

# Physicochemical and Genetic Study of the Crude oils of Different Basins

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**Abstract:** *Petroleum is a mixture dominantly of hydrocarbons with varying proportions of non-hydrocarbon constituents and traces of organometallic compounds. Generally Petroleum has an average composition of 85% carbon, 13% hydrogen, and 2% of sulphur, nitrogen and oxygen. Organic geochemistry can be defined as the study of the fate and distribution of carbon compounds in contemporary environments, in Recent and ancient sediments. 'Biological marker' or shortened to 'Biomarkers' or Geochemical Fossils are complex molecules derived from once living organisms they are found in sediments and oil and show little change in structure from their parent molecules. Genetic correlation of petroleum is important to identify source rocks and determines the migration pathways. It is based on the concept that the composition of the organic components in a source rock is transmitted to the oil. The aim of study is to find out the physicochemical and genetic property of petroleum. The Crude oil was collected from different basins of India. To avoid the loss of lighter hydrocarbon preserve the sample. The sample will be fractionated and different fraction will be obtained with the help of HPLC and GC-MS. In this process different Biomarker were obtained which are then expelled to migrate along carrier beds and other conduits to traps.*

**Keywords:** Biomarker, Genetic Characterisation, Kerogen, Geochemical Fossils

## 1. Introduction

Petroleum is a mixture dominantly of hydrocarbons with varying proportions of non-hydrocarbon constituents and traces of organometallic compounds. In general Petroleum has an average composition of 85% carbon, 13% hydrogen, and 2% of sulphur, nitrogen and oxygen. Petroleum is a form of bitumen composed principally of hydrocarbons and existing in the gaseous or liquid state in its natural reservoir. Petroleum is found in sedimentary basins and is accumulated as gas or oil in the porous and permeable reservoir rocks or a fractured sedimentary rock, a fractured igneous rock or a fractured metamorphic rock associated with sedimentary basin. The name geochemistry as an independent field of study is not very old when compared with its parent sciences- geology and chemistry. Geochemistry is helpful for determining the relative and absolute abundances of the elements and of the atomic species (isotopes) in the earth. Organic geochemistry can be defined as the study of the fate and distribution of carbon compounds in contemporary environments, in recent and ancient sediments. Petroleum geochemistry is based on the premise of organic origin of oil and gas where by organic matter derived from dead plants and animals is believed to have been converted to hydrocarbons in the subsurface through various stages of transformations or evolution, viz., diagenesis, catagenesis and metagenesis. Most of the Geo-chemists now agree that the crude oil has a biological origin. The oil is generated from the fine-grained sediments rich in organic matters. The organic matter is provided by marine plankton algae, higher (land) plants and bacteria. All those living organisms consist of a very small number of chemical substances, carbohydrate, proteins, and lipids. The organic matter is modified by low temperature chemical and biological reactions (called diagenesis) that occur during transport to and early burial in the depositional environment. Most of this organic matter is transformed during diagenesis

biodegradation through fungal and bacterial actions into very large molecules, the largest of which are called 'Kerogen'. Oil and gas molecules once formed, can be expelled from the source rock into more permeable carrier beds or conduits which is called 'primary migration'. Migration through these conduits often leads to traps, where hydrocarbon movement ceases and accumulation occurs; this migration is called 'secondary migration'. Crude oils contain metals, particularly nickel and vanadium, in variable amounts from less than 1 ppm in some Paleozoic crudes upto 1200 ppm V and 150 ppm Ni in Boscan crude. Porphyrin pigments were the first step in that part of the organic geochemistry. This is now usually referred to as the study of "biological marker" organic compounds. Biomarkers are also called as geochemical fossils (Eglinton and Cavin, 1967) because of their origin from living organisms. Such compounds may be derived from terrestrial (mostly plants, marine pelagic (mostly plankton) and marine benthonic (algae, bacteria and other microbes). Biomarkers can be used for characterization, correlation, and/or reconstruction of the depositional environment in the same way as macro- and micro-fossils are used by geologists and palynologists. As biomarkers represent a molecular record of life, they can be used for age determination. The main aim of reservoir geochemistry is to understand the distribution and origin of the petroleum, water and minerals in the reservoir and account for their possible spatial and compositional variation.

## 2. Experiment

The crude oil samples produced in the different basins of India will be collected for this work to study. The crude oil sample of investigation will cover under the following steps:-

- 1) Collect the sample from the different basin of India

- 2) To avoid the loss of lighter hydrocarbon preserve the sample
- 3) Analysis of samples: (i) Topping of the oils: (ii) Fractionation of oils: (iii) Saturated hydrocarbon analysis: (iv) Aromatic hydrocarbon Analysis (v) Urea Adduction of Saturated Hydrocarbon:

**Table 1:** Details of the Samples taken for Study

| Sr.No. | Name of Samples | Type of the sample |
|--------|-----------------|--------------------|
| 1      | A               | Oil                |
| 2      | B               | Oil                |
| 3      | C               | Oil                |
| 4      | D               | Oil                |
| 5      | E               | Condensate         |
| 6      | F               | Condensate         |
| 7      | G               | Oil                |
| 8      | H               | Condensate         |

### 3. Result and Discussion

**Table 2:** Group Type Composition of the oils/condensates from the study area

**Table 3:** Gas chromatographic data of oils/condensates

| Sr. No. | Sample Name | Type of the sample | Pr/Ph | Pr/nC <sub>17</sub> | Ph/nC <sub>18</sub> | Pr + n C <sub>17</sub> | nC <sub>21</sub> + nC <sub>22</sub> | Cmax |
|---------|-------------|--------------------|-------|---------------------|---------------------|------------------------|-------------------------------------|------|
|         |             |                    |       |                     |                     | Ph + C <sub>18</sub>   | nC <sub>28</sub> + nC <sub>29</sub> |      |
| 1       | A           | Oil                | 5.2   | 1.6                 | 0.32                | 2.04                   | 0.74                                | C29  |
| 2       | B           | Oil                | 6.5   | 1.76                | 0.29                | 2.06                   | 0.68                                | C27  |
| 3       | C           | Oil                | 7.4   | 2.01                | 0.28                | 2.39                   | 0.64                                | C26  |
| 4       | D           | Oil                | 4.9   | 1.15                | 0.26                | 1.69                   | 0.78                                | C27  |
| 5       | E           | Condensate         | 5.3   | 1.8                 | 0.38                | 2.23                   | 2.28                                | C14  |
| 6       | F           | Condensate         | 4.8   | 1.23                | 0.33                | 1.8                    | 4.92                                | C15  |
| 7       | G           | Oil                | 5.6   | 1.63                | 0.3                 | 2.09                   | 0.84                                | C27  |
| 8       | H           | Condensate         | 5.6   | 1.5                 | 0.25                | 1.88                   | 0.72                                | C30  |

Where Pr=Pristane, Ph=Phytane

It is also clear from the gas chromatographic data that saturate/aromatic ratio for the sample is more than 1. The waxy nature and slight odd even predominance of the samples are thought to have resulted from a contribution by terrestrial source organics. Philippi index i.e.  $(C_{21}+C_{22}/(C_{28}+C_{29}))$  ratio for the studied samples varies between 0.64 (lowest) for sample C and highest value of 0.84 sample G. This table also clearly indicates that this ratio is generally more for condensates in the range of 2.28 (sample E) to 4.92 (sample F) except the sample H with a value of 0.72, while all the oil samples are having values <1 except oil sample G which is having value of 0.84. Thus the Philippi index i.e.  $(C_{21}+C_{22}/(C_{28}+C_{29}))$  ratio of < than 1 for most of the oils indicates the terrestrial nature of the source while the condensates are having the contribution of marine organic matter input as well. The high Pr/Ph ratios (4.8-7.4) and Pr/nC<sub>17</sub> (1.15 – 2.1) indicate that the source rock for these oils were deposited in oxic environment (Didyk et al 1978) and were rich in terrestrial organic matter (Tissot and Welte, 1984). Further, the presences of the complete range of the n-alkanes (upto nC<sub>36</sub> and in some cases upto nC<sub>40</sub>) also indicate that all the studied samples are normal, non-biodegraded condensate and oil samples.

Thus on the basis of gas chromatography of the studied oils /condensates the following conclusions can be safely drawn:

| Sr. No. | Sample Name | Type of the sample | Sat%  | Aro % | NSO % | Sat/ Aro |
|---------|-------------|--------------------|-------|-------|-------|----------|
| 1       | A           | Oil                | 67.2  | 23.45 | 9.35  | 2.86     |
| 2       | B           | Oil                | 60.48 | 26.5  | 13.02 | 2.28     |
| 3       | C           | Oil                | 64.48 | 27.52 | 8     | 2.34     |
| 4       | D           | Oil                | 63.9  | 28.56 | 7.54  | 2.24     |
| 5       | E           | Condensate         | 70.5  | 20.25 | 9.25  | 3.48     |
| 6       | F           | Condensate         | 60.05 | 27.5  | 12.45 | 2.18     |
| 7       | G           | Oil                | 62.65 | 30.75 | 6.6   | 2.04     |
| 8       | H           | Condensate         | 45.2  | 42.25 | 12.55 | 1.07     |

Sat = Saturate, Aro=Aromatic, NSO = Nitrogen, Sulphur, Oxygen

On the basis of the above observations it is clearly demonstrated that oils and condensates field have high saturate content (>50%) and condensate sample H (Sat %) 45.20). the saturate/ aromatic ratio for all the studied samples is >1. The relative dominance of saturated hydrocarbons over aromatic hydrocarbons indicates that all the studied oils and condensates and predominantly aliphatic in nature.

- 1) The gas chromatograms of saturate fraction of oil and condensates indicate that these oil/condensates are rich in normal alkanes.
- 2) All the oils and condensates are aliphatic in nature.
- 3) The high Pr/Ph ratios (4.8-7.4) and Pr/nC<sub>17</sub> (1.15 – 2.1) indicate that the source rock for these oils were deposited in oxic environment and were rich in terrestrial organic matter. The cross plots of Pr/nC<sub>17</sub> ratios also corroborate the above view.
- 4) The presence of complete range of normal alkanes upto nC<sub>36</sub> and in some cases up to nC<sub>40</sub> also indicate that these oils/condensates are normal, non- biodegradable in nature.

The principal method used to evaluate biomarkers is a computerized gas chromatography- mass spectrometry using a gas chromatograph coupled with a mass spectrometer with the help of an interface.

Organic matter input and depositional conditions of the sediments that become source rocks exert primary control on the biomarker fingerprints of source rock extracts and crude oils. Biomarkers are present in saturate fractions of oil/bitumen and are used to infer the depositional environment, organic matter input, thermal maturity and even the age of the source rock. Correlations using biomarkers are done by biomarkers fingerprinting and by ratios of biomarker classes and individual biomarkers. Most

common biomarkers identified through GC-MS analysis of the samples are hopanes (identified in mass fragmentograms m/z-191 and steranes identified in mass fragmentograms m/z-217.

**Table 4:** Source Specific and correlation related biomarker parameters in oils/ condensates of the area under investigation

| Sr. No. | Sample Name | Type of the sample | $\frac{C_{29}H}{C_{30}H}$ | Oleanane index | $C_{27}R$ | $C_{28}R$ | $C_{29}R$ | $\frac{C_{27}}{C_{27} + C_{29}}$ |
|---------|-------------|--------------------|---------------------------|----------------|-----------|-----------|-----------|----------------------------------|
| 1       | A           | Oil                | 0.48                      | 20.15          | 24        | 24        | 52        | 0.31                             |
| 2       | B           | Oil                | 0.45                      | 18.44          | 22        | 20        | 58        | 0.28                             |
| 3       | C           | Oil                | 0.51                      | 21.8           | 19        | 18        | 63        | 0.33                             |
| 4       | D           | Oil                | 0.48                      | 20.95          | 24        | 21        | 55        | 0.03                             |
| 5       | E           | Condensate         | 0.53                      | 22.18          | 22        | 18        | 60        | 0.27                             |
| 6       | F           | Condensate         | 0.5                       | 20.04          | 31        | 23        | 46        | 0.4                              |
| 7       | G           | Oil                | 0.45                      | 17.47          | 27        | 22        | 51        | 0.34                             |
| 8       | H           | Condensate         | 0.46                      | 15.94          | 33        | 21        | 46        | 0.41                             |

Oleanane Index =  $\frac{\text{Oleanane}}{C_{30} \text{ Hopane}} \times 100$ ,  $C_{27} R = \frac{C_{27}}{C_{27} + C_{29}}$  Regular sterane,  $C_{28}R = \frac{C_{28}}{C_{28} + C_{29}}$  Regular Sterane and  $C_{29}R = \frac{C_{29}}{C_{27} + C_{29}}$  Regular sterane.

The oleanane biomarker is present in all the oil and condensate samples in varying concentration as shown in the Table 4. It is clearly evident from the table that the oleanane index is more than 15% with its value in the range of 15.94 (minimum) to 22.18% (maximum). Minimum value is observed for sample H and maximum for the sample E. Presence of oleanane in all the (>15%, Table 4) indicates that the oils are generated from terrestrial organic matter with significant contribution from angiospermic plants and suggests tertiary age for these oils (Grantham et al., 1981; Udo and Ekweozor, 1990.)

**$C_{29}$  Hopane /  $C_{30}$  Hopane** ratio is utilized to define the source facies of the oils. In the studied samples, the hopanes mass chromatograms show the dominance of  $C_{30}$  Hopane over  $C_{29}$  Hopane which is a common characteristic of oils which have been derived from clay rich source. The values of this ratio for all the studied samples is <1 varying from 0.45 to 0.53 (Table 4).

Steranes are tetra cyclic saturated biomarkers consisting of six isoprene sub units. They are derived from steroids which are abundant in all organisms. During diagenesis, steroids are converted into steranes through hydrogenations of double bonds and loss of oxygen atom. Despite these changes, sterane structures preserve most of the characteristics of precursor steroid and serve as effective biomarkers. Steranes are valuable correlation parameters of the direct dependence of  $C_{27}$ ,  $C_{28}$  and  $C_{29}$  regular sterane concentrations on their precursor  $C_{27}$  to  $C_{29}$  sterols which are present in different proportions in various organisms. During diagenesis these sterols are converted to the corresponding regular steranes. In general  $C_{27}$  sterols are dominant in marine organisms whereas  $C_{29}$  sterols are more common in terrestrial plants. Steranes are of less value where biodegradation is extreme because the regular steranes are completely destroyed in the late stages of biodegradation. Because of the large number of asymmetric centers in sterols, very complex mixtures of stereoisomers are possible. However the asymmetric carbon at C-17 and C-20 are of greater importance than others. Isomerisation of the  $5\alpha$  (H),  $17\alpha$  (H)  $20R$  configuration ( $\alpha\alpha\alpha$  R) inherited from living organisms results in increasing amounts of the other possible stereoisomers  $\alpha\alpha\alpha$  S,  $\alpha\beta\beta$  R and  $\alpha\beta\beta$  S. Steranes mass chromatograms of the studied oils and condensates indicate the predominance of  $C_{29}$  regular steranes over  $C_{27}$  and  $C_{28}$

steranes establishing the terrigenous nature of the source (Moldowan et al, 1985). Data of regular sterane (Table 4) show to low moderate ( $C_{27}/C_{27}+C_{29}$ ) sterane ratio values (0.27-0.41) again suggesting that these oils and condensates have been generated from dominantly terrestrial source rocks (Peters and Moldown, 1993). The value is lowest for the condensate sample E and the highest for the sample H which is also the Condensate sample.

#### 4. Conclusions

- The results of group type compositional analysis indicates that the oils and condensates of the study area have high saturate content (>50%) and the saturate / aromatic ratio for all the studied samples is >1. The relative dominance of saturated hydrocarbons over aromatic hydrocarbons indicates that all the studied oils and condensates are predominantly aliphatic in nature.
- The Gas chromatograms of saturate fraction of oil and condensates indicate that these oil/condensates are rich in normal alkanes.
- All the oils and condensates are aliphatic in nature.
- The source rocks for these oils are terrestrial in nature and were deposited in oxic environment.
- The presence of complete range of normal alkanes upto  $nC_{36}$  and in some cases upto  $nC_{40}$  also indicate that these oils/condensates are normal, non-biodegradable in nature.
- Hopane mass chromatograms (m/z-191) showing the dominance of  $C_{30}$ Hopane over  $C_{29}$ Hopane and presence of complete range of ubiquitous hopanes suggests the clay rich source for these samples.
- The presence of oleanane biomarker in all the oils/condensates (>15%) indicates the terrestrial nature of the organic matter with very significant contribution from the higher flowering angiospermic plants and the Tertiary age of these oils/condensates).
- The terrestrial nature of the source is also strongly indicated by the steranes distribution in the studied samples. Steranes (m/z-217) are characterized by predominance of the predominance of  $C_{29}$  regular steranes over  $C_{27}$  and  $C_{28}$  steranes establishing the terrigenous nature of the source. Low to moderate  $C_{27}/C_{27}+C_{29}$  a sterane ratio value (0.27-0.41) for these oils/condensates also suggests that they have been generated from dominantly terrestrial source rocks.

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