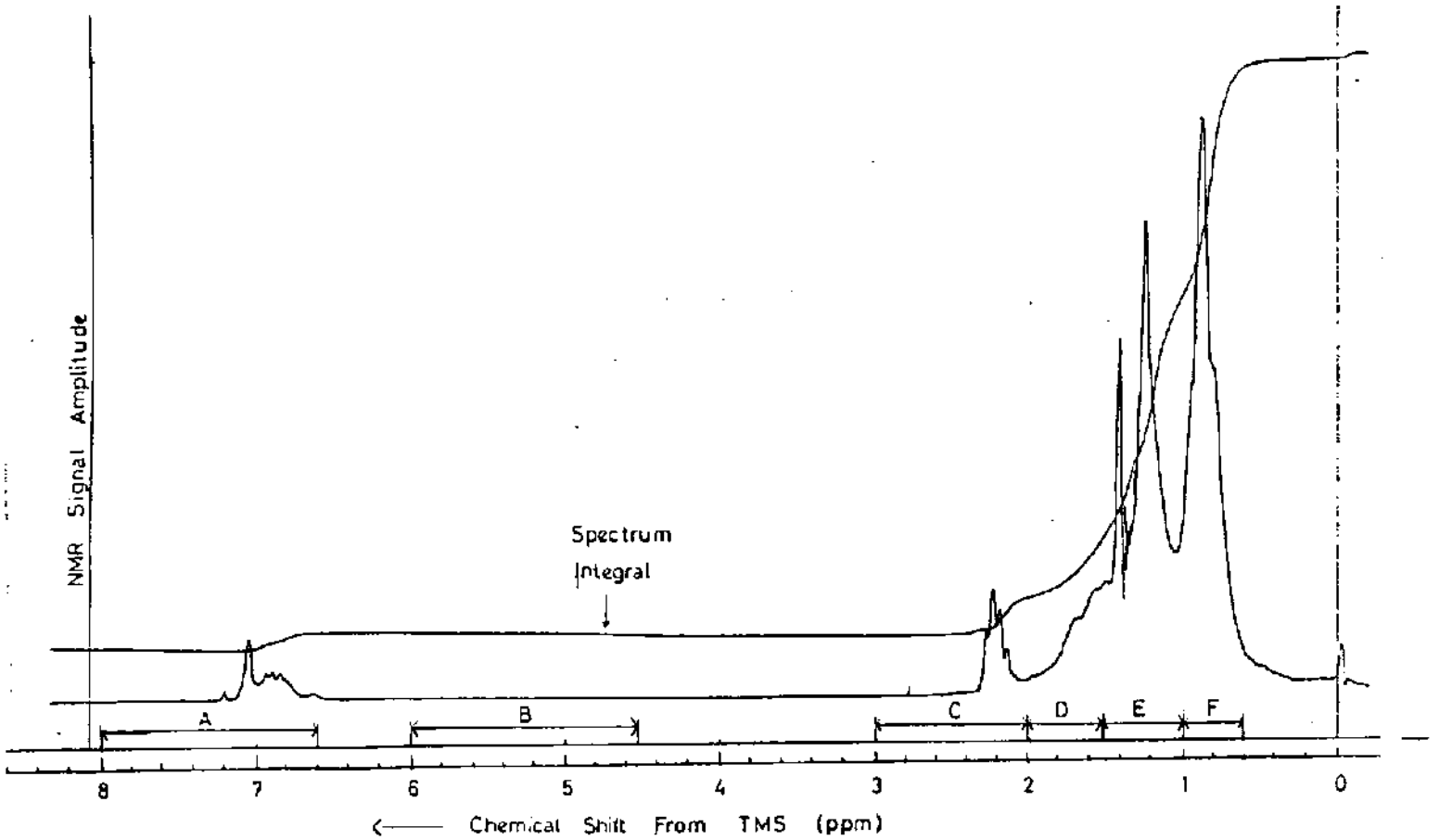


Fig. 3 High Resolution H-NMR Spectrum Of Typical Heavy-Naphtha Fraction

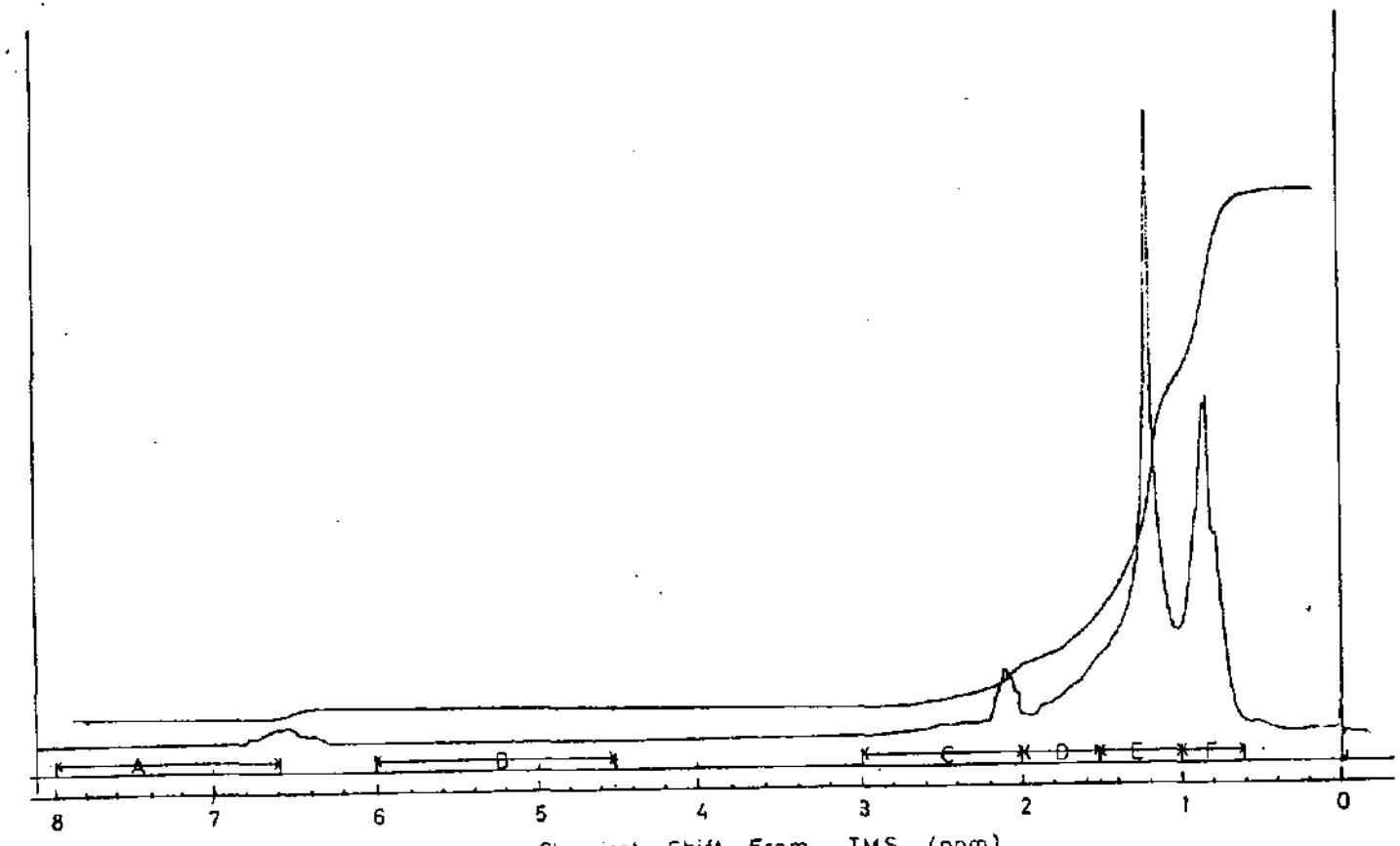


Fig 4 High Resolution H-NMR Spectrum Of Typical A T K Fraction

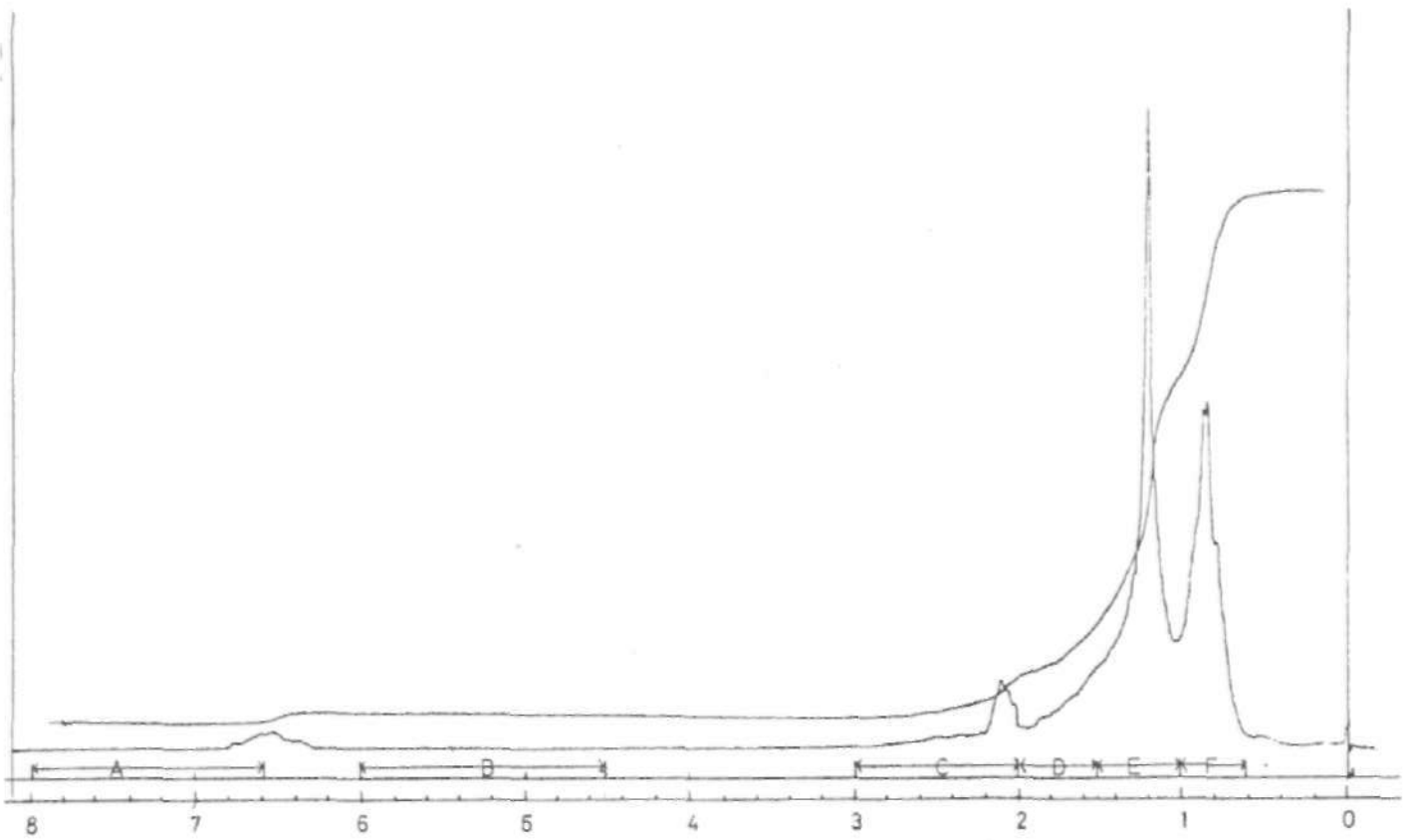


Fig 5 High Resolution H-NMR Spectrum Of Typical Straight-run Kerosine Fraction

TABLE V

INTEGRAL VALUES FOR THE VARIOUS SPECTRAL REGIONS FOR HEAVY - NAPHTHA SAMPLES

SAMPLE NUMBER	WEIGHTS		INTEGRAL VALUES									
			SAMPLE							STANDARD		
	SAMPLE	STANDARD	A	B	C	D	E	F	TOTAL	1	2	TOTAL
1	0.1414	0.1951	4.0	-	7.5	25.0	31.0	50.0	117.5	1.5	3.0	4.5
2	0.1444	0.1529	4.0	-	8.0	24.0	30.0	41.0	107.0	2.5	6.0	8.5
3.	0.1385	0.2659	3.0	0.2	6.0	17.0	13.0	36.0	75.0	4.5	10.0	14.5
4	0.2255	0.2225	3.5	1.0	5.5	18.5	25.5	29.5	82.5	5.0	10.5	15.5
5	0.1967	0.2172	3.5	0.6	5.0	22.0	29.0	43.5	103.0	9.0	21.0	30.0
6	0.2512	0.1402	4.0	0.5	6.0	27.0	32.0	42.0	111.0	15.5	33.0	48.5
7.	0.2538	0.2518	4.0	-	8.0	29.0	35.0	42.5	118.5	5.5	11.0	16.5
8	0.2272	0.1252	5.0	2.0	4.5	20.5	25.5	32.0	87.5	25.0	54.0	79.0
9	0.2380	0.2386	5.0	-	5.5	26.5	34.5	46.0	117.5	1.0	2.0	3.0
10	0.1704	0.2079	5.0	-	8.0	28.0	31.0	36.0	108.0	0.75	2.0	2.75
11	0.1400	0.2262	6.67	-	7.5	20.5	36.0	43.0	113.67	0.83	2.83	.66
12	0.1634	0.2115	5.5	-	6.5	27.5	30.5	42.0	112.0	1.0	2.17	.17
13	0.1754	0.2489	6.0	-	8.0	31.0	32.0	42.0	121.0	1.33	3.35	4.66
14	0.2045	0.2102	5.0	0.25	8.0	32.0	32.0	48.5	125.75	6.0	12.5	18.5
15	0.1863	0.1493	6.5	-	7.0	32.0	36.0	57.0	138.5	1.0	2.0	3.0
16	0.1897	0.2124	5.0	-	6.0	26.0	33.0	47.0	117.0	2.17	5.33	7.50
17	0.3690	0.2547	4.0	-	6.0	25.0	32.0	40.0	107.0	0.67	1.0	1.67
18	0.2712	0.3267	5.67	-	6.0	28.0	35.0	43.0	117.67	1.0	2.33	3.33
19	0.2625	0.4706	4.5	-	7.5	30.5	34.0	40.0	116.5	2.25	5.0	7.25
20	0.1830	0.1813	5.0	-	6.5	32.0	38.0	37.0	118.5	1.0	2.0	3.0

TABLE V CONTD.

SAMPLE NO.	SAMPLE	STANDARD	A	B	C	D	E	F	TOTAL	1	2	TOTAL
21	0.2413	0.2519	4.5	-	6.5	28.0	33.5	37.0	109.5	5.5	11.5	17.0
22	0.2719	0.2120	5.0	.	3.0	33.0	41.0	45.0	132.0	3.0	7.5	10.5
23.	0.2623	0.2270	3.75	-	7.0	26.0	29.0	33.0	98.75	0.635	1.5	2.125
24	0.2813	0.2309	5.0	-	7.0	26.5	40.3	40.0	119.0	5.0	10.0	15.0
25	0.3202	0.3295	5.0	-	7.0	34.0	38.0	41.0	123.0	2.5	5.5	8.0
26	0.2712	0.3267	5.67	-	6.0	28.0	38.0	43.0	117.67	1.0	2.33	3.33
27	0.2896	0.3037	4.5	0.5	7.0	28.0	31.0	38.0	109.0	3.5	6.0	9.5
28	0.3488	0.1868	6.0	-	9.5	33.0	38.5	47.5	134.5	1.25	3.0	4.25
29	0.2855	0.1931	4.0	-	7.5	29.0	39.5	40.0	120.0	5.0	11..5	16.5
30	0.2802	0.4461	3.25	-	8.5	26.5	31.0	33.0	102.25	0.5	1.5	2.0
31	0.2886	0.2322	5.0	-	9.0	33.5	37.5	42.0	129.0	1.5	3.0	4.5
32	0.3000	0.4049	3.5	-	7.0	21.0	40.0	43.5	115.5	0.375	1.0	1.375
33	0.3248	0.3377	6.0	-	10.0	33.5	39.5	40.0	129.0	2.0	5.0	7.0
34	0.2764	0.4247	5.0	-	8.5	31.5	36.0	41.0	122.0	1.0	2.0	3.0
35	0.2636	0.4767	4.5	-	9.5	35.5	37.5	43.5	130.0	1.5	4.0	5.5
36	0.3247	0.5 78	5.0	2.5	8.0	11.0	37.0	40.4	104.0	16.5	32.0	48.5
37	0.3732	0.4520	4.0	0.5	5.0	24.5	30.0	33.0	96.5	2.5	4.0	6.5
38	0.2334	0.2004	6.0	1.5	11.0	31.0	34.0	37.0	120.5	9.0	16.0	25.0
39	0.2037	0.2189	6.0	0.16	8.5	32.5	35.0	42.5	124.6	1.16	2.66	3.82
40	0.2293	0.3273	4.0	0.5	8.5	27.5	34.0	37.5	116.5	6.0	13.0	19.0
41	0.3245	0.3435	4.5	-	11.0	33.5	37.5	42.5	129.0	3.0	5.5	8.5
42	0.3109	0.4227	4.75	-	10.5	33.0	37.0	39.0	124.25	1.5	4.0	5.5
43	0.3668	0.3342	4.5	1.0	8.0	27.5	32.5	34.0	107.5	5.5	12.0	17.5
44	0.2775	0.2483	4.0	1.0	8.5	25.5	30.0	34.0	103.0	2.5	6.0	8.5

TABLE VI

INTEGRAL VALUES FOR THE VARIOUS SPECTRAL REGIONS FOR ATK SAMPLES

SAMPLE NUMBER	WEIGHTS		INTEGRALS									
			SAMPLE							STANDARD		
	SAMPLE	STANDARD	A	B	C	D	E	F	TOTAL	1	2	TOTAL
1	0.1576	0.1648	3.0	0.75	5.5	-	55.0	43.0	106.5	3.0	7.5	10.5
2.	0.1507	0.2748	3.5	-	8.0	-	48.0	48.0	107.5	1.0	3.0	4.0
3	0.1957	0.1164	2.0	0.8	6.0	-	35.0	34.0	77.0	6.0	13.5	19.5
4	0.2450	0.2364	2.5	1.0	5.0	-	45.5	34.0	87.0	6.0	14.0	20.0
5	0.2911	0.2754	3.0	-	6.0	-	56.0	46.5	102.5	2.5	6.0	8.5
6.	0.2773	0.1424	2.5	-	6.0	-	58.0	42.0	108.5	1.0	2.0	3.0
7	0.3446	0.1110	3.0	2.5	6.0	-	64.0	42.0	115.0	12.5	24.5	37.0
8	0.3223	0.1250	4.0	0.75	2.0	-	63.0	43.0	114.0	1.0	2.0	3.0
9	0.2322	0.1973	3.0	0.08	4.0	-	62.0	46.0	115.0	12.0	24.0	36.0
10	0.1378	0.1932	3.5	-	10.0	-	64.0	38.0	115.5	0.75	2.25	3.0
11	0.2840	0.2332	4.75	-	10.0	-	63.0	45.0	122.75	1.0	2.0	3.0
12	0.1898	0.1791	3.75	-	9.5	-	64.5	43.5	121.25	1.0	2.0	3.0
13	0.2723	0.2564	6.5	-	7.0	-	60.5	40.0	107.5	0.75	2.0	2.75

TABLE VII

INTEGRAL VALUES FOR THE VARIOUS SPECTRAL REGIONS FOR STRAIGHT-RUN KEROSINE SAMPLES

SAMPLE NO	SAMPLE	STANDARD	A	B	C	D	E	F	TOTAL	1	2	TOTAL
1	0.3029	0.1717	3.5	-	10.0	-	10.0	40.0	123.5	1.5	3.0	4.5
2	0.3005	0.3868	1.5	-	0.0	-	61.0	49.0	123.5	0.75	2.0	2.75
3.	0.3132	0.1111	3.0	-	10.5	-	59.0	52.0	124.5	1.0	3.0	4.0
4	0.3929	0.2114	2.5	-	10.0	-	53.0	41.0	106.5	1.5	3.5	5.0
5	0.3654	0.1964	3.75	-	9.0	-	63.0	38.0	113.75	1.75	3.0	4.75
6	0.3070	0.1816	3.50	-	9.0	-	52.0	44.0	108.5	1.0	2.0	3.0
7	0.4004	0.3815	2.0	-	9.0	-	30.0	45.5	106.5	1.0	2.0	3.0
8	0.3940	0.2597	3.0	0.5	9.5	-	58.0	53.0	124.0	5.0	11.0	16.0
9	0.3598	0.4277	5.0	-	11.0	-	69.0	45.0	130.0	0.5	2.5	3.0
10	0.2422	0.2193	5.1	0.6	10.0	-	52.0	35.0	103.0	0.6	2.2	2.8
11	0.2052	0.4560	2.5	0.75	10.0	-	61.0	40.0	114.25	4.0	8.0	12.0
12	0.2367	0.2406	3.0	0.5	10.0	-	61.0	43.0	120.5	2.5	5.5	8.0
13	0.3515	0.3212	3.0	-	9.5	-	63.5	40.0	116.0	1.5	2.5	4.0
14	0.3587	0.5893	4.5	1.0	11.0	-	53.0	45.0	114.5	3.5	7.5	10.5
15	0.2718	0.2718	4.0	-	10.0	-	57.0	34.0	105.0	0.75	1.0	1.75

TABLE VIII

HYDROCARBON-TYPE COMPOSTION (VOL %) FROM NMR DATA FOR [illegible] NAPHTHA SAMPLES

SAMPLE NUMBER	PERCENTAGES			H : C	M. wt.
	AROMATIC	OLEFIN	PARAFFIN		
1	9.76	-	90.24	1.76	1.77
2	10.7	-	89.26	1.72	3.92
3	11.74	1.61	86.65	1.79	6.15
4	10.70	6.88	82.42	1.72	15.99
5	8.67	3.46	87.87	1.79	17.44
6	9.01	2.58	88.41	1.72	61.58
7	9.46	-	90.54	1.71	12.15
8	11.75	12.40	75.85	1.67	131.99
9	9.91	-	90.09	1.73	2.02
10	11.61	-	88.39	1.62	1.59
11	14.17	-	85.83	1.73	1.11
12.	11.38	-	88.62	1.65	1.17
13	11.79	-	88.21	1.64	1.98
14	10.53	1.18	88.53	1.68	11.21
15	10.85	-	89.15	1.70	2.04
16	10.27	-	89.73	1.71	2.83
17	9.50	-	90.50	1.70	2.26
18	10.87	-	87.13	1.66	1.80
19	9.86	-	90.14	1.64	2.92
20	9.72	-	90.28	1.61	2.54
21	10.0	-	90.00	1.64	13.26
22	9.62	-	90.38	1.66	7.96
23	10.10	-	90.90	1.64	2.04
24	10.40	-	90.60	1.68	14.20
25	9.73	-	90.27	1.63	3.52

SAMPLE NUMBER	AROMATIC	OLEFIN	PARAFFIN	H : C	M. wt.
26	10.87	-	87.3	1.66	1.80
27	10.59	2.68	86.79	1.70	5.53
28	11.71	-	88.29	1,71	3.28
29	9.34	-	90.66	1.73	14.97
30	10.13	-	89.87	1.70	5.52
31	10.63	-	89.37	1.69	2.62
32	9.36	-	90.64	1.85	4.44
33	12.14	-	87.86	1.67	2.69
34	10.88	-	89.12	1.69	9.59
35	9.91	-	90.09	1.68	1.14
36	12.82	14.07	73.11	1.73	21.98
37	9.68	2.87	87.46	1.65	3.81
38	12.72	6.65	80.63	1.58	16.18
39	11.87	0.72	87.41	1.67	1.57
40	10.28	2.54	87.19	1.75	6.87
41	10.78	-	89.22	1.70	3.97
42	11.17	-	88.83	1.68	1.59
43	10.78	5.07	84.15	1.61	10.21
44	10.86	5.36	83.78	1.63	5.02

TABLE IX
HYDROCARBON-TYPE COMPOSITION (VOL%) FROM NMR DATA FOR ATK SAMPLES

SAMPLE NO	PERCENTAGES (VOL)			H : D	m.wt
	AROMATIC	OLEFIN	PARRAFIN		
1	9.70	5.17	85.13	2.22	6.21
2	12.79	-	87.21	2.25	1.06
3	11.62	0.80	87.58	3.37	27.62
4	10.08	8.30	81.61	2.21	17.03
5	9.85	-	90.15	2.05	5.29
6	10.85	-	89.15	2.17	4.32
7	9.25	3.18	87.57	2.19	78.54
8	8.66	4.78	86.56	2.20	5.58
9	8.15	0.52	91.33	2.22	28.72
10	12.70	-	87.30	2.13	1.31
11	14.19	-	85.81	2.23	2.52
12	12.33	-	87.67	2.56	2.25
13	16.16	-	83.84	2.53	1.85

TABLE X

HYDROCARBON - TYPE COMPOSITION (VOL %) FROM ILR DATA FOR STRAIGHT-RUN KEROSINE

SAMPLE NO	PERCENTAGES (VOL)			H : C	MOL. Wt
	AROMATICS	OLEFINS	PARAFFINS		
1	11.35	-	88.12	2.13	2.35
2	13.22	-	86.78	2.15	7.31
3	11.66	-	88.34	2.22	3.75
4	12.13	-	87.87	2.20	3.76
5	12.69	-	87.31	2.31	3.67
6.	13.34	-	86.66	1.95	1.50
7	10.58	-	89.42	2.25	1.58
8	11.03	3.97	85.00	2.21	3.93
9	14.27	-	85.73	2.11	9.60
10	17.80	4.20	78.00	2.04	1.45
11	11.66	4.37	84.11	2.15	1.34
12	11.36	3.079	85.50	2.15	0.67
13	11.51	-	88.49	2.15	1.34
14	15.37	6.46	78.17	2.11	2.49
15	14.90	-	85.10	2.10	0.54

TABLE XI

HYDROCARBON TYPE COMPOSITION (VOL %) FROM NMR DATA AND CORRESPONDING FIA VAUES FOR HEAVY NAPTHA SAMPLES

	AROMATIC VOL %		OLEFIN VOL %		PARAFFIN VOL %	
	FIA	NMR	FIA	NMR	FIA	NMR
	13.20	10.74	-	-	84.10	89.26
	14.10	11.74	-	1.61	85.90	86.65
	16.60	8.67	-	3.46	83.40	87.87
	13.20	9.01	-	2.58	86.80	88.41
	13.50	9.46	-	-	86.50	90.54
	14.70	9.86	-	-	85.30	90.14
	13.90	9.72	-	-	86.10	90.28
	14.70	10.00	-	-	85.30	90.00
	13.60	9.62	-	-	86.40	90.38
	13.20	10.10	-	-	86.80	89.90
	13.00	10.40	-	-	87.00	90.60
MEAN	13.9727	10.02909	-	0.6955	85.6182	89.4573
STD DEV.	1.0527	0.8955	-	1.261	1.194	1.2845

TABLE XII

HYDROCARBON-TYPE COMPOSITION (VOL %) FROM NME DATA AND CORRESPONDING FIA VALUES FOR ATK SAMPLES

	AROMATIC VOL %		OLEFIN VOL %		PARAFFIN VOL %	
	FIA	NMR	FIA	NMR	FIA	NMR
	17.80	9.70	1.20	5.17	81.0	85.13
	16.90	12.79	0.50	-	82.60	87.21
	18.30	9.85	1.00	-	80.70	90.15
	19.40	9.25	1.00	3.18	79.60	87.57
	15.80	16.16	0.80	-	83.40	83.84
MEAN	17.64	11.55	0.9	1.67	81.46	86.78
STD. DEV	1.3686	2.9322	0.3925	2.3925	1.5258	2.4255

TABLE XIII

SELECTED STATISTICS FROM MULTIPLE REGRESSION OF NMR AND FIA DATA GENERATED BY SUBPROGRAM REGRESSION FOR HEAVY;NAPHTHA SAMPLES

1 F AROMATICS: AROMATIC VOLUME % BY FIA METHOD.

MEANS: 13.9727 Std. Dev. 1.0529

Multiple R	0.5639	Analysis of Variance	DF	SS	Mean Sq.	F	Significance
R^2	0.3179	Regression	3	3.5234	1.1745	1.0877	0.415
Adjusted R^2	0.0256	Residual	7	7.5584	1.0798		
Std. error	1.0391	Coeff of variability	7,4%				

Variable	B	Std Error B	F	BETA	T	95%
A Aromatics	0.2197	0.8592	0.6538 .306	0.1869 .158	0.2557	-1.8119; 2.2513
N Paraffin	0.3253	0.8838	0.1355 .724	0.3969 2.083	0.3681	-1.7645, 2.4151
N Olefin	0.7826	0.9683	0.6532 .446	0.9374 .039	0.8082	-1.5070, 3.0121
Constant A	-17.8727	87.4196	.418 .844		-0.2045	-224.5868, 188.841

TABLE XIII CONTD

2F PARAFFIN: PARAFFINS VOLUME % BY FIA METHOD.

MEAN 85.6182 STD. DEV. 1.194

Multiple R	0.3171	Analysis of Variance	FD	SS	Mean Sq	F	Significance
R^2	0.1005	Regression	3.	1.4333	0.4778	0.2608	0.825
Adjusted R^2	-0.285	Residual	7	12.8231	1.8319		
Std Error	1.3545	Coeff. of Variability		1.6%			

Variable	B	Std Erro B	F	BETA	T	95%
N. Aromatic	.4418	1.1191	.1558 .705	.3313 .0518	.3948	-2.2044, 5.0879
N Paraffin	.4933	1.1511	.1836 .681	.531 .5154	.4285	-2.2287, 3.2053
N Olefin	.2592	1.2612	.4225 .834	.2737 .0021	.2055	-2.723, 3.2414
Constant A	36.8800	113.8650	.1049 .755		.3239	-232.3674m 306.1274

HYDROCARBON-TYPE COMPOSITION (VOL%) FROM "RAW" NMR DATA AND CORRESPONDING FIA VALUES FOR HEAVY-NAPHTHA SAMPLES

	AROMATICS VOL %		OLEFIN VOL %		PARAFFIN VOL%	
	FIA	NMR	FIA	NMR	FIA	NMR
	13.20	11.24	-	-	84.10	88.76
	14.1	12.35	-	0.49	85.90	86.67
	16.60	9,63	-	1.05	83.40	89.32
	13.20	9.45	-	0.79	86.80	89.76
	13.50	9.91	-	-	86.50	90.09
	14.70	10.80	-	-	83.30	89.20
	13.90	10.17	-	-	86.10	89.83
	14.70	10.46	-	-	85.30	89,54
	13.60	10.07	-	-	86.40	89.54
	13.20	10.56	-	-	86.80	89.44
	13.0	10.87	-	-	87.00	89.13
MEAN	13.9727	10.50			85.6182	
STD. DEV.	0.0527	0.8188			1.194	

TABLE XVII

SELECTED STATISTICS FROM MULTIPLE REGRESSION OF "RAW" NMR AND FIA DATA GENERATED BY SUBPROGRAM REGRESSION FOR HEAVY NAPHTHA SAMPLES

1. F - AROMATICS

MEAN: 13.9727 Std. Dev. 1.0527

Multiple R	0.5626	Analysis of Variance	DF	SS	Mean Sq.	F Sig.
R^2	0.3165	Regression	3	3.5071	1.1690	1.0803 0.417
Adjusted R^2	0.0235	Residual	87	7.5747	1.0821	
Std Error	1.0402	Coeff of Variability	7.4%			

Variables	B	Std Error B	F	BETA	T	95% Interval
N-Aromatics	2.1116	5.3896	0.1535	1.6423	0.3918	-10.6326, 16.8229
N-Olefins	3.6789	5.5586	0.4381	1.3414	0.6619	-9.4019, 12.8385
N-Paraffins	1.8660	4.6403	0.1617	1.6630	0.4021	-9.1,65, 14.8558
Constant A	-175.5057	471.7208	0.1384			-12909456, 939.93431

TABLE XVII CONTD.

2. F-PARAFFIN
Mean : 85.6182 Std. Dev. 1.1940

Multiple R	0.4622	Analysis of Variance	DF	SS	Mean Sq	F	Sig.
R^2	0.2136	Regression	3	3.0452	1.0151	0.6338	0.616
Adjusted R^2	-0.1234	Residual	7	11.2112	1.6016		
Std. Error	1.2655	Coeff of Variability	1.5%				

Variables	B	Std Error B	F	BETA	T	95% interval
N-Aromatics	-7.2727	6.5568	1.2302	-4.9870	-1.1092	-22.7771, 8.2317
N-Paraffin	-6.2289	5.6453	1.2175	-4.8946	-1,1034	-19.5780, 7.1200
Constant	79.6288	573.8872	1.5724		1.2539	-637.3857, 207
						.66534

TABLE XVIII

SELECTED STATISTICS FROM MULTIPLES REGRESSION OF RAW NMR AND FIA DATA GENERATED BY SUBPROGRAM REGRESSION FOR ATK SAMPLES

1. F - AROMATICS

MEAN : 17.6400 STD. DEV. 1.36858

Multiple R	0.9975	Analysis of Variance	DF	SS	Mean Sq	F	Sig.
R^2	0.9939	Regression	3	7.4538	2.4846	65.0275	0.091
Adjusted R^2	0.9796	Residual	1	0.03821	0.0382		
Std. Error	0.1955	Coff of Variability	1.1%				

Variables	B	Std. Error B	F	BETA	T	95% interval
N-Aromatic	-4.6326	0.9060	26.1443	-7.8460	-5.1131	-16.1447 ,
			.123	-3.0737		5.8798
N-Olefin	-4.4951	0.9527	22.2598	-2.4006	-4.7180	-16.6009,
			.132	-0.1300		7.6109
N-Paraffin	-4.1044	0.9252	19.6802	-5.6516	-4.4362	-15.8604,
			.141	-20.4135		7.654
Constant A	434.2430	92.2362	22.1651	.	4.708	-737.7241,
			1.130			1606.2181

TABLE XVIII CONTD.

2. F - OLEFINS

Mean: 0.9000 Std. Dev. 0.2646

Multiple R	0.8288	Analysis of Variance	DF	SS	Mean Sq	F	Sig.
R^2	0.6870	Regression	3	0.1924	0.0641	0.7315	0.673
Adjusted R^2	-0.2521	Residual	1	0.0877	0.0877		
Std Error	0.29606	Coff of Veriability	32.9%				

Variables	B	Std. Error B	F	BETA	T	95% interval
N-Aromatics	0.3945	1.3723	0.8262	3.4557	0.2874	-17.0419,178308
N-Olefin	0.6274	1.443	0.1890	1.783	0.4347	-17.1083, 18.9530
N-Paraffin	0.4537	1.4014	0.1048	3.2314	0.3237	-17.3520, 18.2595
Constant A	-43.8393		0.9847		-0.3138	-1818.9240 , 1731.2455

TABLE XVIII-CONTD.

3. F- PARAFFIN

MEAN 81.4600 STD. DEV. 1.5258

Multiple R	0.9995	Analysis of Variance	D.F	SS	Mean Sq.	F	Sig.
R^2	0.99891	Regression	3	9.3019	3.10063	306.4262	0.42
Adjusted R^2	0.9957	Residual	1	0.0101	0.0101		
Std. Error	0.10059	Coeff. of variability	0.1%				

Variables	B	Std. Error B	F	BETA	T	95% Interval	
A-Aromatics	4.2382	0.4663	82.6257	6.4384	9.0899	-1.6861	10.1625
N-Olefin	3.8677	0.4903	62.2293	1.8527	7.8886	-2.3261	0.0976
N-Paraffins	3.6508	0.4761	58.7929	4.5089	7.6677	-2.3790	9.7006
Const. A.	-290.4077	47.4661	37.4326		-6.1182	-893.5273	312.7059

TABLE XIX

PART AND PARTIAL CORRELATIONS FROM REGRESSION OUTPUT

(RAW DATA)

A. HEAVY NAPHTHA

DEPENDENT VARIABLE	OVERRALL		INDEPENDENT		VARIABLES
	MULTIPLE R	R^2	N-OLEFIN	N-PARAFFIN	N-AROMATIC
F-Aromatics	0.5626	0.3165	0.2993	0.0022	0.015
F Paraffin	0.4622	0.2136	0.0753	0.1368	0.0015

B. ATK

F-Aromatics	0.9995	0.9949	0.0194	0.1004	0.8751
F.Olefin	0.8288	0.6870	0.5429	0.1162	0.0259
F-Paraffin	0.9995	0.9989	0.004	0.0639	0.931

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