Petroleum Res. J. Vol. 15 (2003); P. 73–80, 4 Figs.

Evaluation Study for a Number of Libyan Crude Oils and its Products by Using Chemical Composition (^{13}C n.m.r. Spectroscopy Technique) and Some Physical properties

M.A. Abdulaziz* and Abeer Abdul Kader*

دراسة لتقييم مواصفات عدد من خامات النفط الليبي ومنتجاته كيميائياً باستخدام جهاز الرنين النووي المغناطيسي (^{13}C n.m.r.) وكذلك بعض المواصفات الفيزيائية

محمد علي عبد العزيز و عبير عبد القادر الشيخي

باستخدام كل من جهازي الرنين النووي المغناطيسي (^{13}C n.m.r.) ونقطة الغليان الحقيقية (.T.B.P)، تمت دراسة مجموعة من خامات النفط الليبي (آمنة، السرير، حمادة، الظهرة، الزقوط، سيرتكا، راسكو، البريقة) لمعرفة وتقييم مواصفاتها، حيث تم تقطير كل خام إلى خمسة قطفات عند درجات حرارة وضغوط مختلفة بواسطة جهاز نقطة الغليان الحقيقية (ASTM-D 2892-95) وتم تحديد الخواص الفيزيائية لكل قطفة حسب المواصفات القياسية وباستخدام الجهاز الرنين النووي المغنطيسي تم تحديد، نوعياً وكمياً، نسبة المواد العطرية والبرافينية في كل قطفة. وكذلك تم رياضياً حساب عدة علاقات مهمة وهي النسبة المئوية لتوزيع الكربون لكل من المواد البرافينية المستقيمة ومتوسط طول السلاسل البرافينية المستقيمة في جميع قطفات النفوط التي تم دراستها.

من خلال النتائج تم الحصول على معلومات قيمة تبين مواصفات وطبيعة كل نفط خام ومشتقاته والتي ستساعد في تسويق هذه الخامات ومنتجاتها وكذلك إيجاد بدائل متشابه للخامات المستخدمة في الصناعات النفطية وأيضاً معرفة الظروف التشغيلية للمصافي للحصول على المنتجات المستهدفة بالكميات المطلوبة.

Abstract: *In this investigation a number of Libyan crude oils (Amna, Hamada, Sarier, Aldhara, Zaggut, Sirtica, Rasco, Al Brega) were studied by using ^{13} C n.m.r. and true boiling point instrument to evaluate and characterize each crude oil and its products.*

Each crude oil was distilled for five fractions at different temperatures and pressures by using true boiling point instrument (T.B.P.).

As a consequence, a number of physical properties were determined for each crude oil and its products, according to the ASTM standard method, and by applying ^{13} C n.m.r technique, qualitative and quantitative results were obtained as a percentage of aromatic and aliphatic for each fraction. Then by using a number of mathematical calculations, the straight chain aliphatic, Cn straight chain aliphatic and the average chain length are calculated.

It is clear that this valuable information, obtained in this investigation, can be utilized for crude oil marketing, and the development of similar alternatives of crude for petrochemical industries and refineries processes.

* Ras Lanuf Oil and Gas Processing Co. Inc.

INTRODUCTION

Crude oil is a mixture of a huge number of aromatic hydrocarbons and aliphatic hydrocarbons. This mixture contains hydrocarbon with sulphur, oxygen and nitrogen atoms. A method of classifying crude oils is necessary to provide a guide to the quality, and hence value, of the oil. The specific gravity of the crude oil provides a rough measure of the amount of the lighter fractions present. The lower the specific gravity (or the higher of the API gravity, which is an inverse scale) the greater is the yield of the light fractions by simple distillation and hence the higher the price of the crude oil[1]. The quantitative identification of each compound in crude oils is neither practically feasible nor desirable.

Instead of this an overview of the chemical composition of the crude oil can be obtained as average structural parameters using the existing analytical techniques. High-resolution ^{13}C n.m.r. of liquid solution can make an important contribution for coal and oil derived products[2, 3].

However, in the last thirty years the whole field of chemical analysis has developed a base for extremely rapid analysis. Qualitative and quantitative analysis, to single components in very complex natural products, such as petroleum fractions, which were considered impossible, are nowadays carried out as a matter of routine in plant laboratories. Two main factors account for this change; on one hand, the discovery of new separation techniques, for instance chromatographic methods and in particular gas-liquid chromatography and on the other hand, the development in instrumentation which has made possible the production of fast, reliable and relatively cheap instruments, such as n.m.r. , infra-red, uv-visible and mass spectroscopy. But in spite of all the advances, knowledge of the constituents of some petroleum fractions is still very fragmentary, particularly in the region of residual oils and asphalt materials. Further-more, in the case of fractions for which the total analysis is practicable, the very wealth of information possible is difficult to interpret for the purposes of plant design and operation. In such cases use is made of simpler, though still accurate, methods of characterization. One group of such methods uses functions based on a set of physical constants, to describe the factors or indices of the predominant chemical character for the petroleum fraction.

The second group, comprising the methods of structural group analysis, describes the character of the fraction in terms of elements consisting of an imaginary average molecule having the chemical and physical properties of the sum of the individual fraction's component, which is based on their concentration.

Hence, the use of ^{13}C n.m.r. Spectroscopy offers distinct advantages over other methods, as the spectra, which can be recorded in relatively short time, provide detailed compositional characteristics of the crude that are unobtainable by other methods[4].

In this work quantitative and qualitative ^{13}C n.m.r. Technique is applied for a number of Libyan crude oils and their products to study their compositional structure. The TBP was used to distil five fractions for each crude oil. Then a number of physical tests was carried out to correlate them with ^{13}C n.m.r. results. The carbon percentages of (straight chain aliphatic, average chain length, aromatic) were calculated for all crude oil fractions. This paper represents the first step of a research programme in the RASCO laboratory to survey, characterize and evaluate all Libyan crude oil and its products. The obtained results provided plenty of compositional information to be utilised for crude oil characterisation and evaluation. This led to the establishment of analytical technique using n.m.r. Instrument for product quality control tests, crude oil alternative for refineries, petrochemical industry requirements and marketing policy.

EXPERIMENTAL

(1) - True Boiling Point: Three litres of crude oil were distilled in the Fischer autodest 800 (ASTM D-2892) apparatus into five fractions to the eight crude oils as shown in Table 1.

(2) - NMR Spectroscopy: ^{13}C spectra were taken on a Bruker AC/100 MHz super-conducting spectrometer. ^{13}C Fourier transform spectroscopy was performed at 25 MHz. The experimental conditions were: memory capacity used for data

Table 1. True boiling point.

Fraction no.	Temperature range °C (AET)	Pressure
F_1	up to 93	Atmospheric
F_2	93-204	Atmospheric
F_3	204-260	Vacuum pressure of 100 tore
F_4	260-343	Vacuum pressure of 10 tore
F_5	343-400	Vacuum pressure of 2 tore

acquisition 64 k, sweep width 6024 Hz, flip angle 90^0, pulse width 5.7 μs, delay time 15s, acquisition time 5.4s, broad-band proton gated de-coupling, sampling temperature and the sample diameter was 5mm. The ^{13}C n.m.r. spectrum for each of the five fractions of crude oils was carried out in D-chloroform in the presence of $Cr(acac)_3$ as relaxation agent. The experiments were carried out in the inverse gated mode to eliminate the nuclear Over Hauser enhancement. The spectrum was divided into two parts, the aliphatic (0-70 ppm) and the aromatic regions (110-160 ppm)[5,6].

The calculations were carried out by measuring the integral for both regions and the straight chain aliphatic were assigned according to Grant and Lindeman [11].

Cα-Cβ-Cγ-Cn-Cγ-Cβ-Cα: This formula showing the position of the different carbons in the straight chain aliphatic as assigned in the following Table 2.

Table 2. Straight chain aliphatic carbons assignment.

Type	Chemical shift (ppm)	Assignment
Cα	14.2	a-Carbon in straight chain
Cβ	22.9	b-Carbon in straight chain
Cγ	32.2	g-Carbon in straight chain
Cn	29.7	n-Carbon is further removed carbon in straight chain

(3)- Physical Property Tests: All analyses were carried out according to ASTM standard methods.

RESULTS

Physical Properties

As shown in Table 3, some physical properties of the eight crude oils indicate that, all crude oils studied are classified as paraffin crude oils, having API gravity ranging from 35.48 (Zaggut crude) up to 41.84 (Brega crude), the pour point ranging from -3 ^0C (Brega and Hamada crude oils) up to +24 ^0C (Sarier crude) and total sulphur contents are generally low.

The API results in Table 3 show that Brega crude oil has the highest value of API (41.84). This indicates that, Brega crude oil should have the highest yield of light and intermediate distillate. But this is not the case by the TBP distillation result as shown in Table 4. The total yield of the light and intermediate products in Brega crude oil for the five fractions is (68.49 %) which is less than Sirtica crude oil (73.92%) which has API gravity of 39.88. The specific gravity valus of 0.8163 and 0.8266 in Brega and Sirtica crude oils respectively also indicate that Brega crude oil should produce higher yield of light and intermediate distillate

Table 3. Physical properties of the different types of crude oil.

Physical properties	Amna	Sarier	Hamada	Aldhara	Zaggut	Sirtica	Rasco	Brega
Sp. Gr.@15.6 ^0C	0.8384	0.8417	0.8290	0.8433	0.8474	0.8266	0.8328	0.8163
Density @15 ^0C	0.8380	0.8413	0.8286	0.8429	0.8470	0.8262	0.8324	0.8159
API Gravity @15.6^0C	37.20	36.61	39.19	36.29	35.48	39.88	38.40	41.84
R.V.P @ 37.8 ^0C	0.305	0.388	0.297	0.535	0.411	0.562	0.503	0.469
Pour point (^0C)	+ 21	+ 24	3	+ 6	+ 6	3	+ 18	3
Sulphur cont.(wt%)	0.204	0.170	0.080	0.406	0.420	0.399	0.128	0.167
Salt cont. (mg/l)	16.1	14.3	3.5	7.4	8.3	18.2	11	8.3
Viscosity @ 50 ^0C (CSt.)	*	*	*	4.74	4.89	2.88	5.11	2.50

Table 4. The yield (wt. %) for the five fractions to the eight crude oils

Crude Name	F_1	F_2	F_3	F_4	F_5	Total
Amna	4.47	16.51	7.59	15.49	10.47	54.53
Sarier	4.89	16.50	7.75	14.13	10.48	53.75
Hamada	6.00	24.30	9.60	16.90	12.90	69.70
Aldahra	6.45	19.00	9.11	16.77	11.13	62.46
Zaggut	6.00	17.80	10.00	16.20	11.50	61.50
Sirtica	9.45	28.55	9.46	18.16	8.30	73.92
Rasco	6.32	18.31	7.97	16.32	10.26	59.18
Brega	8.56	24.30	11.96	15.85	7.82	68.49

in comparison to the seven crude oils, but this is not the case. On the other hand, the pour point in Brega and Sirtica crude oils has the same value (-3 ^{0}C) which indicates that the physical properties do not give a clear view about the nature and chemical compositions of crude oils. Therefore, further information is still needed about the chemical composition for more understanding of the behaviour of crude regarding its physical properties, products yield and specification.

^{13}C n.m.r. Analysis

The ^{13}C n.m.r. analyses were carried out, carbon distributions for the different types of hydrocarbons were calculated, and some qualitative analyses were also carried out for the five fractions of all crude oils studied.

The aromatic, straight chain aliphatic, Cn and average chain length carbons were calculated and the results are shown in figures 1,2,3,4, respectively and Table 5.

Table 5.Integrated and calculated carbon distribution % for the eight crude's fractions to:
(A)- Aromatic Carbon distribution %.
(B)- Aliphatic (straight, branched and cyclo-alkanes) carbon distribution %.
(C)- Straight chain aliphatic carbon distribution %.
(D)- Cn (further remote carbon) for straight chain aliphatic carbon distribution %.
(E)- Average chain length for straight chain aliphatic carbon distribution %.

Fraction	(A) - Comparison of aromatic carbons % in the fractions for the eight crudes							
number	Amna	Sarier	Hamada	Aldahra	Zaggut	Sirtica	Rasco	Brega
1	3.0	2.4	2.8	1.2	1.8	1.73	1.53	2.36
2	8.2	5.57	7.6	8.5	8.8	4.39	4.09	12.9
3	9.69	10.68	15.4	10.8	15.6	7.38	12.59	15.7
4	13.0	11.96	19.2	15.3	16.7	8.29	16.0	16.5
5	13.3	16.27	21.2	18.7	17.4	13.57	17.55	17.13
Fraction	(B) - Comparison of aliphatic carbons % in the fractions for the eight crudes							
number	Amna	Sarier	Hamada	Aldhara	Zaggut	Sirtica	Rasco	Brega
1	97.0	97.6	97.2	98.8	98.2	98.27	98.47	97.64
2	91.2	94.43	92.4	91.5	91.2	95.61	95.91	87.10
3	90.31	89.32	84.6	89.2	84.4	92.62	87.41	84.30
4	87.0	88.04	80.8	84.7	83.3	91.71	84.0	83.5
5	86.7	83.73	78.8	81.3	82.6	86.43	82.45	82.87
Fraction	(C) - Comparison of straight chain aliphatic carbons % in the fractions for the eight crudes							
number	Amna	Sarier	Hamada	Aldhara	Zaggut	Sirtica	Rasco	Brega
1	44.32	26.38	44.8	24.6	21.4	12.19	16.24	24.39
2	48.53	28.06	48.3	21.1	18.2	19.12	23.47	21.91
3	57.5	33.88	49.6	22.1	25.4	25.13	24.99	30.02
4	62.21	42.27	47.1	26.7	29.6	29.78	31.88	30.16
5	70.28	49.34	48	31.5	31.8	32.66	42.66	33.15
Fraction	(D) - Comparison of Cn carbons % in the fractions for the eight crudes							
number	Amna	Sarier	Hamada	Aldhara	Zaggut	Sirtica	Rasco	Brega
1	3	1.80	3.4	0.4	0.4	0.37	2.08	0.44
2	14	4.40	9.9	4.8	3.3	2.71	3.64	3.97
3	19.8	14.34	15.6	8.8	10	7.61	5.55	12.08
4	31.2	23.38	23.7	14.7	16.6	15.93	16.72	17.14
5	45.23	31.88	27.5	20.9	20.7	21.21	28.45	21.78
Fraction	(E) - Comparison of average chain length carbons % in the fractions for the eight crudes							
number	Amna	Sarier	Hamada	Aldhara	Zaggut	Sirtica	Rasco	Brega
1	5.35	4.5	5.5	4.35	4.3	4.53	5.01	4.04
2	7.47	6.65	6.3	7.4	6.5	6.19	6.3	6.38
3	9.12	10.37	8.8	9.8	10	8.59	7.71	10.04
4	12.08	13.44	12.2	13.35	12.87	12.97	11.92	13.89
5	17.44	27.6	14.3	17.5	16.31	16.54	17.74	17.49

From the ^{13}C n.m.r results and correlation with the physical properties results obtained, it is clear that an overview of each crude oil and its products for characterisation and evaluations can be made.

The aromatic carbon percent results (Fig. 1) show that the sum of aromatic content within the five fractions for each crude oil is highest in Brega crude oil (64.59) and lowest in Sirtica crude oil (35.36). The other crude oils studied are ranging in between which, are [Hamada (64), Zaggut (60.3), Aldhara (54.5), Rasco (51.76) and Amna (47.19) and Sarier (46.88). Secondly, the distribution of the aromatic content within the fractions for each crude oil indicates the properties of light and heavy products for every crude oil. For example, the results show, that apart from F_I in Amna crude oil, which has 3% aromatic carbon and 2.36 % aromatic carbon for F_I in Brega crude oil, the aromatic carbon % in the remaining fractions is higher in Brega crude oil in comparison to Amna crude oil. Thus, Brege crude oil has higher aromatic content. But the coated results of conradson carbon results[9] are showing that the values are 1.9 wt% and 1.5 wt% for Amna and Brega crude oil respectively. If the aromatic content only is considered, these results are in contradiction with the aromatic carbon %. But the aromatic types and nitrogen content for these crude oils should be considered. Then, the nature for both crude oils and its product quality can be characterised.

In addition, the Cn % value results (Fig. 3) for the five fractions of Amna and Brega crude oils are clearly showing that Amna crude oil fractions have higher value than Brega crude oil. This indicates that Amna crude oil has longer chain length paraffin distribution and higher average chain length (Fig. 4). The straight chain carbon % results (Fig. 2) are showing that Amna crude oil fractions contain higher values in comparison to Brega crude oil fractions.

This clearly demonstrates how its physical properties behavior can characterize each product and yield %, *etc.*

Accordingly, Amna is classified as a paraffin crude oil with a total sulphur content 0.2 wt% and has low yield of light fraction, which is similar to Sarier crude oil. Amna light naphtha has low iso-alkane and cyclo-alkane compared to Sirtica and Brega crude oils.

Therefore, Amna light naphtha has modest octane number, if compared with Sirtica's and Brega's crude oil light naphtha. Hence Amna light naphtha is not a preferred cat-reformer feedstock, but is an excellent feed stock for olefins production. A comparison and evaluation of all eight crude oils and their products are reported in detail [10].

Furthermore, Sirtica crude oil is an intermediate crude oil, having a gravity of 39.88 ^{0}API, total sulphur content of about 0.4 wt. % and pour point of -3 ^{0}C. This crude has the highest value of light and intermediate distillate, which is 73.92% yield, compared to the other seven crude oils. Sirtica crude oil also has the lowest aromatic carbon percent (Fig. 1) in comparison to the other seven crude oils. The highest aromatic carbon percentages were shown by Hamada and Brega crude oils. However, the aromatic carbon percentage distributions within the five fractions for the eight crude oils to characterise their products were shown clearly in (Fig. 1). Sirtica crude oil results in (Fig. 2) for the straight chain

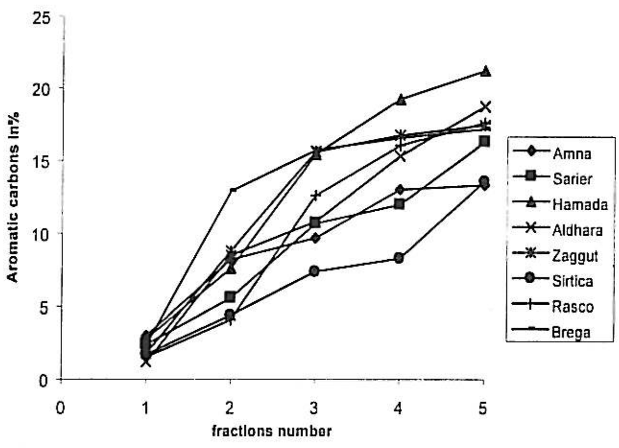

Fig. 1. Comparison of aromatic carbons in the fractions for the eight crude oils.

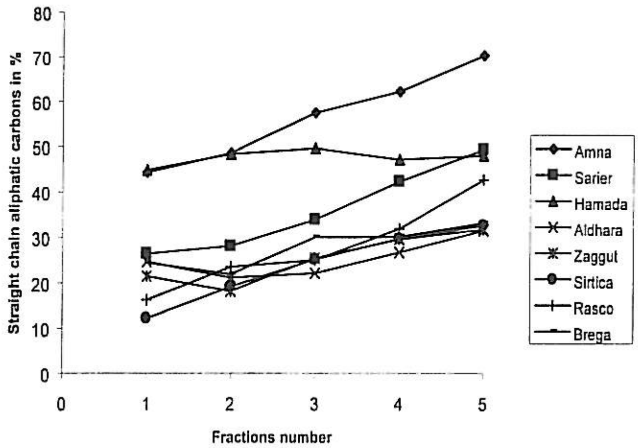

Fig. 2. Comparison of straight chain aliphatic carbons in the fractions for the eight crude oils.

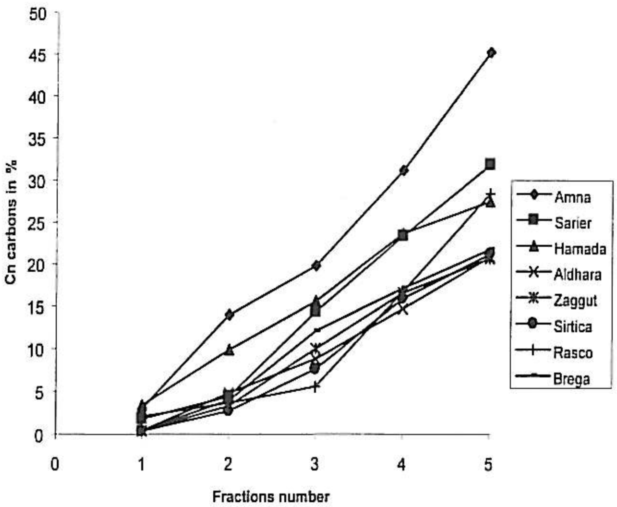

Fig. 3. Comparison of Cn carbons in the fractions for the eight crude oils.

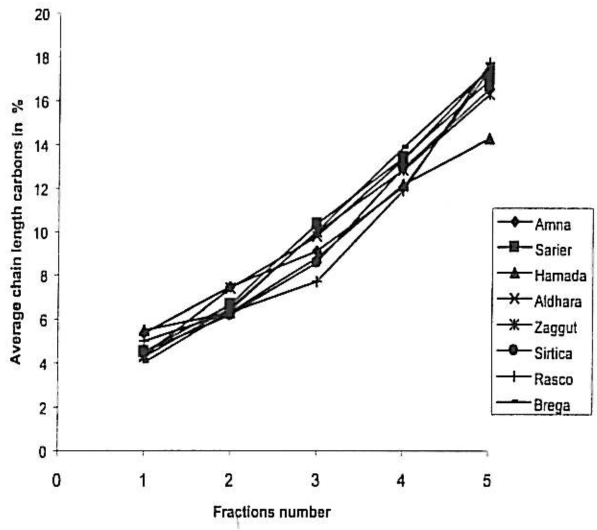

Fig. 4 Comparison of average chain length in the fractions for the eight crude oils.

aliphatic carbon percentages are the lowest for all five fractions in comparison to other crude oils fractions, which makes it high in iso-aliphatic and naphthenic carbons percentages, especially F_2. So, heavy naphtha have a high octane number, which is not good for olefin production, but is an excellent feed stock for aromatic production.

The great content of straight chain aliphatic in the light fraction (F_1 and F_2) in Aldhara and Zaggut (Esidera crude oil) makes it a good alternative for Rasco crude oil to produce the olefins. It also enables the Rasco refinery to produce a wider range of jet kerosene with a suitable freezing point and high quality gas oil to withstand low temperatures. Sulphur content in crude oil and its distribution within the fractions should be considered for the specification. However, Rasco crude oil has less sulphur content (0.167 wt%) than Aldhara and Zaggut (Esidera crude oil) which, consist o.535 and 0.411 wt% respectively.

Finally, all tabulated results and figures obtained from ^{13}C n.m.r. Provide an enormous amount of information to characterize and evaluate all eight crude oils and their products.

CONCLUSION

1- The quantitative ^{13}C n.m.r. for the five fractions of the eight crude oils gives a good view about the carbon distribution of aliphatic and aromatic compounds within each crude oil.
2- The n-paraffin carbon are the highest in Amna, Hamada and Sarier crude oil respectively.
3- Amna crude oil is an unsuitable feed stock for gas oil production. The percentage of n-paraffin carbons indicates that the obtained gas oil will have bad cold properties.
4- Rasco crude oil (Sarrier and Mesla feed for Ras Lanuf oil refinery) can be classified as moderate parafinic oil within the seven studied crude oils.
5- Aldhara and Zaggut (Esidera crude oil) are the best alternative for Rasco crude oil among all crude oil studied.
6- The obtained results in this study indicate that the n.m.r. technique is a good and quick analytical tool for structure characterisation of crude oils. The obtained information can be used to:
   - Predict some important properties of the distilled products.
   - Choose the refining processes and conditions of crude oils.

REFERENCES

[1] Hobson, G.D., *Modern Petroleum Technology*, part 1.

[2] Bartle K.D and Jones, D.W., 1978. *Analytical Methods for Coal and Coal products* Academic Press, New York.

[3] Dreeskamp, H., Potempa, T., and Müller, A., 1989. Aspects of quantitative ^{13}C n.m.r- spectroscopy of high boiling oil residues and coal tar pitches, *Fuel*, **68**, 972-976.

[4] Alhakimi,G., Abeer,A. Abdulaziz, A. and Gebrils, S.,1999. Structure characterization of seven Libyan crude oils by ^{13}C n.m.r., The Sixth Mediterranean Petroleum Conference and Exhibition, November 23-25, 1999, Tripoli -Libya.

[5] Sarowha, S. and Singh, I., 1984. Recent trends in the analysis of petroleum residues by NMR spectroscopy, *Journal of Scientific and Industrial Research*, **43**, 570-575.

[6] Misbah-ML-Hasan, M. Farhat Ali and M. Arab, 1989, Structural characterization of Saudi Arabian extra light and light crudes by ^{1}H and ^{13}C n.m.r. spectroscopy, *Fuel*, **68**, 801-803.

[7] Clutter, D.R., Peterakis,L., Stenger,R.L., and Jensen,R.K.,1972. Nuclear magnetic resonance spectrometry of petroleum fractions carbon-13 and proton n.m.r. characterization in terms of average molecule parameters, *Anal. Chem.*, **44**, No. 8, 1395-1404.

[8] James N. shoolery and William L. Budde, 1976. Natural abundance carbon-13-n.m.r. spectrometry for crude oil and petroleum product analyses. *Anal. Chem.*, **48**, No.11, 1458-1461.

[9] National Oil Corporation (NOC) 1994. *International Marketing, Evaluation of Libyan Crude Oils.*

[10] Abdulaziz,M and Abeer,A.,2000. *Crude Oil Characterisation and Its Products Evaluations by Using ^{13}C n.m.r. Technique and Some Physical Properties.* Technical Report I, Ras Lanuf Gas and Oil Processing Co., Libya.