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Chemical composition (saturate fraction) of western Iraq natural bitumen

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ABSTRACT

This study aims to explore the main components of bitumen in western Iraq as a natural resource of heavy oil. The raw bitumen studied was fractionated into asphaltene and maltene, and then the maltene was separated into saturated, aromatic and polar fractions. Fourier Transform Infrared (FT-IR), ^{13}C NMR, Scanning Electron Microscopy–Energy Dispersive (SEM–EDX) and Gas Chromatography (GC) were used to characterize the organic components of the bitumen. Hypothetical average molecules have been diagnosed including bitumen, asphaltene and aromatic according to ^{13}C NMR methods. The results indicate that the saturated, aromatic and polar compounds in bitumen are 8.24%, 55.67% and 9.93% respectively, while the asphaltene is 26.56%. The bitumen studied contains a relatively high amount of asphaltenes and aromatics fractions, potentially due to a thermal maturation of organic material in the well. However, it may be modified as crude oil derivatives because it contains certain aliphatic hydrocarbons.

Selection and peer-review under responsibility of the scientific committee of the 3rd International Conference on Materials Engineering & Science.

1. Introduction

The study area is located between latitudes 33°32′00″ and 33°42′00″, and longitudes 42°25′00″, 42°55′00″ Western Iraq, as shown in Fig. 1. Geological classification, Fatha formation falls western Iran and extends to the Iraqi-Iranian borders and it is of lower Miocene age. The oil geologists for the Kirkuk oil field proposed the divisions of the Fatha formation. Various bitumen kinds with aragonite and celestite are existent in the basal marl of the Fatha formation near Hit city (Western Iraq) and likely have the same origin. These deposits subsist along the Abu Jir zone characterized by active asphalt seepages [1,2].

Bitumen is a major fraction of crude oil that can be extracted industrially by non-destructive distillation. In some parts of the world, bitumen originated through complicated natural processes, where the crude oil was pushed to the surface of the earth through cracks and fractures [4–6]. Bitumen has a complex chemical composition consisting of many saturated and unsaturated organic fractions. The chemical components, molecular weight, and molecular associations of bitumen are dependent on the area of formation. The main components of bitumen are maleness and asphaltenes [7–12]. Maltenes consist of oils and resin, while asphaltenes are composed of carbenes and Carboids [13]. In addition to fractional distillation methods, light solvent from C_5-C_7 as well as petroleum ether are used to separate the components of bitumen [14]. Bitumen is classified into three types according to its rheological properties, which include viscous flow asphalt (sol-asphalt), strongly elastic asphalt (gel-asphalt), and slightly elastic asphalt (sol–gel-asphalt) [15]. Bituminous materials isolated from crude oil has been studied using X-ray spectroscopy, Fourier-transform infrared spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy to determine its structure [16–19]. To expand its scope of application, bitumen has been modified by several methods including catalysis treatment with polymers to change its chemical structure with the aim of producing paving asphalt with improved rheological properties [20–22].

Bitumen springs have attracted the interest of research attempting to resolve problems encountered in the use of tar water, such as gas emissions and their impact on living organisms [23,24]. However, the organic and aromatic constituents of bitumen were not considered in these studies. Muwafaq et al used asphalt and asphaltene particles extracted from natural bitumen from Western Iraq to produce activated carbon [25–27]. Increasing desire for crude oil has made the world to seek alternative and

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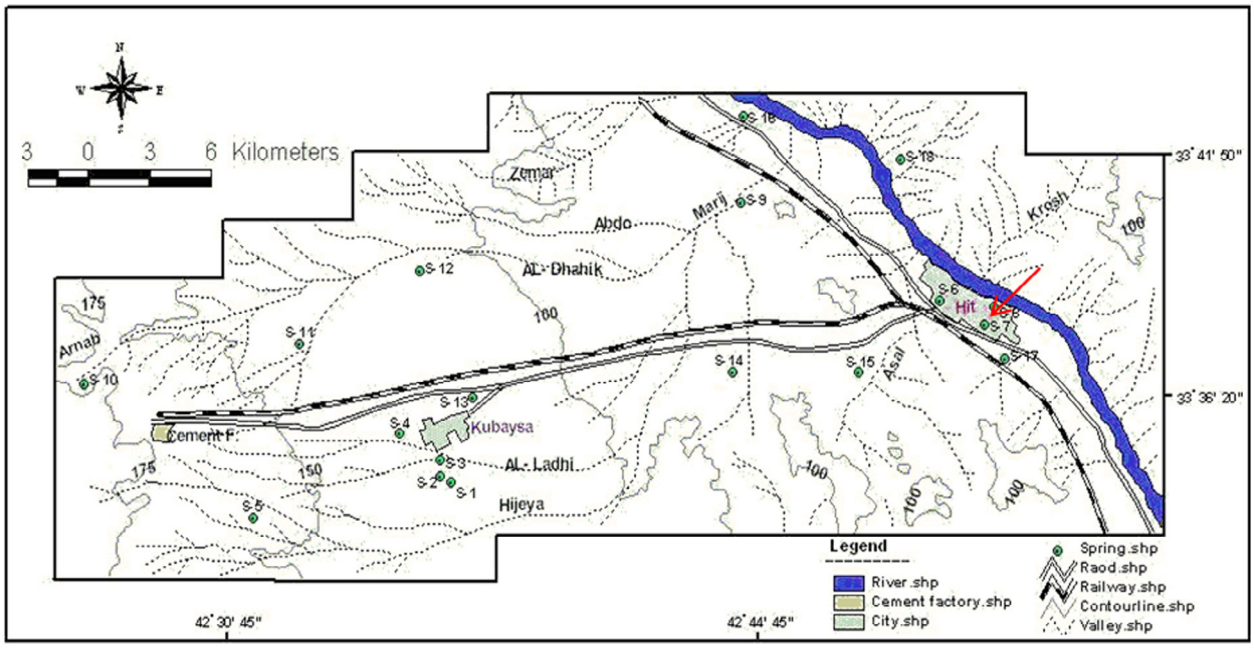

Fig. 1. Location map of the studied area [3].

sustainable sources of energy in order to promote energy sources [28]. Natural bitumen is now one of the natural sources of petroleum derivatives. Although thermal decomposition of bitumen is used to produce light petroleum products, this depends on the composition of the bitumen [29]. In order to determine its chemical components, therefore it is essential to diagnose the chemical fractions for organic matter in bitumen [30]. The bitumen identified in this work is obtained from a natural bitumen springs in western Iraq, which produces hundreds tonnes of bitumen daily, that used in the local flatness and paints as it has low selling price. Therefore, The present study explores the structural parameters of bitumen fractions, namely asphaltenes, saturates and aromatics of bitumen samples, with the aid of information from combined analytical techniques in order to economically feasible highlight from that resources.

2. Experimental

2.1. Preparation of fractions

Five grams of the bitumen sample were stirred with 200 mL of n-pentane in a round bottom flask for a duration of 2 h at a room temperature (20 °C) followed by reflux for 3 h. The soluble matter

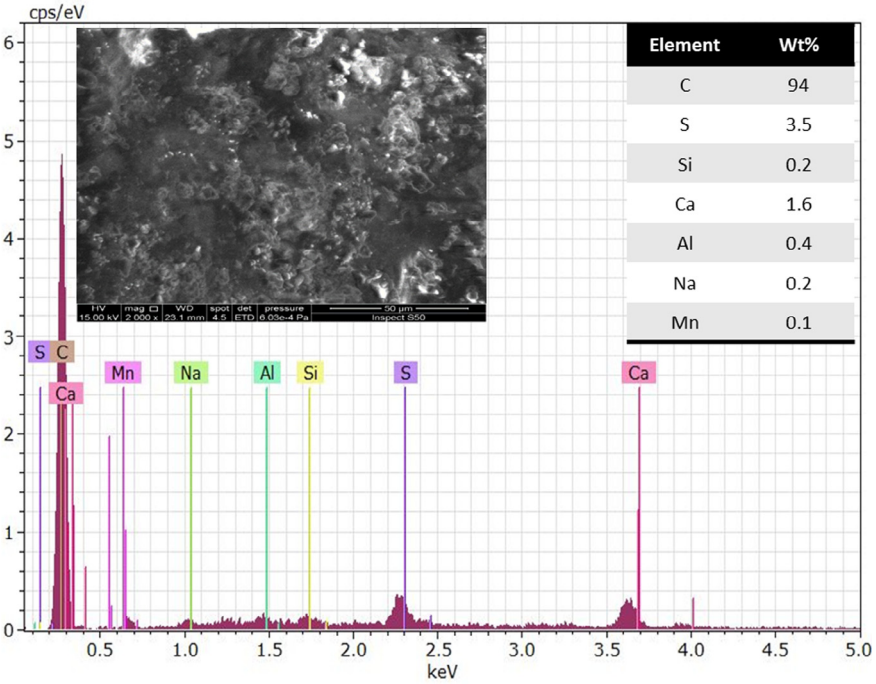

Fig. 2. EDX -SEM of the saturate Sub-fraction.

was separated from the precipitated asphaltene by filtration and then dried and weighed [31]. A 140 cm long glass column packed with silica gel was used to achieve a separation of saturates and aromatic hydrocarbons content of the maltene fraction (1:40 maltene and pentane) [4].

2.2. Analysis of fractions

The resonance spectra of ^{13}C NMR was obtained using Bruker - Ultra shield 300 MHz, Germany. The deuterium signal of the solvent was used as lock signal. Spectral width of 3400 Hz and pulse width of 3 us (with flip angle of 30.0) were used for the procedure. The free-induction decays were accumulated to 32 k [32]. Quantitative ^{13}C NMR spectra was obtained for 10 mm diameter tube containing 1.5 mL of the above prepared sample after the addition of the relaxation agent (19 mg of Chromium (III)- acetyl acetonate Cr (Ac Ac)$_3$ to remove the difference in carbon relaxation time). For the ^{13}C NMR spectra, the spectrometer was operated at 75.47 MHz, spectral width of 17250 Hz, pulse width of 8 us and flip angle of 80.0. The frequency domain spectrum was obtained in 16 k data points. Inverse gated technique was applied to suppress Nuclear Over Hauser effect (NOE), with 16 s waiting time between each interval. The decoupling was put in effect for very short time (0.004 Sec) before the pulse [33]. Fourier Transform Infrared (FTIR) spectra were recorded on a Pye Unicom SP3-300 infrared spectrometer. The sample was prepared as a thin solid film by precipitating its solution in chloroform on the KBr disc. The morphology and components of bitumen were also characterized using Scanning Electron Microscopy (SEM), coupled with an EDX. Gas Chromatography (GC) analysis were carried out on a Pye-Unicam PU-4800 Video chromatographic control centre using a 0.25 mm + 25 mm capillary column (Fused silica) well packed with SE-30. The column was programmed between 80 and 300 °C, with an increasing temperature rise of 2 °C/min. Detector and injector temperature was set at 350 °C. The carrier gas, N_2 flows at rate of 1 mL/min. Carbon and hydrogen contents were determined with the standard combustion method using a Perkin Elmer model 240C elemental analyser.

3. Results and discussion

The basic physicochemical characteristics reveals that bitumen has 232 °C Flash point, 1.02 Specific Gravity and 3.39% Ash Content. These results indicate that most of the saturated compounds in the natural bitumen studied suffered serious oxidation reactions over a long period due to exposure to different weather conditions. Most deposits of heavy oil (bitumen) contain mix of organic components, small amounts of traces elements and other contaminants. The SEM image as shown in Fig. 2 reveals that raw bitumen is a mass of homogeneous hydrocarbons, which appears mostly as plain surface and does not have any noticeable features in surface morphology. EDX analysis also shows that the essential elements in bitumen molecules are 94% carbon atoms and 4% hybrid atoms (sulphur, nitrogen, and so on). This result indicated the bitumen investigated has lest amount from sulphur compared with Cerro Negro (Venezuela) 4%, Boscan (Venezuela) 5.7%, Athabasca (Canada) 4% and Qayarah (Iraq) 8.4% [34].

After removal of the asphaltene fraction from the studied sample, which was found to be 26.56%, separation via solvents was applied to obtain the following fractions: 8.24% saturate molecules, 55.67% aromatic molecules, and 9.93% polar molecules. The differences between the two models are significant that the Agbabu reside has contained higher concentrations of saturated fractions and less asphaltenes [35]. Thus, Agbabu bitumen is easier to process and transport as compared to under consideration sample (western Iraq natural bitumen).

Table 1
The components of the saturate sub-fraction.

Peak No.	C_n	Conc.%
1	C_{18}	1.07
2	C_{19}	1.77
3	C_{20}	2.45
4	C_{21}	3.16
5	C_{22}	3.22
6	C_{23}	2.47
7	C_{24}	6.63
8	C_{25}	4.79
9	C_{26}	4.71
10	Iso-C_{27}	5.53
11	C_{27}	7.31
12	Iso-C_{28}	0.64
13	C_{28}	5.99
14	Iso-C_{29}	3.76
15	C_{29}	5.48
16	Iso-C_{30}	3.54
17	C_{30}	9.56
18	C_{31}	7.10
19	Iso-C_{32}	0.90
20	C_{32}	4.56
21	Iso-C_{33}	1.96
22	C_{33}	1.19
23	Iso-C_{34}	0.63
24	C_{34}	3.15
25	Iso-C_{35}	1.95
26	C_{35}	2.83
27	Iso-C_{36}	2.54
28	C_{36}	1.35

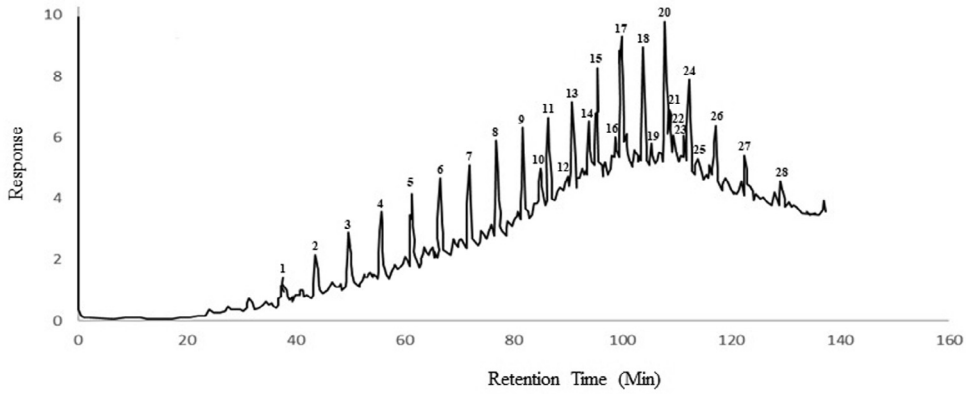

Fig. 3. Gas chromatogram of the saturate Sub-fraction.

The saturate sub-fractions were analysed using gas chromatography. Typical chromatogram of the saturate sub-fractions of bitumen is shown in Fig. 3. It can be seen that n-paraffin, from C_{18} to C_{36} are present. The quantitative evaluation (Table 1) of the chromatogram was performed using the internal calibration method (n-C_{12} standard). The studied model exhibited heavy biodegradation due to its seeping nature that exposed this oil to the air and hence bacterial attack [36]. Therefore, these oils are heavy due to the loss of their light fractions (C_1-C_{18}).

The characteristic bands of natural bitumen structure can be labelled to aliphatic, aromatic and polar groups. The spectroscopic study is one of the major factors in organic chemistry, by which the identity of the compounds is known depending on the functional groups. Infrared radiation absorption occurs through electronic excitation in most organic compounds, and these excitations are sufficient to cause vibration and stretching in the bonds. In qualitative analysis, the FT-IR absorption spectrum of an organic compound is one of the distinctive physical properties that it contains multiple peaks that can be used for comparative purposes and then discloses the molecular structure of the compound. The FT-IR spectrum of the saturate fraction (Fig. 4) indicates that the compositional molecules/compounds include a long paraffinic chain $(CH_2)n$ with $n = 4$ (absorption peak at 707 cm^{-1} and 1900 cm^{-1}). The isoparaffins and cycloparaffinic consist primarily of hydrocarbon structures with paraffin chains, in which one or several hydrogen atoms are replaced by naphthenic rings or isopropyl groups [37]. The peak at 635 cm^{-1} indicative presence of the C–S groups. The adsorption peaks at 740–875 cm^{-1} linked with the aromatic bending vibration (C–H) and the stretching vibration at 3075 cm^{-1} indicated the presence of the aromatic group (=C–H) in the bitumen structure. Another peak at 1583 cm^{-1} due to the stretching vibration of C=C in the aromatic structure (Sp^2); also the symmetrical vibration at 1321 cm^{-1} and the asymmetrical vibration at 1457 cm^{-1} indicated the presence of ($-CH_2$-) and ($-CH_3$) in bitumen as an aliphatic form. In addition, the aliphatic bands at 2865 and 2920 cm^{-1} are appeared C–H stretching vibrations of Sp^3 for symmetric and asymmetric, respectively of

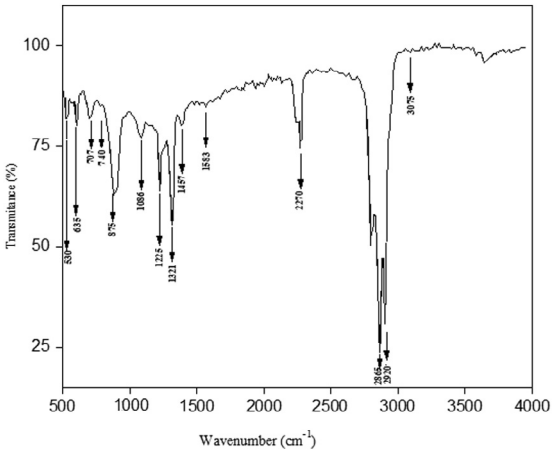

Fig. 4. FT-IR Spectrum of saturate Sub-fraction.

Table 2
Equations used for the calculation of average molecular parameters from ^{13}C NMR.

Parameter	Description	Equation
N	Carbon per alkyl side chain	$\frac{H_\alpha+H_\beta+H}{H_\alpha}$
R	Naphthenic rings per substation	$H_{Al}/2H_\alpha$
F	Carbon-hydrogen weight ratio of total alkyl group	2n /(2n + T-2r)
$\%C_{Al}$	Percent aliphatic carbon	fH_S % H_T
$\%C_A$	Percent aromatic carbon	%C - % C_{Al}
$\%C_p$	Percent peripheral aromatic carbon	$(12H_{Al} + fH)$ %H
%As	Percent substitution of aromatic carbon	(f Hα %H) 100/% C_P
C_A	No. Aromatic carbon per average molecule	$7(\%C_A / \%C_P)^2 - 1$
$C_p(C_1)$	No. Peripheral carbon per average molecule	$(\%C_P / \%C_A)\ C_A$
MW	Average molecular weight	$1200C_A / \%C_A$
C_{Al}	No. Aliphatic carbons per average molecule	% C_{Al} MW/1200
R_A	Aromatic rings per average	$1+ (C_A + C_P)/2$
R_s	Alkyl substitutions per average molecule	$\%A_s\ C_P/100$
R_N	Naphthenic rings per average molecule	R
F_a	Aromaticity factor	$\%C_A$ / %C
F_c	Condensation factor	C_p/C_A
X	Hydrogen carbon ratio of alkyl groups	$12/f_c$
H_{Al}	Aliphatic hydrogen per average molecule	nX R

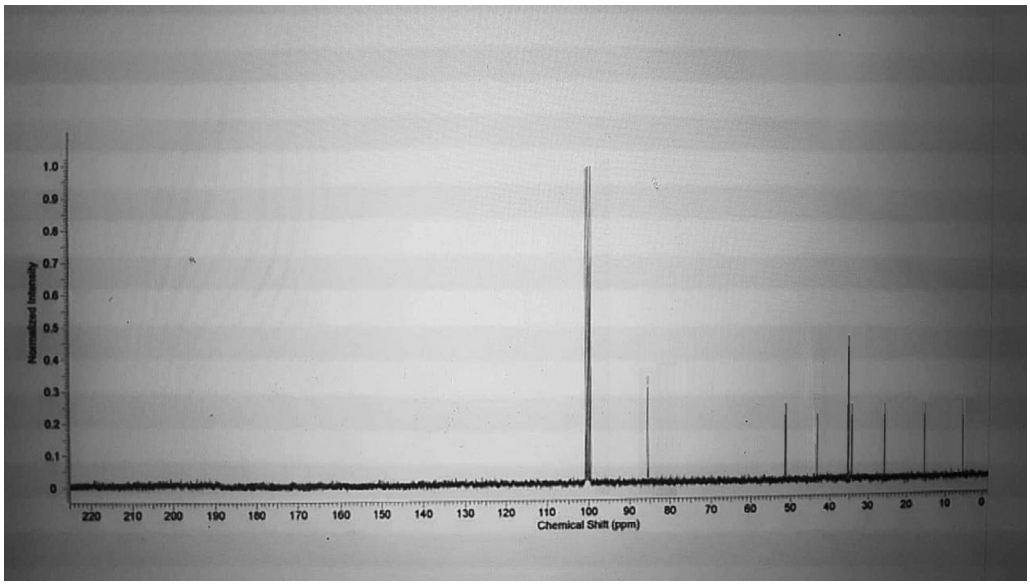

Fig. 5. ^{13}C NMR spectrum of saturate Sub-fraction.

aliphatic components [38,39]. The results of the infrared spectral confirms features are in correspondence with an earlier study on Agbabu natural bitumen [35].

The ^{13}C NMR spectrum of the saturate sub-fraction (Fig. 5) shows five Chemical Shifts δ (ppm) as a singlet form at 8.0, 14.0, 26.0, 37.1, and 43.7 ppm, which are assigned to $-CH_3$ (α), $-CH_2$ (β), $-CH_2$ (γ), $-CH_2$ (δ), and $-(CH_2)_n$ (£) of the normal chain, respectively.

From the ^{13}C NMR spectra, it is evident that for each two methyl groups, there exist 7 methylene groups, so the three chemical shifts δ (ppm) at 85.0, 102, 104 indicative presence of aromatic carbon for the rings. The percentages of normal alkanes, *iso*-alkane and naphthenic alkane fraction were estimated to be 56, 20, and 24%, respectively [40].

Hypothetical Aaverage Molecular Structure (HAMS) of bitumen fractions were determined using the following methods: (A) The average molecular parameters (AMP) for asphaltene and aromatic fractions were estimated based on ^{13}C NMR, elemental analysis and the equations listed in Table 2 and Table 3. The results are given in Table 4. (B) The AMP of the studied fractions were estimated using ^{13}C NMR, elemental analysis and the equations presented in Table 5. Table 6 provides a summary of the results. Since most of the parameters assumed non integer values, the average molecules do not precisely fit the data. Using the aromatic parameters, RA, NO CA and No. C1 it was possible to construct the aromatic carbon framework of the average molecule in each case.

Table 3
Experimental input data for the calculation of average molecular structure of fractions.

Parameter		Bitumen	Asphaltene	Aromatic
Total carbon,	C	81.87	80.743	79.68
Total hydrogen,	H	10.065	7.989	10.267
Aromatic hydrogen,	H_{Ar}	6.45	7.28	5.65
Aliphatic hydrogen,	H_R	93.55	92.72	94.35
Aliphatic hydrogen α to Aromatic rings,	H_α	11.69	21.2	19.27
Aliphatic hydrogen β to Aromatic rings,	H_β	9.68	11.08	10.96
Aliphatic hydrogen α to aromatic rings,	H_α	27.02	22.47	19.93
Aromatic carbon,	C_{Ar}	37.15	50.6	32.12
Aliphatic carbon,	C_R	62.85	49.4	76.88

Table 4
Average parameters calculated for total bitumen and some its sub-fractions using ^{13}C NMR.

Amp	Bitumen	Asphaltene	Aromatic
n	8	4.4	4.9
r	0.41	0.5	0.29
f	5.93	6.04	5.75
$\%C_{Al}$	56	44.7	55.7
$\%C_A$	25.87	36.04	23.7
$\%C_p$	14.76	17.2	18.34
$\%A_s$	47.3	59.2	61.9
C_A	20.5	29.7	10.97
$C_p(C_1)$	11.7	14.2	8.4
C_{Al}	44.3	38.84	25.48
R_A	5.4	8.75	2.3
R_s	5.53	8.5	5.2
R_N	2.27	4.25	1.5
F_a	0.32	0.45	0.3
F_c	0.57	0.48	0.77
X	2.02	1.97	2.09
H_{Al}	89.4	73.7	53.25
MW	950	989	549.0

To define the extent of aromatic rings condensation, the number of internal quaternary aromatic carbon atoms, Y, could be calculated from the expression Y = 6 + No. CA - 2 No. C.

A negative value indicates that the aromatic ring system is not fully condensed, while a positive value indicates fully condensed structures. From the aliphatic parameters; n, x (H/C), Rs and Rn> the remainder of the average molecule can be determined for each sample.

The HAMS obtained by method A are shown in Fig. 6. The HAMS for the aromatic, bitumen and asphaltene fractions were found to fully condensed. The HAMS for the three fractions determined by method B were found to be fully condensed (Fig. 7). The latter structures are more accurate in comparison with HAMS obtained by method A, especially for bitumen fractions containing high molecular weight components, because of the precautions taken to ensure reliable quantitative ^{13}C NMR data. However, these hypothetical molecules should not be taken literally, as they do not necessarily actually exist in the fractions. Hence, they should be regarded as conceptual models that provide a convenient basis for comparing the structures of petroleum fractions. Results on the polar fraction will be reported in a future communication.

Table 5
Equations used for the calculation of average molecule parameters from ^{13}C NMR [33].

Parameter	Description	Equation
N	Carbon per alkyl side chain	$\frac{H_\alpha+H_\beta+H}{H_\alpha}$
F	Carbon-hydrogen weight ratio of total alkyl group	C C_{Al} H H_{Al}
X	Hydrogen carbon atomic ratio of alkyl group	12/ tc
C_A	Percent aromatic carbon	C C_{Ar}
C_I^S	Percent substitution of aromatic carbon	C C_{Al}/ n
C_I^U	Percent unsubstitution of aromatic carbon	12H_{Ar} H
$C_1(C_P)$	Percent nonbridge aromatic carbon	$C_i^s + C_i^u$
No.C_A	Aromatic carbon per average molecule	C_A M / 1200
No.C_1	Aromatic non bridge carbon per average molecule	C_1 M / 1200
R_A	Aromatic rings per average molecular	(No.C_A No. C_1 + 1)/2
A_s	Percent substitution of aromatic rings	100 C_i^s/ C_1
R_s	Alkyl substitutions per average molecule	A_s No. C_1 /100
R	Naphthenic ring per substitutions	H_{Bn} / 2H
P_N	Naphthenic rings per substitutions	$R_{s\ r}$
No.C_{Al}	Aliphatic carbons per average molecule	nR_s
No.H_{A1}	Aliphatic hydrogen per average molecule	nX R

Table 6
Some average parameters calculated for studied fractions using ^{13}C NMR.

Amp	Bitumen	Asphaltene	Aromatic
N	8	4.4	4.9
f	5.49	5.4	5.2
x	2.2	2.2	2.31
C_A	30.4	40.86	25.59
C_I^S	6.43	9.10	11.10
C_I^U	7.79	6.98	6.96
C_1	14.22	16.08	18.06
No.C_A	24.1	33.7	11.7
No.C_1	11.25	13.25	8.3
R_A	7.4	7.95	2.7
A_s	44.2	56.6	61.5
R_s	5.08	7.5	5.1
r	0.44	0.5	0.28
P_N	2.2	3.85	1.43
No.C_{Al}	40.6	33	22.95
No.H_{A1}	89.4	57.7	72.6

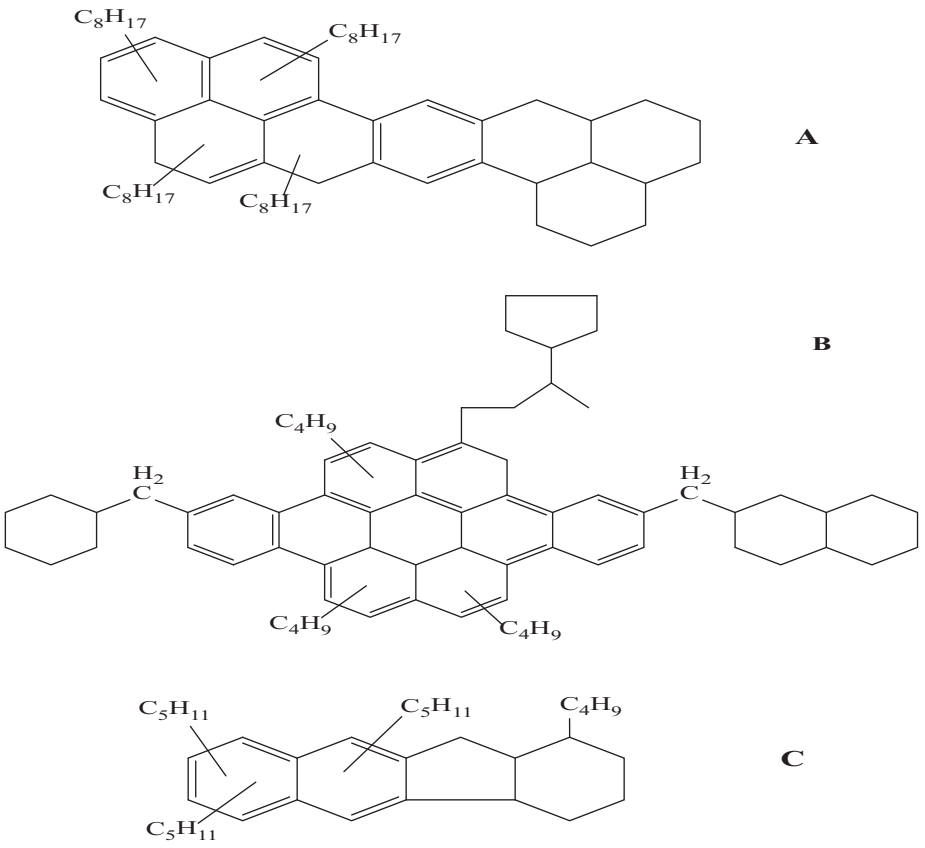

Fig. 6. Hypothetical average molecular structure of A-Bitumen, B-Asphaltene, C-Aromatic fractions according to method)A).

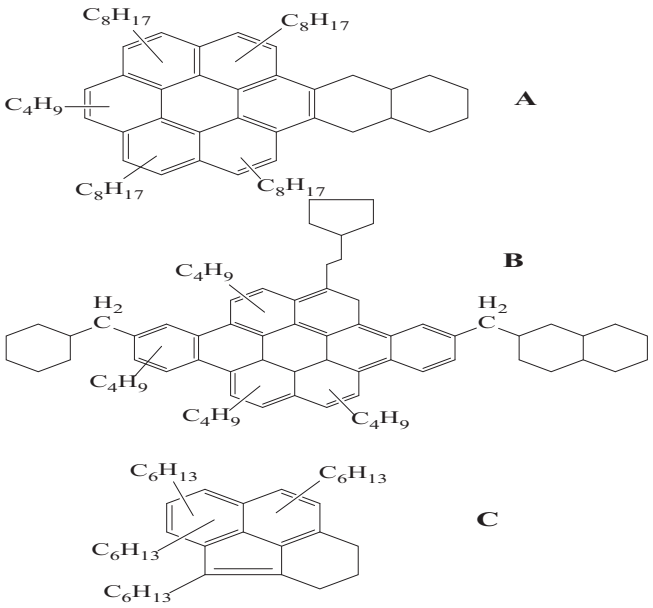

Fig. 7. Hypothetical average molecular structure of A-Bitumen, B-Asphaltene, C-Aromatic fractions according to method)B).

4. Conclusion

The organic structure of the sample under this study was fractionated into asphaltenes, saturates, aromatics and polar fractions. The results indicate that the saturate, aromatic and polar percentages are 8.24, 55.67 and 9.93, respectively. It can be concluded that the origin of liquid bitumen (viscous) is petroleum. However, the hydrocarbon fractions were evaporated over the years because of their proximity to the surface of the earth, resulting in the presently determined organic fractions.

CRediT authorship contribution statement

Marwan Mohammed Farhan: Conceptualization, Methodology, Validation, Investigation, Writing - review & editing, Project administration. **Muwafaq Ayesh Rabeea:** Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Rasim Farraj Muslim:** Software, Formal analysis, Writing - original draft. **Tahseen Ali Zidan:** Conceptualization, Formal analysis, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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