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NOVEL STUDY FOR CHEMICAL COMPOSITION OF AL-AHDAB CRUDE OIL

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ABSTRACT

Thisn research included determination of chemical composition of al-ahdaab crude oil (kute- Iraq) using liquid – solid chromatography. The current researched included to separation the component of crude oil by column chromatography was packing with alumina (AL_2O_3) as a stationary–phases and several solvent as a mobile phase. . The results of crude oil fractionations were 17.01% Asphaltene, 82.99% Maltene, which separated to (Paraffinic) (saturated) 44.11%, Aromatic 30.11% and Resin 4.20%. Crude oil fractionation were characterized using Nuclear Magnetic Resonance H^1NMR and Fourier Transform Infrared Spectrometer FT-IR to determine the chemical composition of each part, which is that represents the first study and a novel results. This study also clarified the paraffinic compounds are represented the main part of materials in crude oil composition.

1. INTRODUCTION

Iraqi oil considers as one of the foremost discovered in the middle east region. BaBa kirkir field is still more manufacturing than the other oilfield although its old age where it has discovered in 1927. Moreover AL-Ahdab field is one of the recently discovered oilfield, and it still in its tentative product stage. This oilfield locates in the middle of Iraq(kute governorate). Crude oil or petroleum is naturally occurring mixture that occur in the earth in liquid form,[1-3] consisting predominantly of hydrocarbons with other element such as sulphur, nitrogen, oxygen, etc. appearing in the form of organic compounds which is some cases form complexes with metals. Elemental analysis of crude oil shows that it contains mainly carbon and hydrogen in the approximate ratio of six to one weight [4].

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Crude oil is a complex mixture and has different components of hydrocarbon groups as colloidal systems having a disperse phase composed of asphaltenes and resins. The precipitation of asphaltenes depends on the colloidal stability of these complex systems. Among the different factors that influence the stability of crude oils. In general the presence of similar weight percentages of saturates, aromatics, and asphaltenes are considered signs of similar asphaltene stability. Crude oil is easily transportable source of energy, concentrated and flexible from of fuel. At the beginning of the 20th century the industrial revolution had progressed to the extent that the oil industry became the major supplier of the energy largely because of the arrival of automobile. The oil achieved a primary importance as an energy source on which the world economy depends [5].

In order to understand the physical properties and chemical composition behavior of such complex

mixtures, it is necessary to characterize the chemical structure of these mixtures the chemical composition of a crude oil is classified according to its SARA content (Saturates, Aromatics, Resins, and Asphaltenes). Generally these groups each with individual sub groupings, different components consisting of mainly hydrocarbons and some trace metals. Crude oils vary widely in their physical and chemical properties. They may be straws colored, green, brown or black, the last three being the most common colors [6,7].

The chemical composition importance of determining the optimization processes of referring, elicitation, and industrials of petroleum products because it represents in clear image the physical and chemical properties of oil which especially use to design the system of oil refinery and production [1-3]. Molecular types in crude oils range from nonpolar, nonaromatic hydrocarbons to highly aromatic hydrocarbons, the molecular structures of which contain varying amounts of certain so-called heteroatoms, predominantly oxygen, nitrogen, and sulfur, together with parts-per-million amounts of metals because the number of molecules in crude oils with different chemical structures is extremely large, determination of crude oil composition by separation into its molecular components [4].

There are many reports on researches about the chemical composition of crude oils that have been reported to hydrocarbon contain [8- 10].

The objective of this research is to elucidate the chemical composition of each fractionated components for crude oils from AL-Ahdab field, using liquid- solid chromatography, and ^{1}HNMR, FT-IR spectroscopy due to characterization of functional group.

2. EXPERIMENTAL

Raw Materials:

Crude oil sample from AL-Ahdab field (kute - governorate) was used in this study. The obtained crude stored in sealed glass ampoules in the dark, in air. The physiochemical properties of crude oil sample were determined such as: API gravity = 25.21, Total Acid Number mg KOH/gr Sample = 0.11 and Total Base Number mg KOH/gr Sample = <0.05.

Chemical and reagent:

The chemically pure grade n-Pentane, n-Heptane, Toluene, Methanol, Benzene and n-Hexane were used as the solvent of precipitant and fractionation, for all samples were purchased from sigma- Aldrich Co. Alumina and CCL_4 from Fluka Co. Instrumentation and Measurements:

Methodology:

Several experimental were carried out to fractionation of Crude oil to the main parts using Column Chromatography and common methods of Separation – Chromatography. All work reported was performed with standard laboratory equipment**.**

^{1}H-NMR Spectra:

^{1}H-NMR spectra were recorded at 500.13 MHz for protons on a Bruker 500MHz Avance 111, spectrometer operating at room temperature. The sample solutions were prepared in chloroform-d ($CDCl_3$) and tetramethylsilane (TMS) was added to the sample as an internal reference.

FT-IR Spectra:

Fourier-transformed infrared spectroscopy sodium chloride (NaCl) polish discs (25 X 2 mm) were used to analyze oil samples under (FTIR) spectrometry.

Background spectra were obtained by scanning two clean discs simultaneously in the instrument. One drop of used oil was placed between of two NaCl disc was placed in a Perkin-Elmer Spectrum -100 FTIR instrument and solid materials as KBr discs four scans were carried out in the 4000–400 cm^{-1} range.

Fractionation and Separation of Crude oil:

SARA Separation: Many attempts have been made to separate crude oils into groups or classes of compounds. The SARA-separation is an example of such group type analysis, separating the crude oils in four main chemical classes based on differences in solubility and polarity. The four SARA-fractions are the saturates (S), aromatics (A), resins (R), and the asphaltenes (A). The SARA based on removal of asphaltenes by precipitation with a paraffinic solvent such as n-pentane or n-heptane before to chromatographic separation of the remaining crude oil on alumina [11].

Deasphaltening:

The Separation of asphaltenes was carried out by two steps First : removal of the insoluble materials in crude sample. In a 500ml flask 10g of crude sample and 40ml of CCL4 was added. Mixture was shacked for 30 minutes, than filtrated to product insoluble materials. Secondly: In a 500ml flask soluble of Crude oil sample, normal hexane was added, mixture was shaked at room temperature for 1.5 hour to ensure the full solubility of Crude sample, Asphaltene precipitation occurs when an excess of n-pentane is added to mixture, then filtrated through the use of ashless paper No (42) mm by a Buchner funnel, the precipitate was washed until less for the color drops ensure complete. Asphaltene was separated in the precipitate part and soluble are Maltenes part.

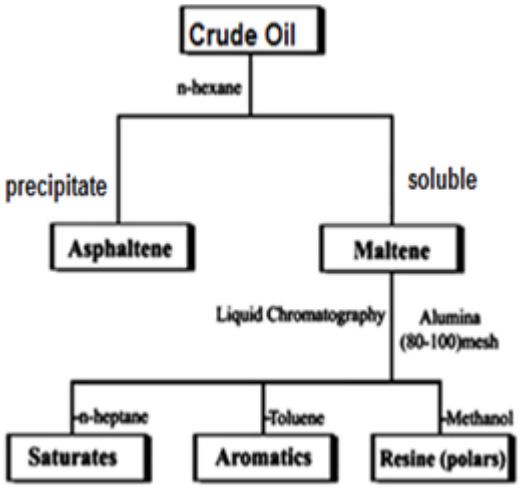
Liquid- solid chromatography separation of Crude Oil:

Fractionation of Maltenes by Column Chromatography:

The soluble part (maltenes) was evaporated at room temperature to get a test sample (dry maltenes) and several stationary phases were used for laboratory fractionation column by using n- hexane, into the SARA method enables the separation of maltenes into groups (Saturated ,Aromatic, Resin and Asphaltine) This method is an extension of column liquid -solid chromatography to get more precise separation, packed columns are employed. packed under vibration. ASTM (D3279).

General Procedure:

A 100 × 2 cm glass column was used for the present work. Column Chromatography packed (mobilizes) under vibration in the activated stationary phase (alumina), was activated at 350 ºC for 2hrs. Maltens part of 8g was dissolved with a small amount of n-heptane then transferred to the chromatography column. First part of a saturated hydrocarbon was fractionated by using n-heptane as solvent. Second part of aromatic was separated by using toluene. Third part of resin separated using methanol, once fractionation processes finished of the three parts with change color. The three fractions were collected and the solvents were removed from them by distillation. Samples were further dried under vacuum to measure their weights to estimate the kinds of each fraction part. The speed of the coming down drops was an (5) drops rate per minute in all fractionation process at the chromatography column as shows Scheme**.1**



Schematic.1. illustration of SARA test

Fractionation by alumina (Al_2O_3): A 50g of alumina (80 - 100 μm) where activated at 350 ^oC for 3hrs then mixed with a small amount of n-heptane (emulsion) to ease transfer to the column due to good packing without gaps and bubbles. Maltens part 8g was dissolved with n-heptane, Paraffin compound (saturated) part was coming down with pale yellow colures. Fractionation side red when the coming down drops which received of eluent (heptane) become colorless, then toluene had been added to fractionate the aromatic part which has orange color. Fractionation of the last part (Resin) which high polarity was complete carried out by methanol. The product was of orange- red color. The fractionation when the eluent drops become colorless. Three samples were collected and then distilled, dried and evaporated for measuring the weights of fractions and determined the kinds of every fractionated part of petroleum crude.

3. RESULT AND DISCUSSION

There are many parameters that is operational in the separation of crude oil constituents such as (polarity, aromaticity, molecular weight, solvent power, time required to allow the recipitating/extracting, temperature, pressure, ratio of the precipitating/extracting). SARA separation is convenient and inexpensive and has been utilized extensively in the oil industry. Crude oils from AL-Ahdeb field exhibit a wide range of physical and chemical properties and the SARA-separation can be seen to give information somewhat between that obtained by elemental analysis and analysis for individual molecules. The chemical composition of crude oils will in the following to be discussed on the SARA-fractions. Table.1 shows a summary of the main characteristics of the studied crude oils [12].

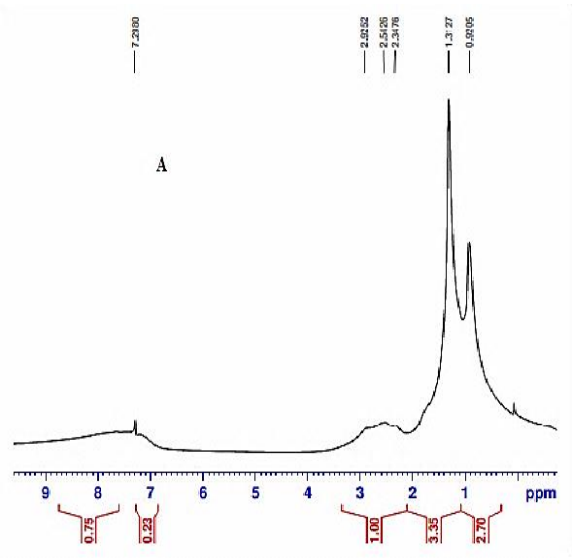


Table.1. Wt. % of fractionation part come from SARA test

Solvent used	Expected of isolated materials	Alumina Wt %
Heptane	Paraffinic	44.11
Toluene	Aromatic	30.11
Methanol	Resin	4.20
Hexane	Asphaltene	17. 01
CCl_4	insoluble	0,7
-- -- - -	Residue	2.9

Quantitative analysis of the ^{1}HNMR:

Proton Nuclear Magnetic Resonance ^{1}HNMR Spectroscopy has been applied to petroleum chemistry to provide details information of the hydrocarbon chemistry of raw petroleum and its various products [13].

^{1}HNMR can be an useful tool due to investigation of distribution hydrogen type and molecular mobility it was found the type of H % in Crude sample at Table 2. Study was achieved by using the area under the curve and by identifying the absorption of protons. Which include aromatic hydrogen H_a at chemical shift with rang between 6.5 - 8.5 ppm . naphthenic hydrogen H_n at rang 1.4- 2.2 ppm. Methylene hydrogen H_{my} of paraffin compound at rang 0.9 -1.8 ppm, methyl hydrogen H_{me} at ring 0.5 -1.4 ppm, hydrogen of alpha aromatic ring Hα at 1.7 - 3.4 ppm. Through Information from the values of the ^{1}HNMR results obtained the methylene hydrogen of paraffin compound $H_{my\%}$ a higher percentage in asphaltene part of AL-Ahdeb crude oil. The different types of hydrogen atoms are given in Table 2 [14].

Table.2. distribution of proton H % by 1HNMR Spectroscopy of Asphaltene

Type Hydrogen%	H_{my}	H_{me}	H_n	Hα	H_a
Asphaltene sample	47.86	21.50	13.65	9.18	7.80

Figure.1 ^{1}HNMR spectra of Asphaltene

From this figure 1, one could observe that asphalten contains a high proportion of methylene groups. Followed by methyl groups, and that the ratio of naphthenic protons to the alpha aromatic are close together in the relative distribution[15].

The fractionated parts of maltenes (paraffinic, aromatic, resin) which separated with column chromatography, by using alumina an a stationary phase

The H^{1}NMR profile of maltenes fractionation part have been provided in table 3 and figures (2- 4).

Table.3. distribution of proton H % by ^{1}HNMR Spectroscopy of maltenes fractionated

Type Hydrogen%	H_{my}	H_{me}	H_n	Hα	H_a
paraffin sample	46.54	34.33	8.12	4.53	4.65
Aromatic sample	47.67	17.53	8.65	7.89	12.67
Resin sample	34.23	15.65	10.54	7.42	10.61

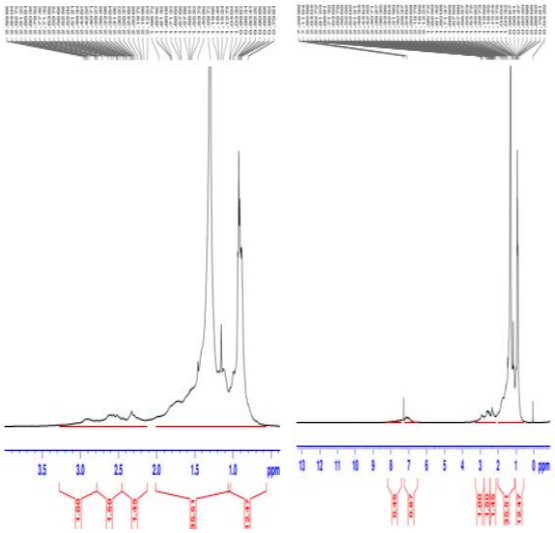


Figure.2. ^{1}HNMR spectra of paraffin

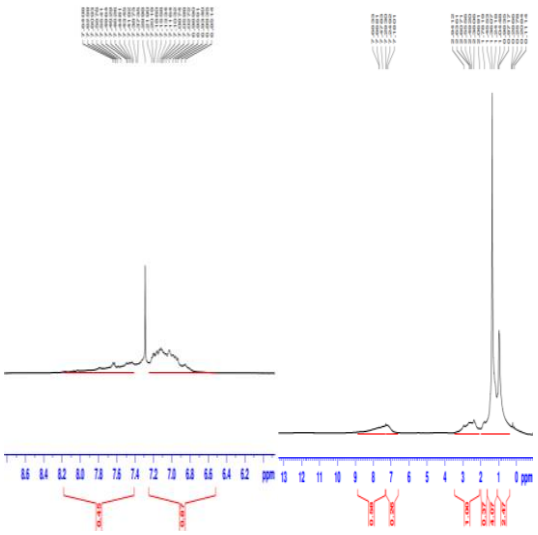


Figure.3. 1HNMR spectra of aromatic

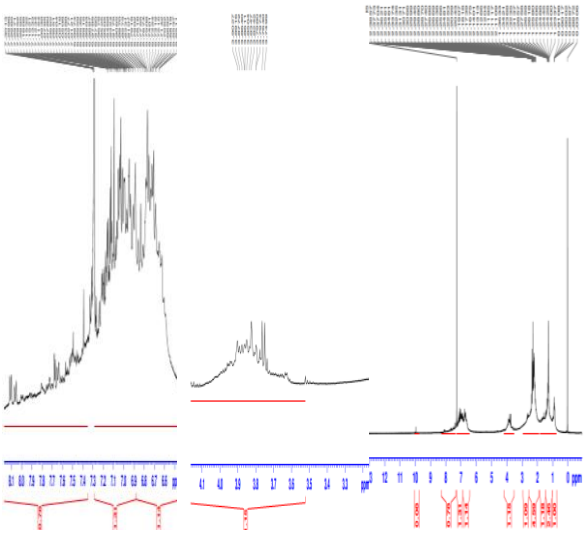


Figure.4. ^{1}HNMR spectra of resin

AL-Ahdab crude oil fractions using FTIR transmission spectra (inverses of absorbance spectra) which showed absorption of asphaltene band (KBr disc)cm^{-1} from figures.5. Absorbance peaks of the following functional groups: aliphatic CH_2 and CH_3 stretch, aromatic C-C ring-breathing stretch, methyl CH_3 asymmetric and symmetric stretches, carbonyl and carboxyl stretch, pyrrolic NH stretch, and sulfoxide stretch. In addition, many of the spectra contain one of the following absorbance's: free OH stretch from 3424 to 3436cm indicate of phenolic and Alcohols OH stretch, and amide-carbonyl stretch. Each of these absorbance's has been ca**re**fully identified in the spectra large absorbance intensities for aliphatic CH_2 and CH_3 stretches in the wavelength range from 2800 to 3000 cm^{-1}, significant absorbance for symmetric and asymmetric CH_3 bending modes in the wavelength range from 1350 to 1500 cm and aromatic C-C ring-breathing stretches at a frequency of about 1600-1605cm^{-1}, asymmetrical stretching vibration CH_3 to 1411-1450cm^{-1}, Sulfoxide (C_2S=O-) from 1029 to1032 cm^{-1} and peak at 806 cm $^{-1}$ out-of-plane vibration of ring C-H.

However, the paraffinic fractionated was confirmed by FTIR spectrum Figure.5. More detailed information of the chemical structure of paraffinic obtained by following the absorptions of C-H stretching in the alkanes 3000 to 2840 cm^{-1}. The band at 2923 cm^{-1} indicate of vibration of CH_2 methyl groups, that at 2857cm^{-1} attributed of CH_3. The band located at 1623cm to amide stretching, vibrations for C-H at 1515 cm $^{-1}$ indicate the methylene (-CH2-) chains, the band from 1461 to 1403cm^{-1} stretching of CH_3, band at 1110 to 1033 cm^{-1} for C-O bending and 674 cm^{-1} for C-C vibration out of the plane [16].

The aromatic C-H stretching band, which occurs between 3100 and 3000cm, did not appear on the spectra due to the weak C-H stretch in aromatic compounds, band at 1407cm^{-1} attributed to asymmetry bend of CH_3, the band at 1330cm is indicative of H-C=C- groups and a new band appeared at 1037cm^{-1} which are related to the C—C aromatic, since low boiling aromatics are depleted relative to saturated compounds.

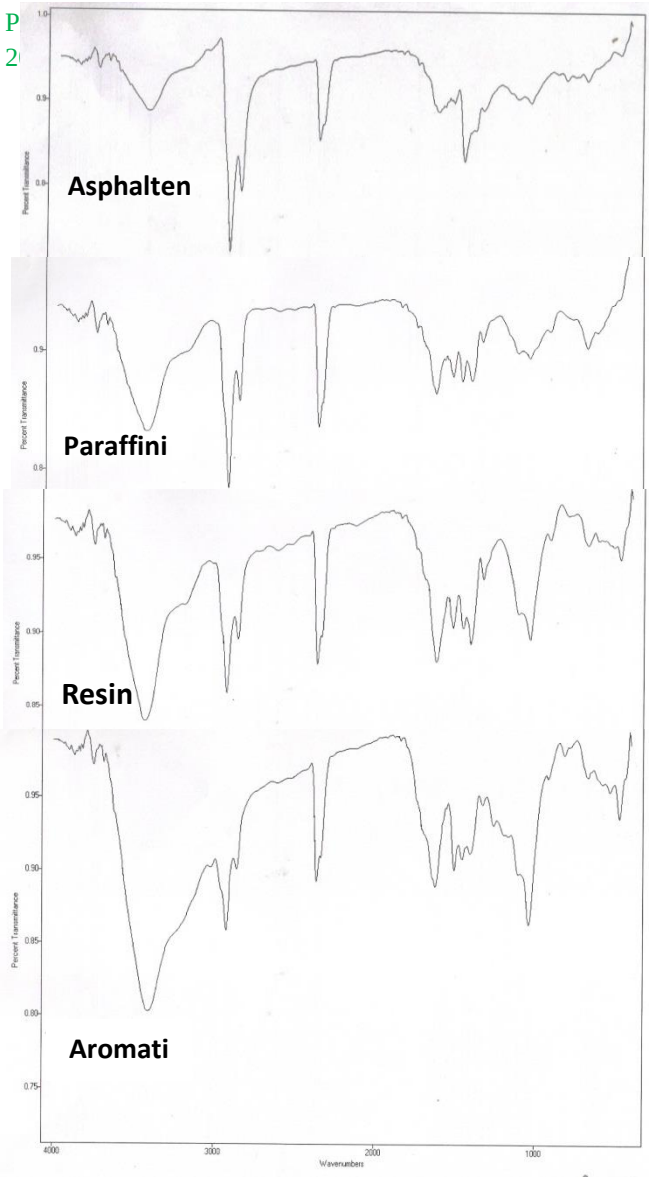


Figure.5. FTIR spectra for SARA extraction of AL-Ahdab crude oil.

The resin fractionated is the oil component and has polar aromatic compounds. The absorption band located at 1508cm^{-1} Indicate the presence of C— H aromatic, bands related to –CH_2 CH_3 vibrations appear in the1454 cm^{-1}, observed band at 1261 cm^{-1} was -CH_2-CH_2-vibration**,** the band occurred at 917 and 817cm^{-1} are representing hydrocarbons C-C in the aromatic ring or polyaromatic polar compound and observed band in the 671 and 558cm^{-1} attributed to C-X aliphatic halogen compound [17].

Combining structural analysis results obtained from elemental analysis, FTIR and ^{1}HNMR of fractions, the possible hypothetical molecular structure for asphaltene, paraffinic, aromatic and resin are represented as in figures (1-5) which were successfully method for determination of crude oil component.

4. CONCLUSIONS

This study has shown that $^{-1}$HNMR and IR spectroscopy, several important structural parameters are proposed and calculated through the analysis of quantitative ^{1}HNMR and FTIR spectra including the number of alkyl chain substituents to aromatic rings of crude oil, which has been used for characterization and determination of diverse compositions of AL-Ahdab crude oil were separated into compound classes via SARA technique to four fractionated of different structure.

The high content of paraffinic and low resin supported that AL-Ahdab crude was medium crude oil. Hypothetical structures for four fractions were proposed paraffinic structure was contained long aliphatic compounds. The aromatic fraction consisted of aromatic ring with branched paraffin's, the resin part was composed of fused polar aromatic groups with branch paraffin. Asphaltene was the most complex compositions. However the present study was a novel and has provided insight in to the chemical structure of AL-Ahdab crude oil.

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دراسة جديدة للهندسة الكيميائية من نفط الأحدب

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الخلاصة:

تضمن هذا البحث تحديد التركيب الكيميائي للنفط الخام في حقول الاحدب (كُوت- العراق) باستخدام كروماتوغرافيا السائل - الصلب .كان البحث الجاري المتضمن لفصل مكون النفط الخام بواسطة عمود كروماتوغرافي هو التعبئة مع الألومينا (AL2O3) كمراحل ثابتة والعديد من المذيبات كمرحلة متنقلة . .كانت نتائج تحليل النفط الخام 17.01٪ Asphaltene، 82.99٪ Maltene ، التي فصلت إلى برافين مشبع 44.11٪ ، وارومانتيك30.11 ٪ وراتنج 4.20٪ .تم تصنيف تجزئة النفط الخام باستخدام الرنين المغناطيسي النووي H1NMR و مطياف الأشعة تحت الحمراء لتحديد التركيب الكيميائي لكل جزء ، والذي يمثل أول دراسة ونتائج جديدة .كما أوضحت هذه الدراسة أن مركبات البارافين تمثل الجزء الرئيسي من المواد في تركيبة الزيت الخام.