

Study of the Parameters and Bio-Markers of Crudeoils

I. P. Pandey

Indra Prasad Pandey, Harish Chandra Joshi, Ashish Tyagi, Sadhana Tiwari & Nitika Garg
Oil Extraction, Environmental & Disaster Management Lab., Department of Chemistry D.A.V. (P.G.) College,
Dehradun – 248 001, Uttarakhand, India

E-mail: ippande@gmail.com

Abstract: Geo-chemical Fossils are derived from living organisms and are complex compounds containing C,H and other elements. These compounds show the structures indicating that these are the components of living organisms. Geochemical fossils find their applications in correlations of oil. Organic matter input, depositional environment and biodegradation. The occurrence of biological marker in crude oil is studied qualitatively as well as quantitatively. Several ratios and specified ranges of parameters are the basis of classification and geo-chemical characterization of different types of crude oils.

Keywords: Molecular fossils; Isoprenoids; Biomarkers; n-alkanes.

Introduction

The crude oil or petroleum is a mixture of gaseous, liquid and solid hydrocarbon compounds. The petroleum occurs in sedimentary rock deposits throughout the world and also contains small quantities of Nitrogen, Oxygen and Sulphur containing compound as well as trace amount of metallic constituents. Thus petroleum or crude oil is defined as, "Naturally occurring mixture of hydrocarbon, generally in a liquid state, which may also include compounds of Nitrogen, Oxygen, Sulphur and other elements."

Whenever an oil and gas are struck in the basin, it is necessary to know about the genetic class of the oil and gas. The genetic class of the oil implies that the oil is terrestrial or marine oil. The genetic class of the gas indicates whether the gas is a thermal or biogenic.

Most of the Geo-chemists now agree that the crude oil has a biological origin. The organic matter is provided by marine plankton algae, higher (land) plants and bacteria. Organic matter is mixture of varying proportions of amorphous sapropelic organic matter, algal remains plants resins, degraded wood, cuticles, spores and pollen grains. The type of organic matter deposited and incorporated in sediments depends largely upon the natural association of the various groups of organism are basically composed of the some chemical constituents such as lipids, proteins, carbohydrates and lignin in higher plants. All those living organisms consist of a very small number of chemical substances, carbohydrates, proteins, and lipids.

These chemical fossils can also be termed as geo-chemical fossils, molecular fossils, biological markers or

biomarkers. The geo-chemical or molecular fossils are derived from living organisms and are complex containing principally carbon, hydrogen and other elements.

Molecular fossils find their applications in correlations of oils; oil to source correlation, assessment of maturity, organic matter input, depositional environment and biodegradation.

Biomarkers are derived from chlorophyll, bacteriochlorophylls and carotenoids in living organisms are found in ancient rocks and petroleum.

Bulk parameters of crude oils like A.P.I. gravity is the basic parameter to classify the crude oils, n-alkane-isoprenoid ratios, carbon preference index (CPI) and other ratios would be discussed. The main classes of biological marker are: n-alkanes, iso and anteiso-alkanes. C₁₀ branched alkanes, a cyclic isoterpenoids, tri cyclic diterpenoids, steroids and pentacyclic triterpenoids, polyterpenes, aromatic hydrocarbons and many other nitrogen, oxygen compounds.

1. Parameters (Efficient tools for the characterization of crude oils)

1.1 API gravity

API gravity is reported in °API. API gravity is a measure of density or specific gravity. The relation between specific gravity and API gravity is shown by the following Equation:

$$141.5 \\ \text{API} = -131.5 \\ \text{Specific gravity}$$

The API gravity of pure water is 10° . If gravity is less than 10° API indicates the oil is denser than pure water. Normal oil has API gravity ranges from 25° to 45° . API gravity is less than 20° the oils are biodegraded, high content in sulfur or both.

1.2 Sulfur content

Sulfur content expressed as weight percent. Most of the oils are of low sulfur content, containing less than 0.5% sulfur. Sulfur content can be raised during biodegradation. Most of the sulfur resides in the asphaltene fraction, incorporated into the ring structure of large aromatic molecules.

1.3 Isotope ratio

Isotope ratio measured by mass spectroscopy and it is reported in permil. Natural variations in isotope ratios are great enough to permit utilization of isotopes in correlations. The isotope ratio is most commonly used is $^{13}\text{C}/^{12}\text{C}$. On the average oils are about 20/00 more negative or lighter than kerogen. Bitumen are also about 20/00 more negative than the kerogen. This indicates that isotopic fractionation occurs during catagenesis and that effects during expulsion and migration are far less pronounced.

1.4 Carbon Preference Index (CPI)

CPI is used for the measure of the strength of the odd-Carbon predominant in n-alkanes. If the number of odd and even carbon members is equal the CPI is 1.0. If odd carbon homologs, predominate the CPI is greater than 1.0. However, the concentration of n-alkane decreases with increasing carbon number the longer carbon homologs are given more weight in calculation.

1.5 n-Alkane

n-Alkane can be measured by Gas Chromatography of the saturated hydrocarbons fraction. Alkane distribution is sensitive to variation but it provides an idea about the maturity of oils. As maturity moves up chain length becomes shorter. Less maturity waxy oil possesses larger amount of normal alkanes. Accurate result can be obtained by separating n-alkane from the branched and cyclic saturated hydrocarbon by urea adduction or molecular sieving prior to gas chromatography analysis.

1.6 n-Alkane/Isoprenoid ratio

On green river shale experiment, Cummins [et.al](#) (1965) reported that concentration of phytane decreases with increasing depth but the concentration of Isoprenoids from $i\text{C}_{15}$ - $i\text{C}_{18}$ was found to increase. Presence of Isoprenoids from $i\text{C}_{11}$ - $i\text{C}_{18}$ in crude oils is due to scission of phytyl side chain (G.W.M. Lijimabch, 1975). Thus the presence of lower Isoprenoids ($i\text{C}_{15}$ - $i\text{C}_{18}$) is attributed to catagenetic effect on maturation of organic matter. Thermal maturity of oils is also assessed by using the

ratio $i\text{C}_{16+}/i\text{C}_{18}/i\text{C}_{20}$ (phytane) and also by the ratio of $i\text{C}_{15}+i\text{C}_{16}+i\text{C}_{18}/\text{Pr}+\text{Ph}$ with increasing thermal maturity. Pristane/n-heptadecane and phytane/n-octadecane ratio generally decreases as more normal alkanes are generated by cracking maturity assessment needs to be seen in the light of other technique because of limitation of alkane profile.

1.6.1 Pristane/Phytane Ratio

Pristane/Phytane Ratio is often used as maturity parameters (Welte et. al, 1975). This ratio suffers from the uncertain effects of thermal maturation. This ratio has been utilized in association with percentage of aromatic proton (R. Alexander, R.I. Kagi & G.W.Woodhouse, 1978). Formation of pristane and phytane is supposed to depend on the redox potential of the depositional environment of the source material. Hydrolysis of chlorophyll during early sedimentation yields phytol.

Value of Pristane/ $n\text{C}_{17}$ is < 0.50 in case of oils formed from source rock deposited in open water conditions.

Pristane/Phytane ratio could be employed for source organic matter and depositional environment. In general the value of this ratio is found to be < 1.0 in anoxic marine sediments. Its value ranges from 1-3 coals have value greater than 3.

Generally Pristane/Phytane ratio greater than 3 is thought to be associated with terrigenous bed with oxidizing conditions. According to Volkman and Maxwell (1986) Pristane/Phytane ratio > 3 indicates that terrestrial organic matter input under oxic conditions. Value less than 0.60 show anoxic commonly hypersaline environments. Value of this ratio in the range of 0.8 to 2.50 should not be used as an indicator of paleoenvironment without other supporting data.

High Pristane/Phytane value could reflect the relationship between contributing organic matter and chemistry of depositional environment R 15 oils invariably show this value greater than 4 to 5.74, rest of the oils in this group have lower values than R 15 A oils. R13, R10-3 and RBC have the lowest value in the group.

1.7 Methyl Phenanthrene Index (MPI)

An aromatic hydrocarbon occurs widely in petroleum and source rock organic matter. Transformation of precursor molecules may be brought about by microbial process during diagenesis or during subsequent burial in which these precursor molecules are exposed to the effect of temperature, pressure and catalytic action of mineral matrix.

Phenanthrene is supposed to be derived from steroids and triterpenoids (Mair 1964, Greiner [et.al](#) 1976). Methyl derivatives of phenanthrene are not related to any precursor, these are derived either by methylation of phenanthrene or dehydrogenation of alkylated dihydrophenanthrene (Larter & Allan, 1982).

Methyl phenanthrene found in sediments and oils are -1 methyl phenanthrene (1-MP), 2-MP, 3-MP, and 9-MP. It is held at 2 & 3 – methyl phenanthrenes are derived from 9-MP and 1-MP by rearrangements and also by methylation of phenanthrene. MPI have been related to

vitrinite reflectance within oil generation window. MPI can be calculated as follows

$$1.5(2MP + 3 MP)$$

MPI=

$$P + 1 MP + 9 MP$$

Reflectance can be calculated as

$$R_c = 0.60 MPI + 0.40 \text{ for more reflectance } < 1.35 \%$$

It has been observed that as maturation increases the concentration of 3 MP and 2 MP increases over 1 MP & 9 MP. 3- Methyl and 2- methyl phenanthrene are thermodynamically more stable than 1 & 9 methyl phenanthrene.

2. Biomarkers

2.1 n-Alkane

n- Alkane was the first biomarker to be studied extensively. Their high concentration in bitumen and oils is can be explained by their existence in their part and algal lipids and by their catagenetic formation from long chain compounds. n-Alkane also present in terrestrial plants have odd numbers of carbon atoms like 23,25,27,29. Marine algae also produce n-alkane according to their distribution at C-17 or C-22 depending upon the species present.

CPI (Carbon Preference Index) Value in all oils is very close to unity and seems to be no odd even preference. In crude oils, the high molecular weight alkanes inherited from terrestrial organic matter are normally diluted by hydrocarbons from kerogen degradation and the CPI value remains around 1. The other reasons could be due to mixed organic matter. The low values decreases always indicate maturity. Where terrestrial input is negligible a significant proportion of long chain alkanes may be derived from planktonic algae and bacteria which do not generate a predominance of the odd numbered long chain molecules. The CPI value is near 1.0 even in immature sediments. Generally CPI values have been reported to range between 2 to 5.5 in case of odd to even predominance (Evans 1981)

2.2 Isoprenoids

Isoprenoids generally derived from chlorophyll. Several cyclic or linear compounds known to occur in living plants and animals to lesser extent are formed of isoprene unit. These may also contain one or two aromatic rings.

In geo-chemical studies Isoprenoids term is restricted to an acyclic, branched, saturated molecule with a methyl group on every fourth carbon. Isoprene units are arranged in head to tail linkage. However, Isoprenoids units with head to head and tail to tail linkage are also known to occur (Lycopane and Squalane). In living organisms chlorophyll is attached to phytol side chain through an ester linkage. This is the most spread form of Isoprenoids compounds. As maturity proceeds phytane is generated

by faster than pristane, leading to decreases in the pristane/phytane ratio. During hydrocarbon generation Isoprenoids concentration increases more slowly than n-alkane concentration. Isoprenoids are good indicators that bitumen and petroleum are of liogenic origin.

2.3 Steranes

Steranes are important biological marker found in petroleum and sediments. Steroids is the biological precursors of the Steranes, are present in all organisms. Diagenesis converts the steroids molecules to Steranes hydrocarbon through hydrogenation of double bonds and loss of oxygen atoms. The important use of Steranes as biomarker derived from the sterols having 27, 28 and 29 C-atoms. During diagenesis these sterols are converted to the corresponding Steranes. Sterols in living organisms show configuration 8β (H), 9α (H), 10β (CH₃), 13β (CH₃), 14α (H), 17α (H) 20R. Configuration at C14, C17 and C20 are of greater importance for maturity assessment. C5 and C24 position in sterol consists of α (H) and β (H) configuration. All sterols in living organisms appear to show only 20R configuration. C24 configuration in sterols can be R or S. In sediments and petroleum sterols consists of 24R and 25S (ergostane C28 and stigmastane C29). C5 position in most of sterols contain a double bond which on reduction gives 5α and 5β mixtures favoring 5α . 5β (H) compounds are disregarded for biological marker applications.

2.4 Diterpanes

Diterpanes are important constituents of crude oils and extracts derived from fossil plant resin.

2.5 Triterpanes

Triterpanes are commonly found in oils and bitumen from microorganisms. The common triterpanes are hopane, norhopane, oleanane, ganmacerane, lupine, hopane etc. .The precursors of these two hydrocarbons are hopane and norhopane are unknown. Some bacterial triterpenoids actually have 35C-atoms rather than the 27C-atoms to 30C-atoms in the normal hopane series. Hopane contain from 36C-atoms to 40C- atoms have been reported. Triterpanes are well known biomarkers because of very stable cyclic structure. A large number of triterpanes have been isolated in geological samples and oils. Hopane occurs frequently in geological samples. Hopane series is found in blue green algae and bacteria. Hopanes with 30 C- atoms or less have asymmetric centres at C 21. Hopane with more 30 C- atoms are called homohopanes and contain extended side chain with an additional asymmetric at C 22. Hopane are compound of three stereoisomeric series 17α (H) 21β (H); 17β (H) 21β (H) and 17β (H) 21α (H). Compound in β series are called moretananes. $\beta\beta$ hopnaes occur in living organisms and immature sediments but do not occur in oils due to thermal instability. The compound containing $\alpha\beta$ configurations are found in petroleum ranging C27-C35 owing to their greater thermodynamic stability compared to $\beta\beta$ and $\beta\alpha$. Hopanes are derived from bacteriohopnae-

tetrol, which is found in lipid membrane of prokaryotic organisms.

2.6 Naphthenoaromatics

It is derived from Steranes and triterpanes. These lost their stereo chemical characteristics as a result of catagenetic transformations and can not be related with any precursors.

3. Conclusion

Bulk parameters of crude oils show the compositional resemblance of different oils, which help for co-relating oils. The above parameters will also suggest that type of organic matter is derived from which type of oils. Methyl phenanthrene index indicates the thermal maturity of oils. The n-alkane distribution also give the details of saturated fraction of crude oils will be studied to its

origin. n-alkane/Isoprenoid ratios will be used to understand the paleoenvironment conditions.

Biological markers play an important role in genetic classification of petroleum oils. Here is important data on the source of Biomarkers.

1. Bitumen and crude oils with high contents of waxy n-alkanes have a significant input of terrestrial plant material.

2- Isoprenoids ratios are indicators of diagenetic conditions.

3. CPI values 1.0 is associated with evaporates. Diterpanes have a significant contribution from land plant resin.

In the present investigation the genetic Biomarkers of crude oils from the different classes will be used to understand the origin of hydrocarbon in the area and their maturation and accumulation histories. Biological markers crude oil implies that whether the oil is terrestrial or marine.

Table 1: Important classes of biomarkers are listed

Biomarkers	Precursors
N-Alkane (>C22)	Terrestrials Plant waxes
N-Alkane (C17,C22)	Algal lipids
Isoprenoids (< C20)	Chlorophylls
(> C20)	Lipids or Chlorophylls of hypersaline algae
Porphyryns	Chlorophylls
Steranes	Steroids
Triterpanes	Bacterial triterpenoids
Diterpane	Hydrocarbons in plant resins
Large Naphthenoaromatics	Steroids, Triterpenoids

References

- Alexander, R., Kagi, R.I., Woodhouse, G.W. and Volkman, J.K. (1983): The geo-chemistry of some biodegraded Australian oils: Journal of the Australian petroleum exploration Association (APEA), v.23, pp.53-63
- Bayliss, G.S. (1968) The formation of the Pristane, phytane and related isoprenoid hydrocarbons by the thermal degradation of Chlorophyll. 155th Am. Chem. Soc. Nat.Meet. Div. Petr. Chem. Preprint F.117-131
- Bendoraitis, J.G., J.G. (1974); Brown, B.L. & Hepner, L.S. (1962) Isoprenoid hydrocarbon in Petroleum, Anal.chem., n.34, p.49-53
- Brassel, S.C., Wardroppe, A.M.K., Thompson, I.D., Maxwell, J.R. and Eglinton, G. (1981) Specific acyclic isoprenoids as biological markers of methanogenic bacteria in marine sediments Nature V.290 P.693-696
- Burnham A.K., Clarkson, J.K., Singleton, M.F., Wong, C.M. and Crawford R.W. (1982) Biological markers from green river Kerogen decomposition. Geochemical Cosmochimica Acta, v.46 p.1243-1257
- Connan, J. (1984): Biodegradation of Crude oils in reservoirs, in J. Brooks and D. Welte, eds., Advance in Petroleum geochemistry, volume 1: London Academic press, pp.299-333
- Cummins, J.J., and Robinson, W.E., J. Chem. Eng. Data 9. 304 (1964)
- Eglinton, G. (1993): Fossil Chemistry, Pure Applied Chemistry 34, pp.611-632
- Erdman, J.G., Morris, D.A. (1974) Geo- Chemical correlation of petroleum. AAPG, v.58, p.2326-2327
- Lijmbach, G.W.M. (1975) On the origin of petroleum. Proceedings 9th world petroleum Congress v.2. Applied Science Publisher London, p. 357-369.
- Mackenzie, A.S. (1990): Application of Biological markers in Petroleum Chemistry: Advance in Petroleum Geochemistry volume 1: pp.115-214
- Ourisson, G., Albrecht, P., Rohmer, M. (1984) The microbial origin of fossil fuels. Scientific American, v.251, p.44-51.
- Patterson, G.W. (1971) the distribution of Sterols in algae, Lipids, v.6, p.120-127
- Volkman, J.K. and Maxwell, J.R. (1984) Biological Marker: A Monograph (R.B. Johns ed.) Elsevier. Amsterdam.

14. Waples, D.W., and Machihara, T. (1991) Biomarkers for geologists. AAPG methods in exploration series, No. 9. p. 91.