STUDY OF NON HYDROCARBONS CONTENT OF SOME LOCAL CRUDE OILS

THESIS

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BY

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A C K N O W L E D G E M E N T S

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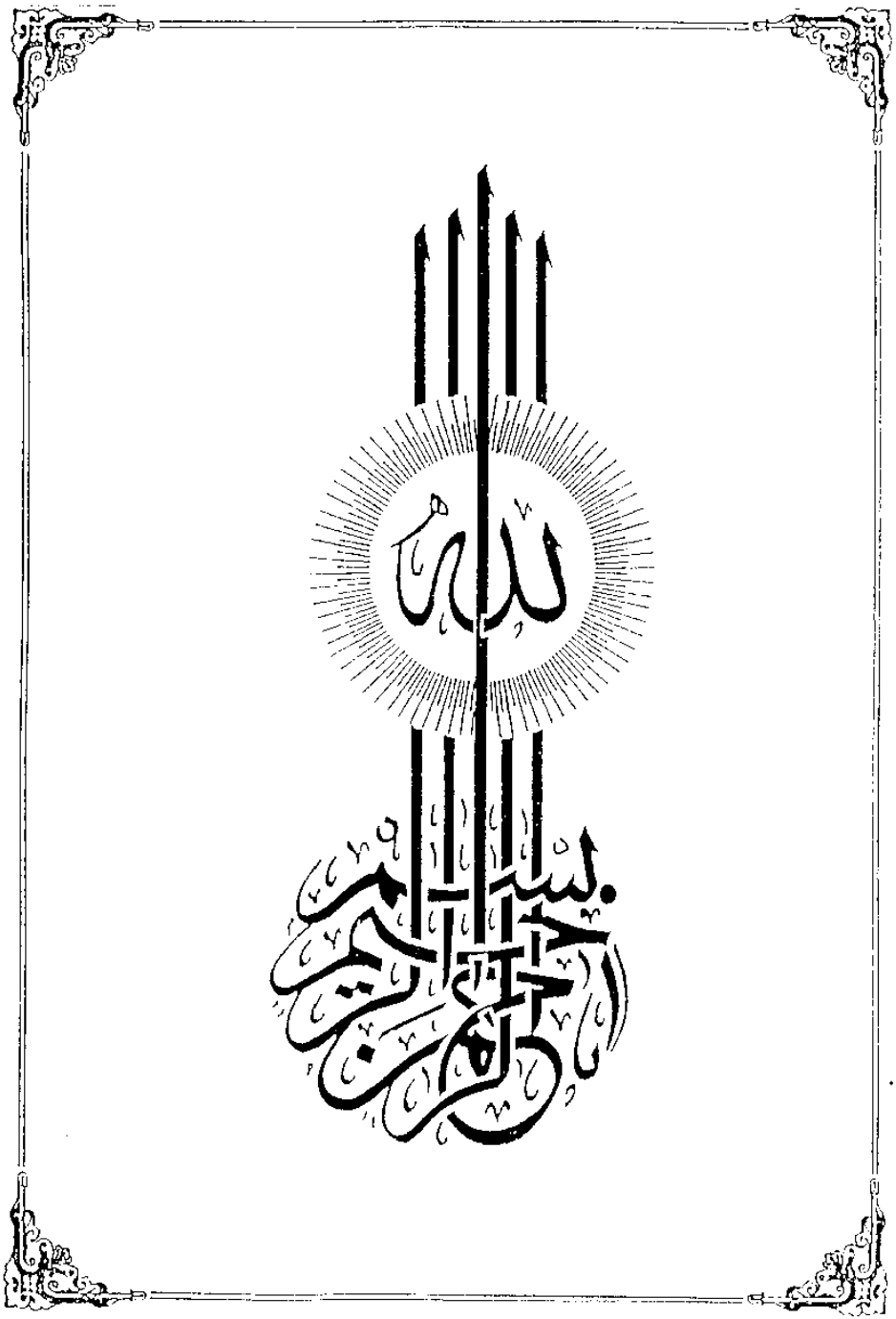

N o t e

Besides the work carried out in this thesis, the candidate has attended post graduate courses for one year in Organic Chemistry including the following topics:

1. Reaction Mechanism
2. Electronic, IR, Mass, and NMR spectroscopy of organic molecules.
3. Organic Reactions
4. Free Radicals
5. Steroids
6. Aromaticity
7. Organophosphorous Compounds
8. Conformational Analysis.

She has successfully passed an examination in these topics.

Prof. Dr. Nazir Erian
Head of Chemistry Department

C O N T E N T

I. Aim of the Work:

The aim of the work was namely to study the non-hydrocarbon content especially nitrogen and sulphur compounds in two Egyptian oil fields Ramadan and Ras-Gharib.

II. Introduction

Crude Petroleum

Petroleum crude differs in its appearance from a light black mobile, viscous liquid to a dark semi solid product. It is generally assumed that all constituents of crude petroleum resulted from aerobic and anaerobic enzymatic degradation of organic matter under suitable conditions of temperature and pressure. It is composed mainly of hydrocarbons with small amounts of non-hydrocarbons[1-6], usually concentrated in the higher boiling fractions of the crude. Some other contaminants may be present such as vanadium and nickel, however small amounts of insoluble materials such as sand and clay may also be present which may have been originated in the drill hole itself[7].

Hydrocarbons:

Four classes of hydrocarbons form the main constituents of the crude petroleum, namely n-paraffinic, isoparaffinic, naphthenic and aromatic types of mixed structures. The pure hydrocarbon types are mainly present in the gaseous and lighter fractions of the crude oils, as the

boiling point of the fractions increases mixed type structures predominate.

Complete separation of each individual hydrocarbon has not been yet attained. However, different techniques were elaborated for the separation and identification of the hydrocarbons in light fractions[8]. In case of heavy fractions[9], methods of structural group analysis are usually made use of, since fractional separation is not an easy work.

Non-hydrocarbons

The non-hydrocarbon constituents of petroleum present to a great extent than expected sulphur, nitrogen and oxygen are rarely present in amounts greater than 1 or 2%[2] as well as traces of metallic compounds[10-13].

It is very important to give certain attention for studying non-hydrocarbon compounds, since it contains acid-forming elements which may cause corrosion of refinery equipment, certain metallic elements may also deposit on hydrocarbon conversion catalysts and adversely affect yields or products distribution. Inorganic materials or tarry oxygenated compounds may deposited in equipment[14].

have a corrosive effect on gas turbins working with residual oil.

A. Nitrogen Compounds

The study of the nature of nitrogen compounds in crude oils has long been of great interest from the stand point of its possible relation to the question of the origin of petroleum. The nitrogen compounds in crude oils originate from the organic material which represents the mother substance of crude petroleum. The nitrogen content[21-23], in crude petroleum occurs in amounts ranging from trace up to slightly less than 1%. Peckman[24] suggested that the amount found in oil might vary with the extend to which the oil has been exposed to air[25,26].

Nitrogen compounds are classified into a basic and non-basic according to their ability to interact with perchloric-acetic acid solution.

Older oils may lost a great part of their nitrogen through the decomposition of high molecular weight bases as they have been subjected to more severe conditions[27,28]. The distribution of nitrogen in fractions is generally the

same as that of sulphur, i.e., they increase with the boiling range of the fractions in which at least 85% of the nitrogen of most crude oils is found to be concentrated in the residue. Generally, the nitrogen content increases as the crude oil becomes more asphaltic. A relation between the nitrogen and carbon residue contents of the crude has been established, the higher the carbon residue content, the higher becomes its nitrogen content[12].

Recently, nitrogen compounds attracted the attention due to a number of reasons among which are their poisoning effects on catalysts as well as storage, colour, stability and gum formation in oil.

(1) The Nature of Nitrogen Compounds in Petroleum

Mabery[29,30] and later on Bailey[31,32] and co-workers investigated different nitrogen bases present in oil distillates.

In 1928 Poth and co-workers[33] concluded that nitrogen compounds in distillates are basic along with non-basic compounds of unknown structure, but in crude oil itself it appears to be non-basic, this is due to the fact that during extraction of nitrogen from crude oil

with 16% sulphuric acid which was not successful.

(a) Basic Nitrogen Compounds

The term "basicity" means the relative availability of the electrons on the nitrogen atom. This property is of great importance as many of the reactions of these compounds take place at the nitrogen atom. The classification of nitrogen compounds into basic and non-basic[34,35] is based on the ability of the nitrogen compound to interact with a perchloric acid-acetic acid solution. The older methods of defining basic nitrogen compounds as those extracted by an aqueous solution of some mineral acids have certain disadvantage.

Hall[36] found that the relative strength of various organic bases can be studied in glacial acetic acid solution.

Further work on a number of bases is done by Albert and co-workers[37]. Fritz[38] has described the titration of a number of weak bases with perchloric acid in acetic acid solution. This titration is used for the classification of nitrogen compounds in a shale oil naphtha by Dineen and Bickel[39] and also for the determination of traces

of basic nitrogen impurities in benzene by Wilson[40].

Basic nitrogen compounds can be completely extracted by 25% aqueous solution of sulphuric acid[41]. Six membered ring compounds are pyridine and quinoline. Some derivatives of pyridine such as acridine and acridone. Amines and anilines[42] can exist but are found in large quantities in higher boiling distillates.

In a typical straight-run stock, basic nitrogen compounds would constitute 25-35% of the total nitrogen content, and according to Ball[43], although the ratio of basic to total nitrogen is high for the lower boiling fractions, it is about 0.3 for the major portion of the crude. It was found that pyridine and quinoline derivatives were the only basic nitrogen compounds present in the lighter straight-run and cracked petroleum fractions.

(b) Non-basic Nitrogen Compounds

The five membered ring compounds are considered as non-basic, e.g., pyrroles, indoles and carbazoles. In domestic heating oil distillates Sauer et al[44] predicted that the pyrroles and indoles are mono- and di-alkyl substituted with 2 or 3 carbon atoms in the alkyl groups.

Some exceptions to the non-basicity of six membered ring compounds are the basic character of hexahydrocarbazole (hydrogenated carbazole derivative) and indoline. Some pyrrole derivatives[37], e.g., 2-methyl-3-ethyl pyrrole pocess also basic character due to the presence of side chain.

Ward et al[45] noted that pyrrolic compounds are concentrated on catalytic oils while thermally cracked oils are characterised by a high concentration of basic nitrogen compounds.

Although nitrogen compounds are present in trace amounts they have still poisonous effects. They reduce the activity of cracking and hydrocracking catalysts because of their polarity and basicity as well as poor storage of fuel due to the gum formation. Also, the poor colour[46] together with colour instability is due to the presence of nitrogen compounds.

Hindrickson[47] showed that the neutral polar materials such as alkyl substituted pyrroles, indoles, alcohols, esters and amides produce all the colour formed in cracked gas oil from California crude.