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Determination of Saturates, Aromatics, Resins and Asphaltenes (SARA) Fractions in Iran Crude oil Sample with Chromatography Methods: Study of the Geochemical Parameters

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Abstract

In this study, Iran crude oil samples (K, L) were separated on the basis of solubility and polarity, resulting in saturates, aromatics, resins, and asphaltenes fractions. The fractions were analyzed by traditional open column chromatography, thin layer chromatography-Flame ionization detector in an Itroscan instrument (TLC-FID) and Gas chromatography with flame ionization detection for the determination of *n*-alkane and isoprenoid distribution in oil samples that are chosen as the most suitable structures for the identification and differentiation of crude oil samples and oil-oil correlations. The precursor organic matters of the analyzed oil samples of K, L are from a low salinity marine carbonate and reduced depositional environment. The studied oil samples were light and appeared to be mostly of type II, III kerogen mixture origin. The Koil sample is moderately mature (OEP and CPI are near 1).

Keywords: *SARA fractions, TLC-FID, Crude oil, Maturity parameters, Geochemical parameters.*

Introduction

Over the last few decades, an increase in the demand for commercial light oil and the decline of the quality of crude oil have been observed [1].The recovery of useful products from petroleum has been for several years an increasingly important task that is based on the understanding of the physicochemical properties of the crude oil mixture. For petroleum fluids composition and properties vary continuously from the simplest structures to macromolecule [2]. The characterization of the heavy fraction is then based on the identification of a number of families with

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certain properties which can be easily distinguishable from each other [3]. While simulated distillation by gas chromatography is a routine means for characterization of the light end, it is not applicable for heavy-end characterization due to inability of GC for characterization of large molecules. Therefore the methods employed rely on solubility and other chromatographic techniques [4]. The SARA procedure [5] modified for characterization of the heavy end as already described by Vazquez and Mansoori [6] was used to separate a sample into four classes of compounds, namely saturates, aromatic, resins and asphaltenes.

The saturate fraction consists of a viscous whitish translucent liquid mainly composed of paraffin's and diamond oils. From the four fractions separated from the heavy-end only the saturate fraction is easily distinguishable and separated from the rest of the oil due to the absence of π-bonds in between saturate hydrocarbon molecules. The aromatic fraction is a viscous reddish liquid composed of aromatic hydrocarbons with various degrees of condensation, alkyl-substitution and heteroatom(i.e. sulfur, oxygen, nitrogen) content forming a continuum with respect to polarity, molecular weight and other properties. The resin fraction is a dark brown colored, thick viscous liquid to semi-solid with a higher degree of condensation and heteroatom content than the aromatics. It plays an important role in asphaltene flocculation [7, 8].

There is however no single approach that can rapidly, reliability and simultaneously characterize crude oil fractions and specific classes of compounds and individual compounds in each fraction. Many standard methods(e.g. ASTM D2007, D4124) had been developed for characterizing the crude oil fractions but the gravimetric quantification of typical fractions proved inadequate [9,10].Coupling fractionation by TLC and quantification using with flame ionization detection (FID), the TLC-FID method developed in the 1970s showed to offer several advantages: (i) simultaneous fractionation crude oil into saturated, aromatic and polar classes, (ii) applicability for the determination of heavy fractions with high boiling points, (iii) low cost, simple instrument requirements and procedure saving. Therefore, TLC method rapidly became extensively applied for analysis of drugs, crude oils, coal-derived liquids [11-13].

The objectives of this paper were: (i) to compare the extraction efficiency of traditional open column chromatography and the TLC-FID Itroscan separations of crude oils into classes of compounds such as SARA,(ii) to identify specific compounds in the light fraction of crude oil using GC, (iii) to explains how certain non-biomarker parameters, such as ratios involving n-alkanes hydrocarbons, are used to assess thermal maturity.

Experimental

SARA Fractionation of Crude Oil

A SARA separation system was developed to characterize crude oils of interest. Crude oil samples (K, L) for this study were obtained from a South west of Iranian source and stored under argon. The asphaltene fraction was precipitated from the corresponding crude oil using n-heptane (HPLC grade, Merck, Germany). To obtain the asphaltene, a slightly modified SARA fractionation procedure was used (Fig 1) [6]. A total of 30 ml of n-heptane/gof crude oil was added. The precipitated portion was filtered and dried under inert gas flow. The sample (with the filter) was extracted with 300 ml of toluene (HPLC grade, Over lack, Germany) until no color changes were observed. The re-dissolved asphaltene fraction was rotary-evaporated and afterward, dried under a continuous stream of nitrogen. The extracted solution (maltenes fraction) was rotovapped until a stable mass was achieved. The dried maltenes were then diluted with n-heptane and mixed with activated alumina (80−200 mesh, Merck, Germany). The slurry was dried and loaded on the top of a glass column, packed with neutral alumina sorbent. In sequence, n-heptane, toluene, and toluene/methanol (9:1, v/v) (HPLC grade, Merck, Germany) mixtures were used to elute saturates, aromatics, and resins. A total of 350 ml of solvent/g of maltenes was used for the chromatographic separation. Thin-layer chromatography was used to monitor the complete separation of each fraction. Finally, the fractions were rotary-evaporated to dryness and then weighed. To have a correct mass balance, the volatile part of the original sample was also determined using rotavap vapor at 26 mbar and 30°C. The obtained mass balance and recovery is presented in Table 1. The reported SARA-values of the low-yield samples in this study are corrected to 100 % by adjusting the saturate and aromatic values. Hence, the evaporation loss from the resin fraction is considered to be negligible.

Table 1. SARA fractions of crude oil samples analyzed with TLC-FID Itroscan and traditional open column chromatography-gravimetry.

Sample	Saturate %Wt		Aromatic %Wt		Resin %Wt		Asphaltene %Wt	
	TLC*	Open column**	TLC	Open column	TLC	Open column	TLC	Open column
K	70.9	78.90	17.0	4.50	11.2	15.6	0.3	1.00
L	72.0	76.10	17.9	5.00	9.20	17.9	0.9	1.00

*Analyzed by TLC-FID Itroscan, **Analyzed by traditional open column chromatography-gravimetry.

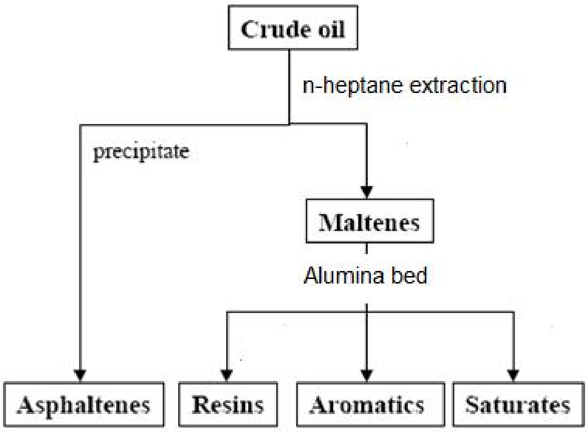
TLC-FID procedure of crude oils

Recently, the TLC-FID method has been substantially improved. Barman showed that a sample loading as low as 5–10μg was optimal regarding signal-to-noise ratio [14]. Karlsen and Larter [15] and Cebolla et al. [16] investigated the effect of scan speed on the FID response, and found that the FID response decreased when increasing the scanning speed. A TLC device (MK-6S, Tokyo, Japan) equipped with FID detector was used to test the TLC-FID method. The S-III chromarod (MKI, Tokyo, Japan) used in this study was 15.2cm long and 1.0mm in diameter and was coated with a layer of silica gel (5μm particle size). During experiments the chromarod was spotted with 1μL of extract, and subsequently was developed with the following program: n-hexane (30 min), 50% (v/v) hexane–DCM (20 min) and 95% (v/v) DCM–methanol (5 min). The chromarod was dried at 40 ◦C for 2 min after each development. For the TLC-FID method, a scan rate of 40 s/scan was used. Air and hydrogen flows were 2000 mL/min and 160 ml/min, respectively.

Whole oil GC analysis

A gas chromatograph capable of oven temperature programming from 35°C to 200°C in 1°C/min increments was used. A heated flash vaporizing could provide a linear sample split injection (for example, 200:1). The associated carrier gas controls could provide reproducible column flows and split ratios. A hydrogen flame ionization detector designed for optimum response with capillary columns (with the required gas controls and electronics) could meet the following specifications: Operating temperature: 100°C to 300°C, sensitivity >0.015 C/g, minimum detect ability: 5*10−12 g carbon/second, linearity >107.

A Varian cp-3800 gas chromatograph was used to analyze the oil samples. The gas chromatograph (GC) was equipped with an auto sampler for injections, a flame ionization detector (FID), and electronic pressure flow controllers to ensure constant flow throughout the oven-heating program. The GC was operated using the following analytical materials and conditions: 1 column (100 m×250 μm I.D×0.5 μm film thicknesses), injector temperature of 250 °C, pressure 283 kPa, split ratio set to 100:1, and FID temperature of 300 °C. The GC oven was programmed from 35 °C with a 13 min initial isotherm, then an initial heating rate program of 10 °C/ min to 45 °C with a 15 min hold time after which the rate was decreased to 1.9 °C/ min to a final temperature of 200 °C with 5 min hold time. Helium carrier gas was used with a minimum purity of 99.999%. The injected sample volume was 0.5 μl. The crude oil was back flushed 0.3 min after injection to remove its heavy components. The assignment of the C7 compounds was based on comparison with chromatogram references provided by the supplier of a commercial mixture of paraffin's, naphthenes and aromatic hydrocarbons (ASTM D- 5134).



Scheme 1. SARA Fractionation According to the Solubility of Each Fraction.

Whole oil GC is a common type of analysis for oil samples. The analysis (Figure 2) will give a complete picture of the hydrocarbons present in the oil and also of the sulphur-containing compositions. It is important to have good resolution for both the light and heavy components.

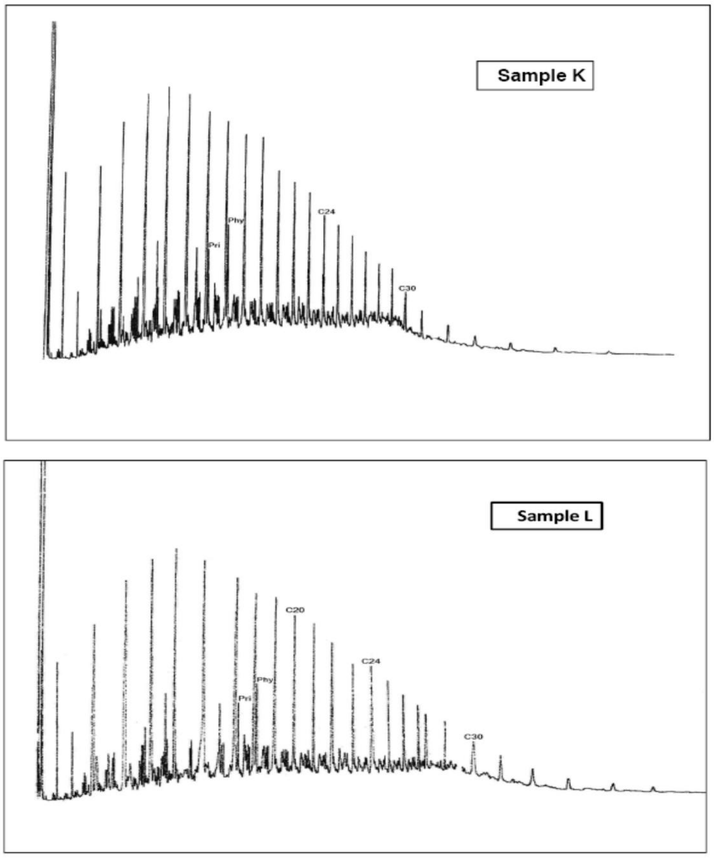


Figure 2. The GC chromatogram for the analyzed oil samples(K,L). Note:(C_9:naphta, C_9-C_{14}:Kerosene, C_{14}-C_{20}:Diesel, C_{20}^+:Residual fuel oil).

Result and discussion

Analysis of crude oil samples

The crude oil samples were fractionated by the traditional and TLC-FID (Itroscan) SARA technique as described by in the experimental section. The experiment was repeated severaltimes and the average results, reported as wt. % are presented in Table 1 and Figure 3. The results obtained from the fractionation of crude oils K, L were compared with each other in this study also oil-oil correlation was performed.

From an overall comparison the two crude oils seem quite similar in composition.

In general, the mass ratios of asphaltenes to resins in crude oils around the world have been found to be quite small, in the range of 0–0.26. For the crude oils under study here the average ratio were found to be 0.02 and 0.09 respectively [17-19].

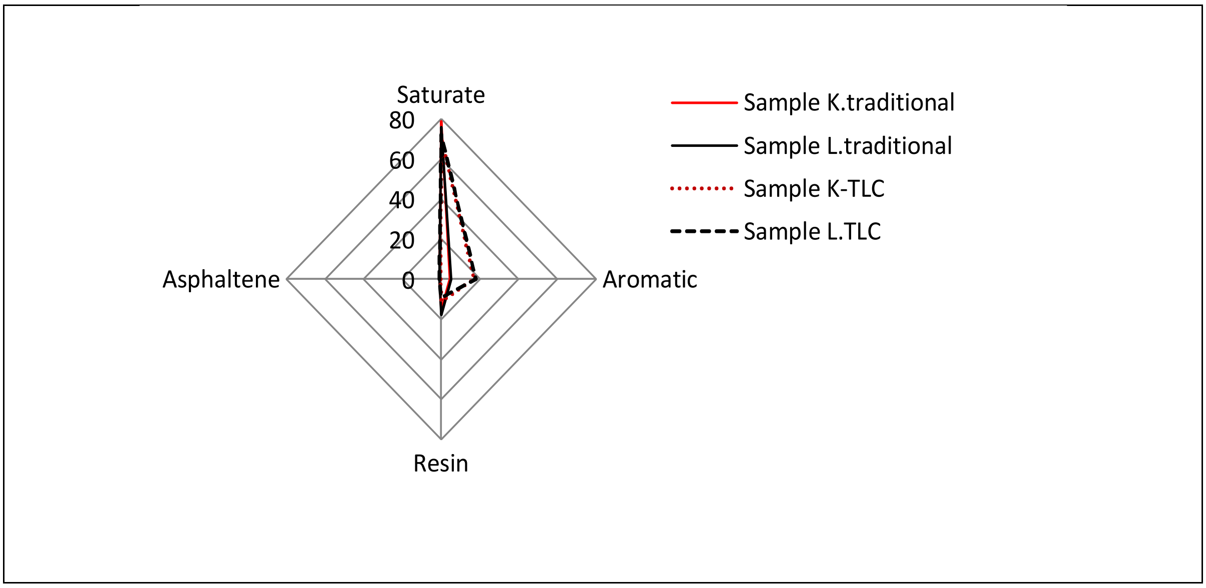


Figure 3. Star diagram (comparative diagram) for SARA fractions of two samples K, L under traditional measurement and modern measurement.

Non-biomarker maturity parameters

This study explains how certain non-biomarker parameters, such as ratios involving n-alkanes hydrocarbons, are used to assess thermal maturity. Various characteristics of petroleum samples can be used to assess their relative level of thermal maturity.

Alkanes & isopronoids (pristine and phytanes)

Isopronoids/n-alkane ratios: specific for maturity but also affected by other processes, such as source and oxidizing, reducing and biodegradation measured using peak heights or areas from gas chromatography(GC data) and type of kerogen, however carbon preference index(CPI) and odd-even preference(OEP) are defined as follows [20]:

$$CPI=\frac{1}{2}\left[\frac{C25+C27+C29+C31+C33}{C24+C26+C28+C30+C32}+\frac{C25+C27+C29+C31+C33}{C26+C28+C30+C32+C34}\right](1)$$

$$OEP=\frac{(C21+6C23+C25)}{(4C22+4C24)}(2)$$

CPI and OEP parameters show the strength of the odd carbon in n-alkanes. According to Table 2 and Figure 4 (geochemical parameters were calculated by the integrated peak area from GC (CPI, OEP, Pri/Phy))

Table 2. The ratios and values of the majority of the used non biomarkers in this study.

Sample	CPI Eq(1)	OEP Eq(2)	Pri/Phy*	Pri/nC17	Phy/nC18
K	0.94	0.54	0.95	0.53	0.48
L	1.10	0.99	0.95	0.54	0.34

*Pristane:Pri, Phytane:Phy.

Broocks noted the presence of the regular isoprenoids pristane (Pri) and phytane (Phy) in crude oils and coal extracts [21]. A mechanism for the production of relatively high concentrations of pristane in oxic type environments and high concentration of phytane in reducing type environments was represented [22]. Thus, the Pri/Phy ratio evolved as an indicator of the oxicity of the initial organic matter's depositional environment. The Pri/Phy ratios are very helpful in determining the pale depositional environment and source of the precursor organic matters of the reservoired oil. It is well known that Pri/Phy ratios>3.0 indicates predominantly non marine source from terrestrial organic matter,(terrigenous plant input) deposited under oxic to suboxic conditions [20, 23].An oil accumulation have Pri/Phy ratio < 0.8 indicates saline to hyper saline conditions associated with evaporate and carbonate deposition, while marine organic matters usually have Pri/Phy<1.5 [20]. As the Pri/Phy ratio for the analyzed oil samples (K, L) are 0.95, 0.95 respectively, therefore a marine influence on the type of the source organic matters can be detected. The plot of the Pri/nC_{17} and Phy/nC_{18} values for the analyzed sample on the specific plot in the Figure 4 indicated a mature marine source of organic matter (mostly type II, III kerogen mixture) deposited in a reduced condition with less effect of biodegradation.

Kerogen is a mixture of organic chemical compounds that make up a portion of the organic matter in sedimentary rocks. It is insoluble in normal organic solvents because of the huge molecular weight of its component compounds. The soluble portion is known as bitumen. When heated to the right temperatures in the Earth's crust, (*oil window* ca. 60–160 °C, *gas window* ca. 150–200 °C, both depending on how quickly the source rock is heated) some types of kerogen release crude oil or natural gas, collectively known as hydrocarbons (fossil fuels). When such kerogens are present in high concentration in rocks such as shale they form possible source rocks. Shales rich in kerogens that have not been heated to a warmer temperature to release their hydrocarbons may form oil shale deposits [24]. All types of kerogen are introduced in Figure 4.

Level of thermal maturity

The gas chromatogram of the saturated hydrocarbon fractions shows a shift in the normal alkane distribution to lower carbon numbers (Figure 2), reflecting relatively a moderate level of thermal maturity, The analyzed oil samples are light samples (Table 1 and Figure 3) this can be interpreted according to Justwan [25] in terms of increased type II, III kerogen mixture contribution. CPI can offer valuable information on the maturation of source rocks and reservoired oil. High CPI values (above1.5) always refer to relatively immature samples. Low CPI values, however, do not necessarily mean higher maturity; they can also mean a lack of higher n- alkanes stemming from terrestrial input. The measured CPI values for the studied oil samples (K,L) are respectively equal to 0.94 and 1.1 which means that they are moderately mature oils.

In practice, the OEP can be adjusted to include any specified range of carbon numbers. Some examples of CPI and OEP variations are shown above (Eq1, Eq2). CPI or OEP values significantly above (odd preference) or below (even preference) 1.0 indicates low thermal maturity. Values of 1.0 suggest, but do not prove, that an oil or rock extract is thermally mature. CPI or OEP values below 1.0 are unusual and typify low-maturity oils or bitumens from carbonate or hyper saline environments. Organic matter input affects CPI and OEP. However in this study OEP of K, L oil samples are 0.54 and 0.99 respectively, one can conclude that L sample has lower maturity.

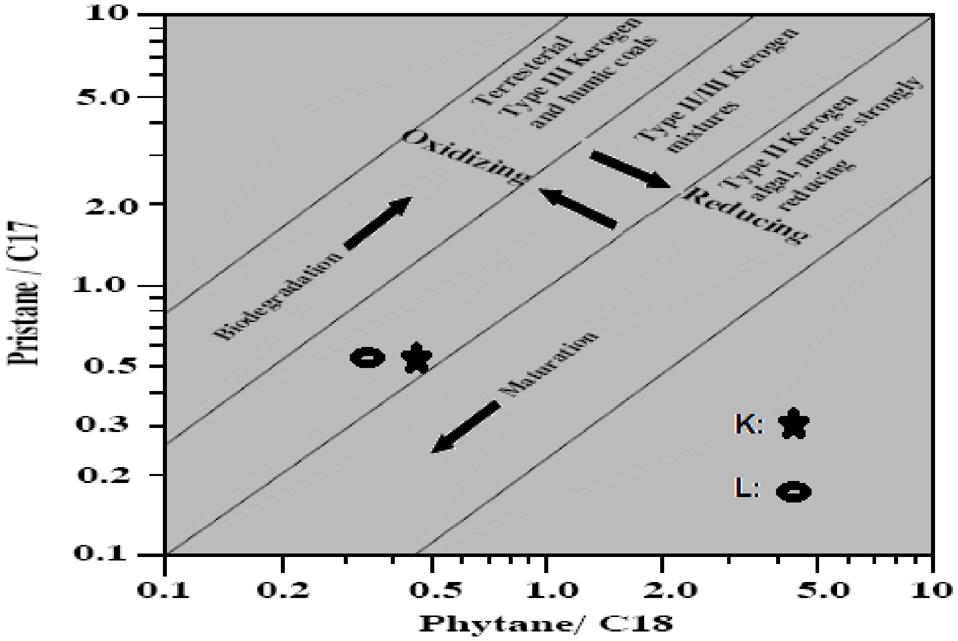


Figure 4. Pristane/C_{17} versus Phytane/C_{18} diagram for the studied oil samples. Note:Type I Kerogen: Sapropelic (containing alginate), Type II Kerogen: Planktonic (marine),Type II Kerogen: Sulfurous (similar to Type II but high in sulfur, Type III Kerogen: Humic(Land plants (coastal)).

Conclusion

This has resulted in the observation that crude oil SARA-data can be determined both from modern method (TLC-FID Itroscan method) in a fast and simple manner compared to the more tedious traditional open column chromatography-gravimetry method.

The precursor organic matters of the analyzed oil samples of K, L are from a low salinity marine carbonate and reduced depositional environment. The studied oil samples are light and appear to be mostly of type II, III kerogen mixture origin. The Koil sample is moderately mature (OEP and CPI are near 1).

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References

[1] E.J. Swain, *Oil Gas J.*, 93 (2), 37 (1995).

[2] A.M. McKenna, J.M. Purcell, R.P. Rodgers, A.G. Marshall, *Energy Fuels*, 24, 2929 (2010).

[3] S.S. Betancourt, G.T. Ventura, A.E. Pomerantz, O. Viloria, F.X. Dubost, J. Zuo, G. Monson, D. Bustamante, J.M. Purcell, *Energy Fuels*, 23, 1178 (2009).

[4] K.J. Leontaritis, G.A. Mansoori, *Int. J. Pet. Sci. Technol.*, 2, 1 (1989).

[5]D.M. Jewell, E.W. Albaugh, B.E. Davis, R.G. Ruberto, *Ind. Eng. Chem. Fundam.*, 13 (3), 278 (1974).

[6] D.Vazquez, G.A. Mansoori, *J. Pet. Sci. Eng.*, 26, 49(2000).

[7] A. Gaspar, E. Zellermann, S. Lababidi, J. Reece, W. Schrader, dx.doi.org/10.1021/ef3001407, *Energy Fuels* (2012).

[8] G.A. Mansoori, *KU Int. J. Sci. Technol. Trans.*, B 1 (2002).

[9] B.N. Barman, *J. Chromatogr.* Sci., 34, 219 (1996).

[10] B.K. Sharma, S.L.S. Sarowha, S.D. Bhagat, R.K. Tiwari, S.K. Gupta, P.S. Venkataramani, *J. Anal. Chem.,* 360, 539 (1998).

[11] S. Chopra, F.J. Ahmad, R.K. Khar, S.K. Motwani, S.M. Zeenat Iqbal, S. Talegaonkar, *Anal. Chim. Acta* 577, 46 (2006).

[12] J. Vela, V.L. Cebolla, L. Membrado, J.M. Andrés, *J. Chromatogr. Sci*., 33, 417 (1995).

[13] N.C. Shanta, *J. Chromatogr.,* 624, 21 (1992).

[14] B.N. Barman, *J. Chromatogr. Sci*., 34, 219 (1996).

[15] D.A. Karlsen, S.R. Larter, *Org. Geochem*., 17, 603 (1991).

[16] V.L. Cebolla, J. Vela, L. Membrado, A.C. Ferrando, *J. Chromatogr. Sci*., 36, 479 (1998).

[17]S.J. Park, G.A. Mansoori, Proceeding of UNITAR/UNDP *4th International Conference on Heavy Crudesand Tar Sands*, Edmonton, Alberta, Canada, August (1988a).

[18] S.J.Park, G.A. Mansoori, *International J. Energy Sources*, 10, 109 (1988b).

[19] V.A.M. Branco, G.A. Mansoori, L.C. De Almeida Xavier, S.J. Park, H. Manafi, *J. Pet. Sci. Eng*., 32, 217 (2001).

[20] K.E. Peters, C.C. Walters, J.M. Moldowan, "The Biomarker Guide", Second Edition, Volume II, Biomarkers and Isotopes in Petroleum Systems and Earth History, United Kingdom at the Cambridge University Press, 684 (2005).

[21] J.J. Broock, R.E. Summons, "Sedimentary Hydrocarbons, Biomarkers for Early Life, in Holland, H.D. and Turekian, K.K. (eds.), Treatise on Geochemistry", Vol. 8, Biogeochemistry, Elsevier, Amsterdam, 425 (2004).

[22] R.P. Philp, "Formation and Geochemistry of Oil and Gas, in Holland, H.D. and Turekian, K.K. (eds.), Treatise on Geochemistry", Vol. 17, Sediments, Diagenesis and Sedimentary Rocks, Volume Editor, F.T. Mackenzie, Elsevier, Amsterdam, 425 (2004).

[23] K.E. Peters, M.G. Fowler, *Organic Geochemistry*, 33, 5 (2002).

[24] Oxford English Dictionary, 3rd Ed. (2003).

[25]H. Justwan, B. Dahl, G.H. Isaksen, I. Meisingset, *Journal of Petroleum Geology*, 28, 241 (2005).