A Novel Study for Chemical Composition of Al-Ahdaab Field Crude Oil

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Crude oil Fractionation Chemical composition Al-ahdaab.	This research included determination of chemical composition of al-ahdaab crude oil (kute- Iraq) using liquid – solid chromatography method. The current study involved separation the components 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 fractionations were characterized using Nuclear Magnetic Resonance ^{1}HNMR and Fourier Transform Infrared Spectrometer FT-IR to determine the chemical composition of each part, which is that represents the first study and novel results. This study also clarified the paraffinic compounds are the main part of materials in the crude oil composition.

Introduction

Iraqi oil considers as one of the foremost discovered in the Middle East region. Baba Kurkur Field in Iraq is still more manufacturing than the other oilfield although its old age where it has discovered in 1927. Moreover, AL-Ahdeb 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 (Mustafa *et al.,* 2011; Mahinpey *et al.,* 2010; Mamdouh *et al.,* 2012), consisting predominantly of hydrocarbons with other element such as sulphur, nitrogen, oxygen, etc. appearing in the form of organic compounds which is in 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 (Bouhadda *et al.,* 2007). 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 percentages weight of saturates, aromatics, and asphaltenes are considered signs of similar asphaltenes 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, because of the arrival of automobile. The oil achieved a primary importance as an energy source on which the world economy depends (Enekwe *et al.,* 2013). To understand the physical properties and chemical composition behaviour 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 (May- Elena *et al.,* 2003; Joseph *et al.,* 1997). 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 (Mustafa *et al.,* 2011; Mahinpey *et al.,* 2010; Mamdouh *et al.,* 2012). 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 (Bouhadda *et al.,* 2007). There are many reports on researches about the chemical composition of crude oils that have been reported to hydrocarbon contain (Carmen *et al.,* 2000; Odebunmi *et al.,* 2000; Ren Wenpo *et al.,* 2006). The objective of this study is to elucidate the chemical composition of each fractionated for crude oils from AL-Ahdeb field using liquid- solid chromatography, and ^{1}HNMR, FT-IR spectroscopy are used to characterize of functional groups.

Experimental

Raw Materials: Crude oil sample from AL-Ahdeb 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/g Sample = 0.11 and Total Base Number mg KOH/g 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 500 MHz 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 analyse 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 in the form of 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 the chromatographic separation of the remaining crude oil on alumina (Trejo *et al.,* 2007).

De-asphalting: The Separation of asphaltenes was carried out by two steps Firstly: removal of the insoluble materials in crude sample. In a 500 mL flask 10 g of crude sample and 40 mL of CCL$_4$ was added. Mixture was shacked for 30 minutes,

then filtrated to product insoluble materials. Secondly: In a 500 mL flask soluble of crude oil sample, normal hexane was added, mixture was shacked 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 dry maltenes and several stationary phases were used for laboratory fractionation column by using *n*-hexane, SARA method enables the separation of maltenes into groups (Saturated, Aromatic, Resin and Asphaltene) 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 glass column (100 × 2 cm) was used for the present work. Column Chromatography packed (mobilizes) under vibration in the activated stationary phase (alumina), was activated at 350 ^{o} C for 2hrs. Maltenes part of 8 g 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 colors. 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 in Scheme.1

Fractionation by alumina (Al₂O₃): A 50 g of alumina (80 - 100 *μm*) where activated at 350 °C for 3hrs then mixed with a small amount of *n*-heptane (emulsion) to ease transfer to the column to get a good packing without gaps and bubbles. Maltenes part 8 g 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) becomes colorless, then toluene had been added to fractionate aromatic part which has orange colors. 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.

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 precipitating/ 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 (Elham *et al.,* 2013).

Quantitative analysis of the ¹HNMR

Proton Nuclear Magnetic Resonance ¹HNMR Spectroscopy has been applied to petroleum chemistry to provide details information of the hydrocarbon chemistry of raw petroleum and its various products (Ren Wenpo *et al.,* 2006). ¹HNMR can be a 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 $H\alpha$ at 1.7 - 3.4 ppm. Through Information from the values of the ¹HNMR results obtained the methylene hydrogen of paraffin compound $Hmy_\%$ are a higher percentage in asphaltene part of AL-Ahdeb crude oil. The different types of hydrogen atoms are given in Table 2 (Ahammed *et al.,* 2011). 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 (Akmza *et al.,* 2011). The fractionated parts of maltenes (paraffinic, aromatic, resin) which separated with column chromatography, by using alumina a stationary phase The ^{1}HNMR profile of maltenes fractionation part have been provided in table 3 and fig 2- 4. AL-Ahdeb 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 3436 cm^{-1} indicate of phenolic and Alcohols OH stretch, and amide-carbonyl stretch.
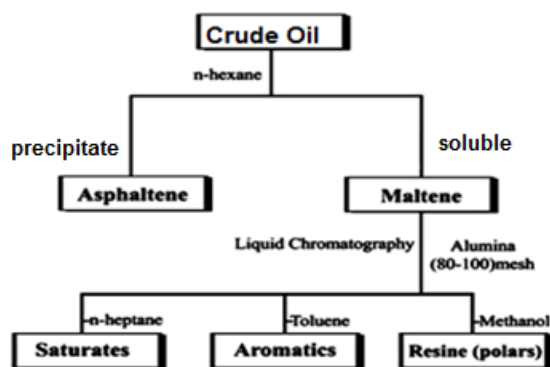
Scheme.1 Illustration of SARA test

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

Solvent	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

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

Hydrogen Type	H_{my}	H_{me}	H_n	$H\alpha$	H_a
Asphaltene sample	47.86	21.50	13.65	9.18	7.80

Table.3 Distribution of proton H % by 1HNMR Spectroscopy of maltenes fractionated

Hydrogen Type	H_{my}	H_{me}	H_n	$H\alpha$	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

Fig.1 HNMR spectra of Asphaltene
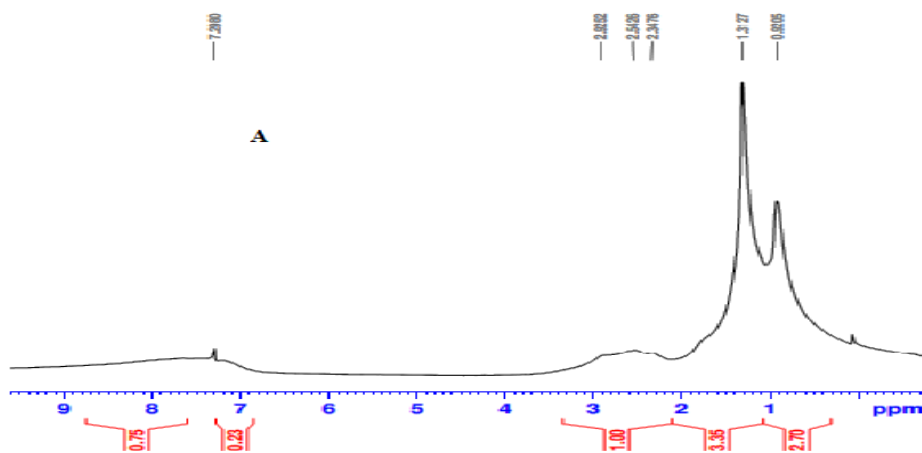
Fig.2 1HNMR spectra of paraffin
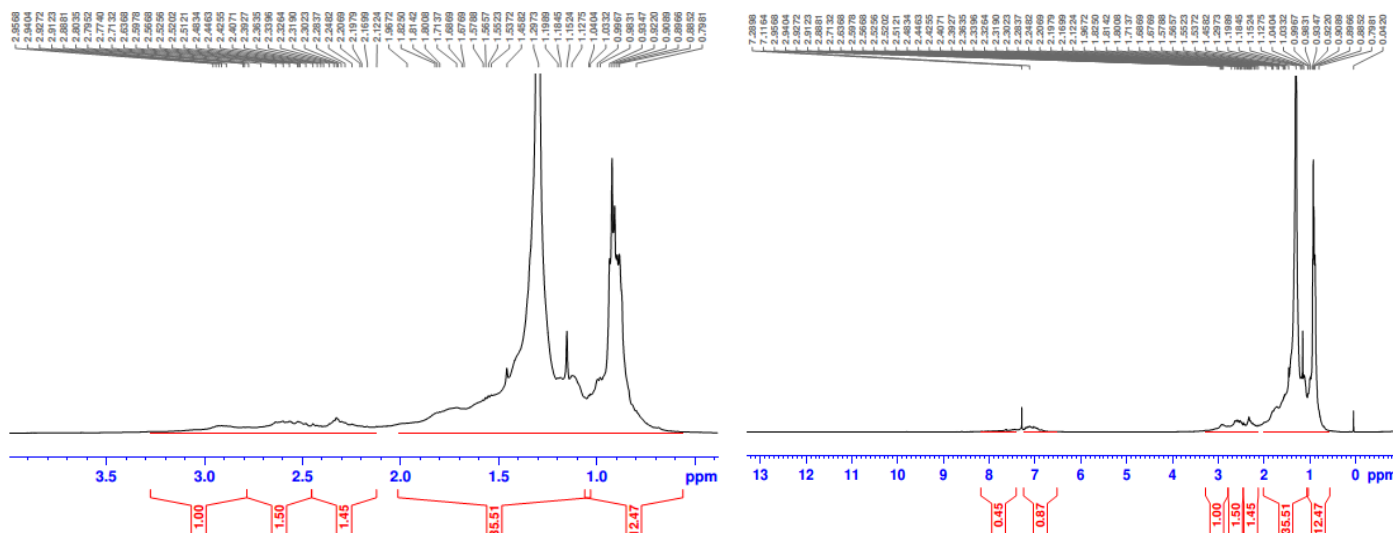
Fig.3 1HNMR spectra of aromatic
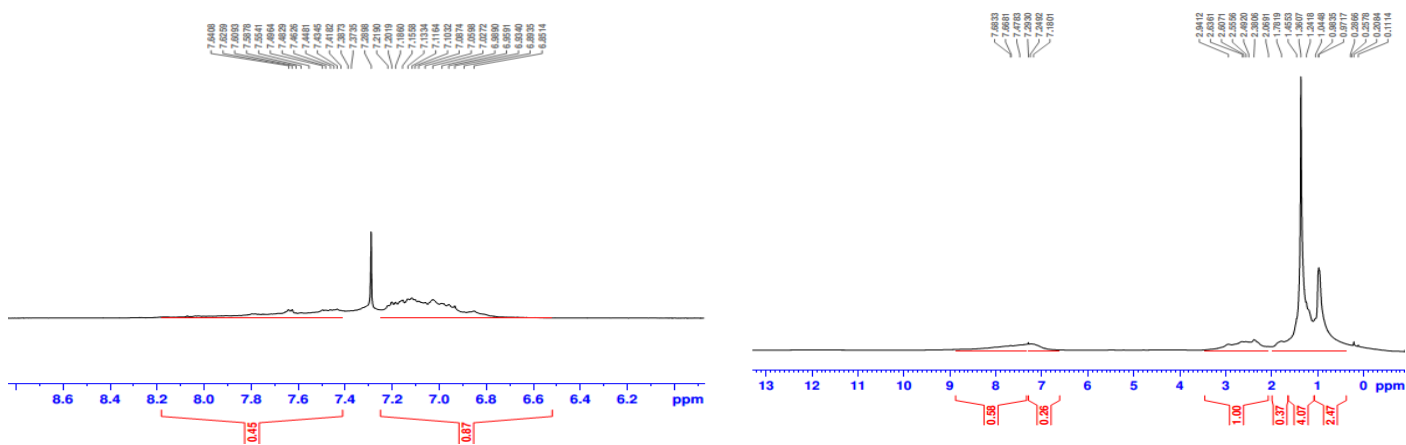
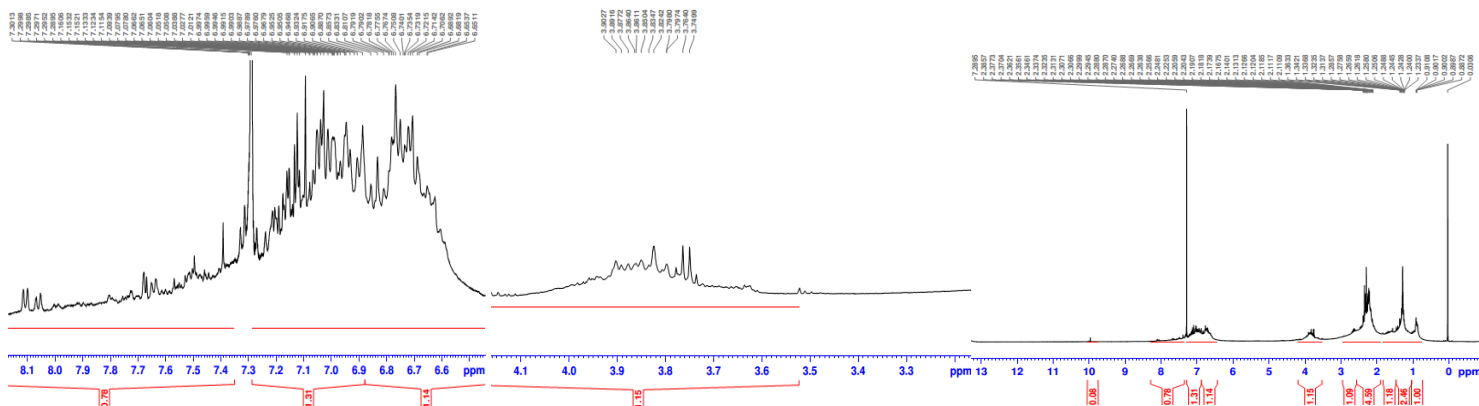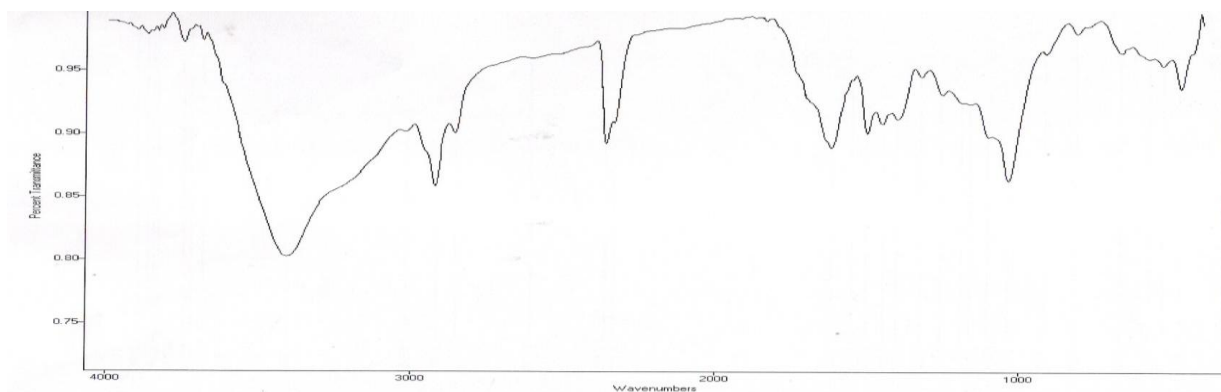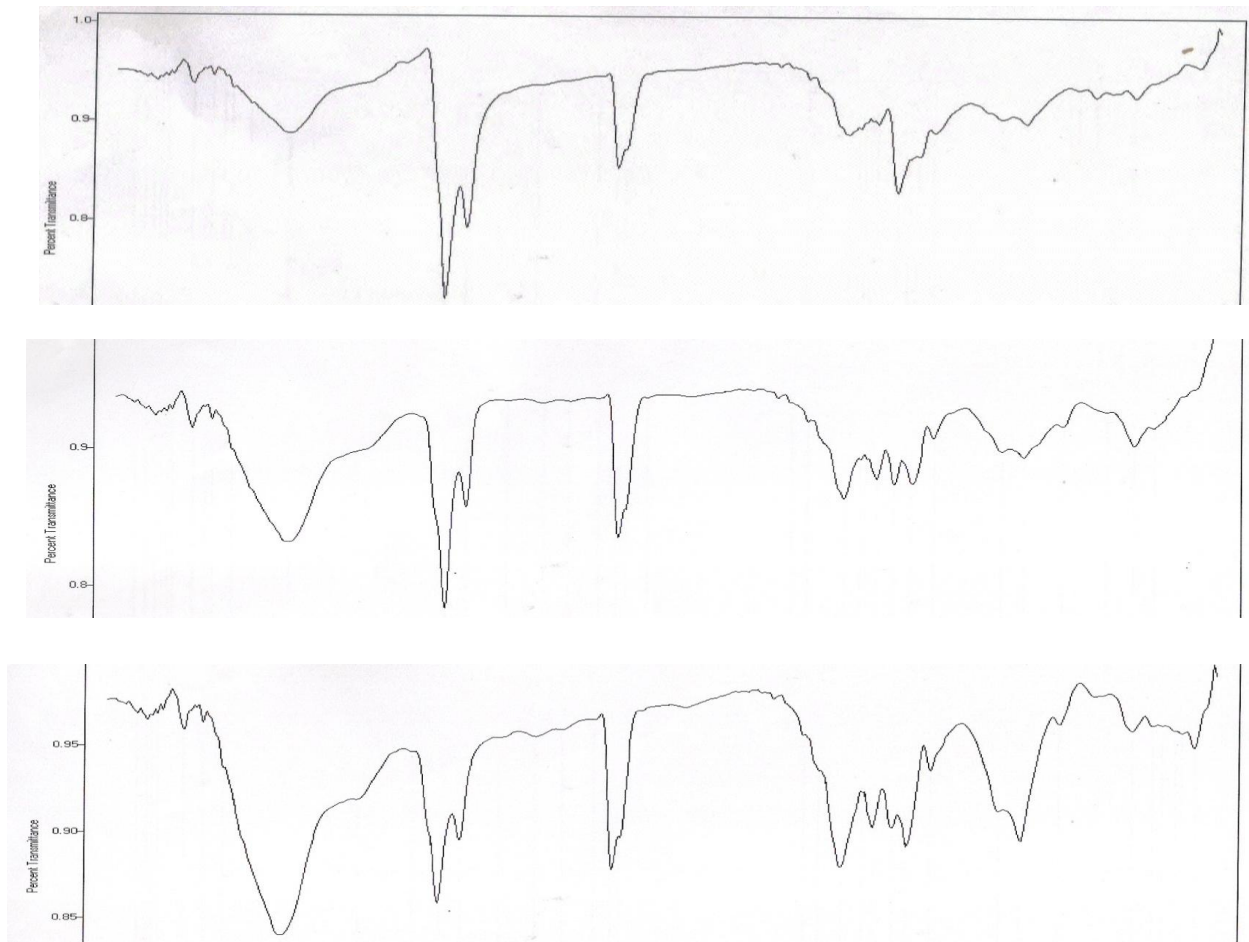**Fig.4** 1HNMR spectra of resin

Fig.5 FTIR spectra for SARA extraction of AL-Ahdeb crude oil

Each of these absorbance's has been carefully 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 1600-1605 cm, asymmetrical stretching vibration CH_3 to 1411-to 1450cm, Sulfoxide ($C_2S=O-$) from 1029 to1032cm and peak at 806 cm 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} indicates of vibration of CH_2 methyl groups that at 2857 cm^{-1} attributed of CH_3. The band located at 1623 cm^{-1} to amide stretching, vibrations for C-H at 1515 cm^{-1} indicate the methylene (-CH_2-) chains, the band from 1461 to 1403 cm^{-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 (Fredericks *et al.,* 1985). The aromatic C-H stretching band, which occurs between 3100 and 3000 cm^{-1}, did not appear on the spectra due to the weak C-H stretch in aromatic compounds, band at 1407 cm^{-1} attributed to asymmetry bend of CH_3, the band at 1330 cm^{-1} is indicative of H-C=C- groups and a new band appeared at 1037 cm^{-1} which are related to the C—C aromatic, since low boiling aromatics are depleted relative to saturated compounds. The resin

fractionated is the oil component and has polar aromatic compounds. The absorption band located at 1508 cm^{-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 817 cm^{-1} are representing hydrocarbons C-C in the aromatic ring or polyaromatic polar compound and observed band in the 671 and 558 cm^{-1} attributed to C-X aliphatic halogen compound (Silverstein, 1991). 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.

Conclusions

In this study 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-Ahdeb crude oil which were separated into compounds classes via SARA technique to four fractionated of different structures. The high content of paraffinic and low resin supported that AL-Ahdeb 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-Ahdeb crude oil.

References

Ahammed, M.A., Tighe, S. 2011. Asphalt pavements surface texture and National Research, Council, Ottawa, in press, Volume 39 1-9.

Akmza, S., Iscan, O., Gurkaynak, M.A., Yasar, M. 2011. The Structural Characterization of Saturate, Aromatic, Resin, and Asphaltene Fractions of Batiraman Crude Oil, *Petroleum Sci. Technol.,* 29: 160–171.

Mamdouh, T., Ghannama, Basim Abu-Jdayil. 2012. Rheological properties of heavy & light crude oil mixtures for improving flow ability, *J. Petroleum Sci. Engi.,* 81: 122–128.

Bouhadda, Y., Bormann, D., Sheu, E., *et al.* 2007. Characterization of Algerian Hassi-Messaoud asphaltene structure using Raman spectrometry and X-ray diffraction, *J. Fuel,* 86: 1855-1864.

Carmen Garcia el, M., Carbognani, L., Orea, M., Urbina A. 2000. The Influence of Alkane Class-Type on Crude Oil Wax Crystallization and Inhibitors *Efficiency J. Petroleum Sci. Engi.,* Vol.25, No.3-4, pp.99-105, ISSN 0920-4105.

Elham Keshmirizadeh, Somayeh Shobeirian, Mahmoud Memariani. 2013. Determination of Saturates, Aromatics, Resins and Asphaltenes (SARA) Fractions in Iran Crude oil Sampl, Study of the Geochemical Parameters, *J. Appl. Chem. Res.,* 7(4): 15-24.

Enekwe, Chukwudi Benedict, Okoro, Hyceinth Akpa. 2013. Analytical studies of poor performance of research, Volume 3, Issue 3.

Fredericks, P.M., J.B. Lee, P.R. Osborn and D.A. Swinkels. 1985. Materials characterization using factor analysis of FTIR spectra.Part2: mathematical and statistical consideration *.Appl. Spectroscopy,* V39, No.2, pp311-315.

Joseph, D., McLean and Peter, K. Kilpatrick. 1997. Comparison of Precipitation and Extrography in the Fractionation of Crude Oil Residua, *Energy & Fuels,* 11: 570-585.

May- Elena Dominguez-Rosado and John Pichtel. 2003. Chemical characterization of fresh Weathered motor oil, *Proceedings of the Indiana Acad. Sci.,* 112(2): 109–116.

Mahinpey, N., Murugan, P., Mani, T. 2010. Comparative kinetics and thermal behavior: the study of crude oils derived from Fosterton and Neilburg Fields of Saskatchewan, *Energy Fuels,* 24(3): 1640–1645.

Mustafa Versan Kok. 2011. Characterization of medium and heavy crude oils using thermal analysis techniques, *Fuel Processing Technol.,* 92: 1026–1031.

Odebunmi, E.O., Ogunsatin, E.A. 2000. Characterization of crude oil and petroleum products elution liquid chromatographic separation. *Bull. Chem. Soc. Ethiop.*, 6(2): 115-132.

Ren Wenpo, Shan Honghong, Yang Chaohe. 2006. Characterization of Average Molecular Structure of Heavy Oil Fractions. *China Petroleum Processing and Petrochem. Technol. Ren Wenpo Yang,* Vol. 13, No. 3, pp 1-7.

Silverstein, R.M., G.C. Bassler, and T.S. Morile. 1991. Spectrometric Identification of Organic Compounds,' John Wiley and Sons Inc, New York, N.Y.

Trejo, F., Ancheyta, J., Morgan, T.J., *et al*. 2007. Characterization of asphaltenes from hydrotreated products by SEC, LDMS MALDI, NMR, and XRD, *J. Energy & Fuels,* 21(4): 2128-2121.