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Table of Content

1. **Learning outcomes**
2. **Introduction**
3. **Chemical Composition of Petroleum**
4. **Classification of Crude Oil**
5. **Types of Organic Matter and Hydrocarbon Generation**
   - **5.1 Types of Kerogen**
   - **5.2 Maturation of Kerogen and Formation of Petroleum**
   - **5.3 Oil Window**
   - **5.4 Formation of Petroleum in different depth zones in the subsurface**
   - **5.5 Van-Krevelen plot and kerogen maturation**
6. **Summary**

1. Learning outcomes

After studying this module, you shall be able to:

- Know about compositional variability of Petroleum and broad chemical constituents.
- Learn about types of organic matters involved in hydrocarbon generation and maturation of organic matter in different depth/temperature zones in the subsurface.
- Know about quality and maturation of organic matter for hydrocarbon generation.

2. Introduction

The word 'petroleum' is derived from a Greek word, which means "rock oil". Petroleum is used since ancient times for various purposes. Crude oil is a mixture of several thousands of hydrocarbon compounds of various molecular weights. Although petroleum can form by inorganic processes, organically formed petroleum is much more significant. Petroleum consists almost entirely of hydrogen and carbon, which has the ratio of 1.85 hydrogen atoms to one-carbon atoms in crude oil. Sulphur, nitrogen and oxygen comprises up to 3% of most petroleum.

In its strict sense, petroleum includes only crude oil, but it occurs as liquid, gaseous and solid hydrocarbons (table 1). Petroleum may occur as solid state in forms of tar sands, natural asphalt, gibsonite, albertite, grahamite, oil sands and oil shales. These are known as non-conventional hydrocarbon resources. The liquid state of petroleum includes the conventional heavy and light crudes and condensates. Condensates occur in the form of gases in the subsurface, but converts to liquid in the surface. Gaseous petroleum includes conventional hydrocarbon gases, methane hydrates, swamp gas, coal bed methane, shale gas.

Table 1: Different states of petroleum

State of petroleum	Examples
Solid	gibsonite, albertite, natural asphalt, tar sand, oil shale
Liquid petroleum	conventional light crude oil and heavy crude oil condensate
Gaseous hydrocarbon	conventional (natural gas) unconventional (methane hydrate, swamp gas, coal bed methane, shale gas)

3. Chemical Composition of Petroleum

Petroleum is essentially made up of carbon and hydrogen. The other elements that may be present are Nitrogen, Sulphur and Oxygen. A very small amount of metal is occasionally detected in liquid hydrocarbon. Hydrocarbon compounds maybe classified as Paraffins, Naphthenes, Olefins, Aromatics, Naphtheno-aromatics and ashphaltic compounds.

3.1 Paraffins: Paraffins are alkanes or straight-chained hydrocarbon. They are saturated hydrocarbon having the general formulae C_nH_{2n+2}. They form a homologous series where the next compound of the series is obtained by adding CH_2 to the previous compound (Fig. 1). The members of this series having low n value, i.e. from 1 to 4 are gaseous namely, methane, ethane, propane and butane. The paraffins with n values from 5 to 17 occur as liquid form. As the n value of paraffin increases, its wax content increases and ultimately it converts into a semi-solid form. Branched chain paraffins are known as isoparaffins. Although the chemical formula of the straight chain and branched chain paraffin are the same (Fig. 2), physical properties of crude oil, like boiling point vary. Thus the boiling point of normal butane is (-0.5^{o}C), while in case of isobutane it is -12^{o}C.

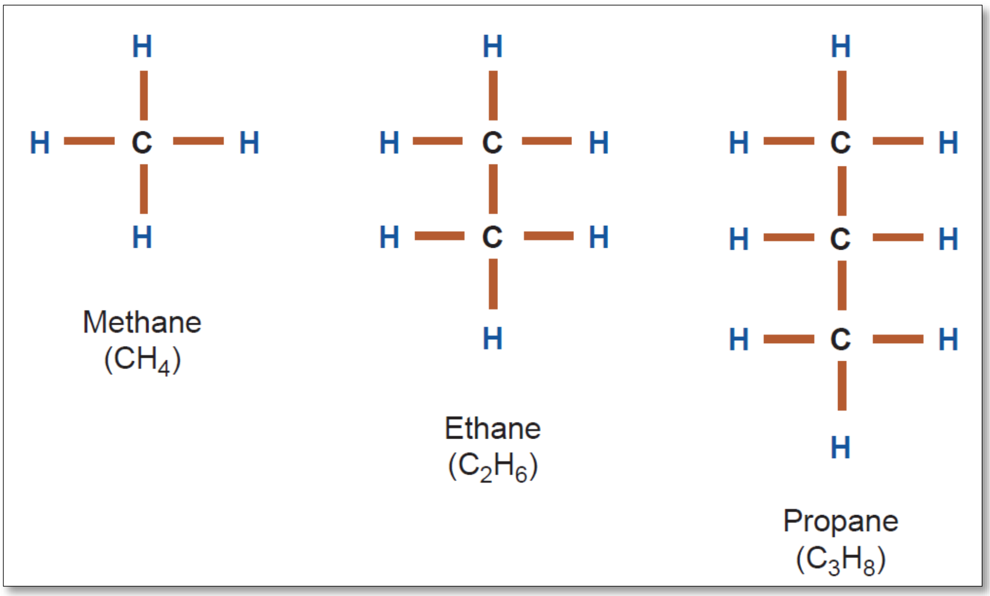


Fig. 1 Example of alkanes (after Jahn et al., 2008).

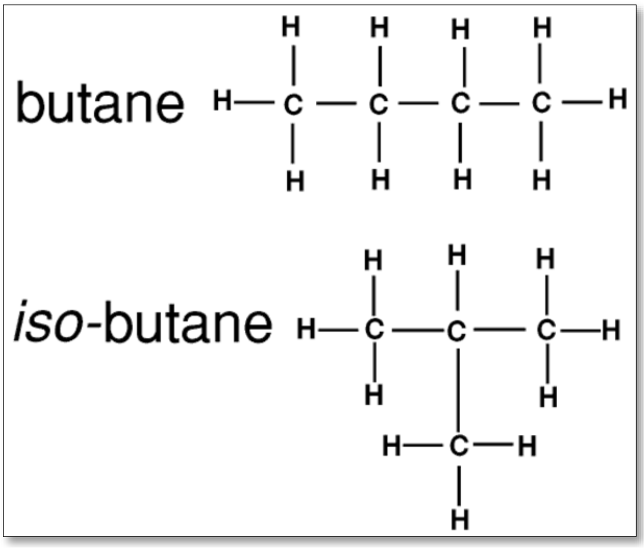


Fig. 2 Isomers of butane (n-butane and iso-butane).

3.2 Naphthenes: Naphthenes are cyclo-alkanes consisting of saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula C_nH_{2n} (Fig.3). Naphthene is the most common hydrocarbon compound of crude oil constituting about 50%. Cycloalkane rings larger than C_7 or smaller than C_5 are not found in crude oil. The hydrocarbon rings may merge together to form complex molecules.

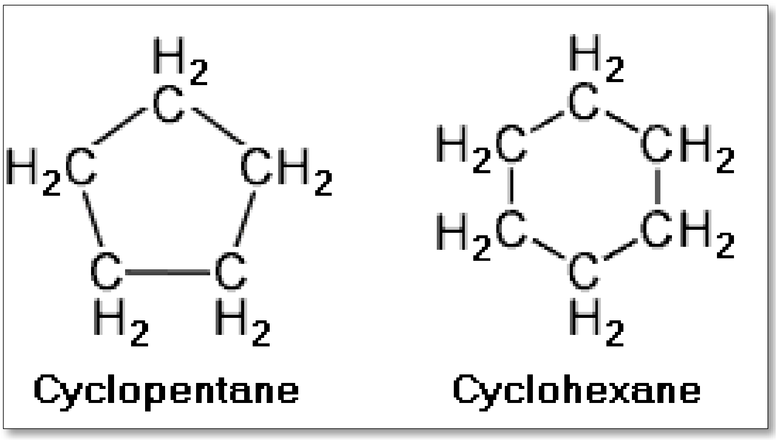


Fig. 3 Examples of Naphthene).

3.3 Olefins: Olefins are unsaturated alkenes containing double bonds in their structure (Fig. 4). They are isomer of cycloalkanes with the general formula C_nH_{2n}. They are very rare in crude oils.

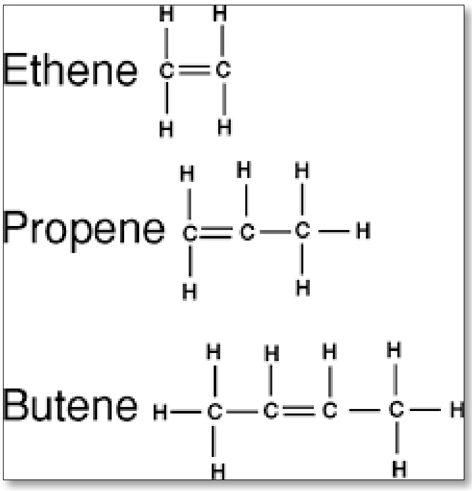
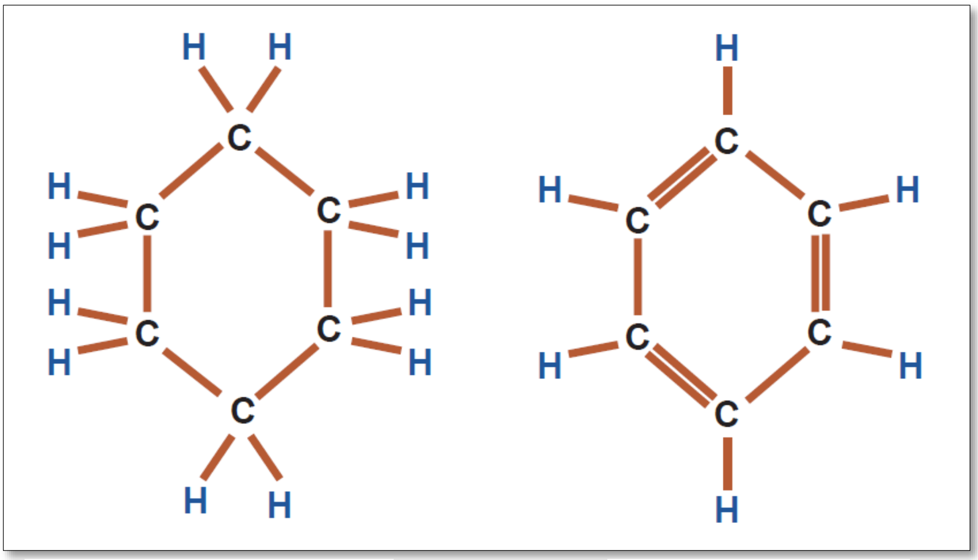


Fig. 4 Olefins (ethene, propene, 2 butene, 2, 4 pentadiene).

3.4 Aromatic Hydrocarbons: The aromatic hydrocarbons are unsaturated hydrocarbons, which have one or more six-carbon rings, called benzene rings, to which hydrogen atoms are attached having the general formula C_nH_{2n-6} (Fig.5). They react to add H or any other element to ring and gain stability. Aromatic hydrocarbons are mainly found in the heavy fraction of the crude. Toluene is the most common form of this variety. The smell of crude oil is related to the presence of aromatic compounds.



Cyclo-Hexane (C_6H_{12})
(Naphthene Series)

Benzene (C_6H_6)
(Aromatic Series)

Fig. 5 Example of aromatic hydrocarbon and its comparison with naphthene for the same carbon number (after Jahn et al., 2008).

3.5 NSO Compounds: NSO-compounds include nitrogen, sulphur or oxygen in the molecular structure of the hydrocarbon. They are mainly present in the heavy (large molecule) residual fractions of petroleum. The most important sulphur compounds are thiols and thiophenes. The free sulphur range in natural crude oils is less than 0.5-5% of petroleum. The nitrogen Compounds that may be present are pyridines, quinolenes, and indoles. The range of nitrogen in natural crude oils is 0.25 to 0.8%. The common oxygen compounds that are present in petroleum are organic acids, alcohol, phenol, esters etc. The range of oxygen in natural crudes is $<0.1\%$ to 2% of oxygen.

An overall chemical composition of petroleum is shown in Table 2. The common hydrocarbon present in petroleum is diagrammatically represented in Figure 6.

Table 2: Composition of crude oils based mainly on hydrocarbon groups in weight percent (modified from Selley, 2014).

Type	Paraffinic	Naphthenic	Aromatic	Asphaltic
Paraffinic	40	48	10	2
Paraffinic - Naphthenic	36	45	14	5
Average crude oil	30	49	15	6
Naphthenic	12	75	10	3
Mixed Asphaltic	8	42	27	23
Asphaltic	5	15	20	60

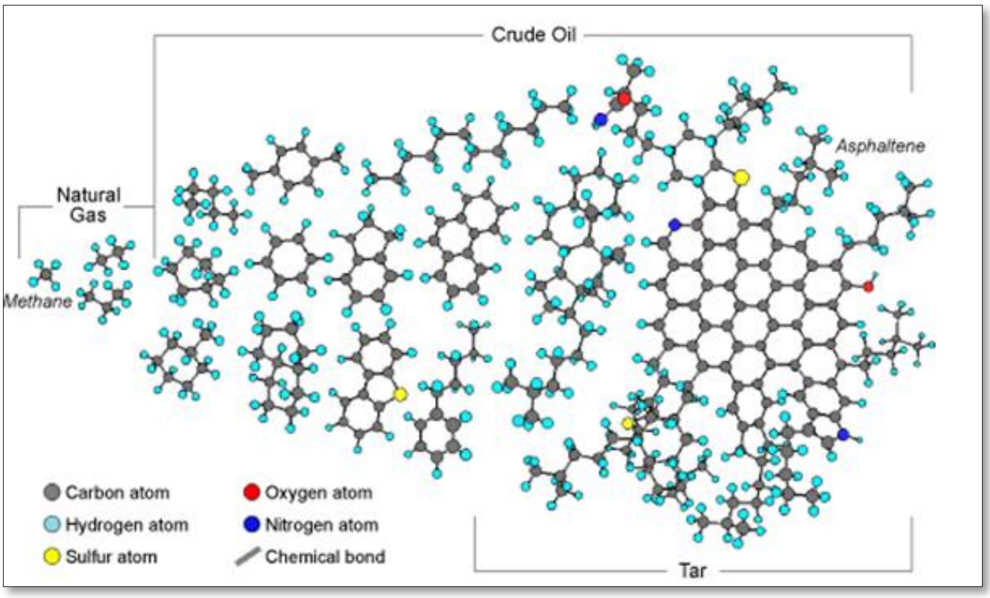


Fig. 6 Schematic representation of chemical compounds present in the petroleum (source USGS energy research website).

4. Classification of Crude Oil

Natural crude oils are classified according to their density for commercial purposes. The density of crude oil is measured generally in API units. The American Petroleum Institute gravity, or API gravity, is a measure of specific gravity of crude oil compared to water. API values are used to compare densities of various petroleum-based liquids. API gravity is a dimensionless quantity mathematically but is referred to as 'degrees'.

The formulae for API is

$$API\ gravity = \frac{141.5}{specific\ gravity} - 131.5$$

The specific gravity of oil fractions is usually determined at 15.6°C. API gravity values of most petroleum liquids range from 10 to 70 degrees. API values of some hydrocarbons are given below (Fig. 7). Crude oil is classified as light, medium, heavy, and extra heavy according to its measured API gravity (Table 3). The API values of crude oil are compared with their specific gravity in Fig. 7.

API gravity greater than 10 indicates that it is lighter than water. API value less than 10 indicates extra heavy crude oil, which sinks under water. As the API gravity of crude oil decreases, it becomes dark (Fig. 8).

Table 3: Types of crude oil as per API value.

	API values	Density (kg/m^3)
Light crude oil	API >31.1^0	<870
Medium crude oil	$22.3\text{-}31.1^0$	870-920
Heavy crude oil	API<22.3^0	920-1000
Extra heavy crude oil	API<10^0	>1000

On the basis of its sulphur content crude maybe referred to as sweet if it contains relatively little sulphur, or sour if it contains substantial amounts of sulphur.

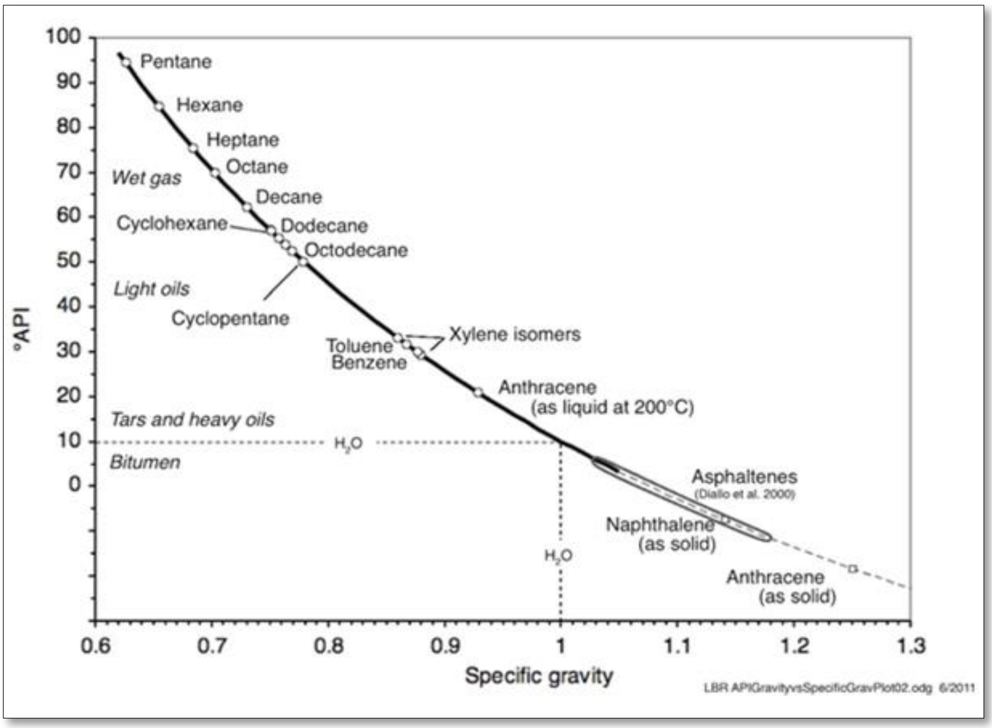


Fig. 7 API value of some hydrocarbon compounds and the relationship between API gravity and specific gravity (modified from Hunt, 1997).

Fig. 8 Light, medium and heavy crude oils showing different colors.

Crude oil is refined into useful products like petrol, kerosene, diesel, naphtha, fuel oil and lubricating oil by the method of distillation in a refinery. Crude oil is separated into fractions by fractional distillation. The crude oil fractions at the top of the fractionating column have lower boiling points than fractions at the bottom. All of the fractions are processed further in other refining units.

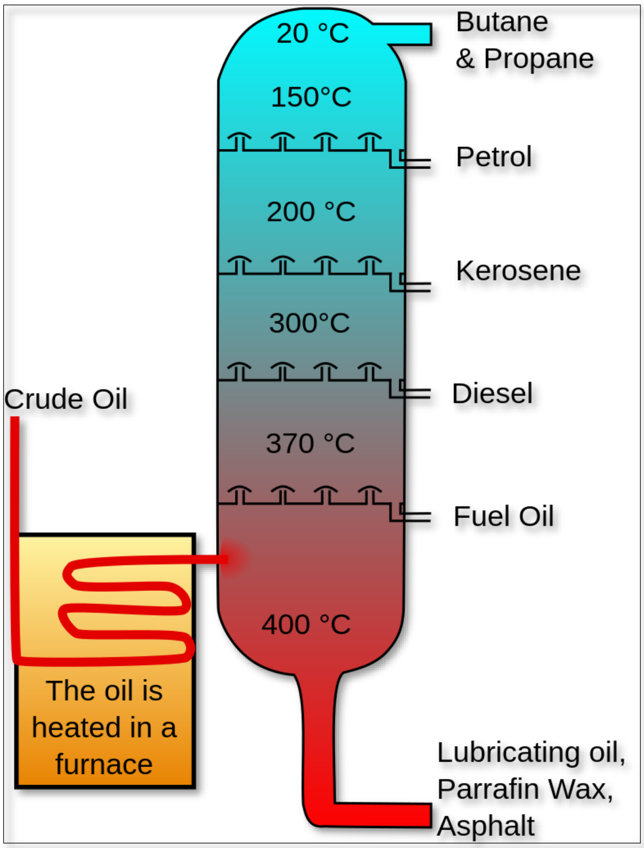


Fig. 9 Distillation of crude oil in a distillation tower.

5. Types of Organic Matter and Hydrocarbon Generation

There are two theories regarding the origin of petroleum, inorganic and organic. The stable isotope ratios of carbon and hydrogen clearly distinguish petroleum formed by two mechanisms mentioned above. While petroleum may be associated with igneous deposits in trace amount, the origin of most petroleum is linked organic matters. Organic matter may be of two types, autochthonous (produced in the depositional environment) or allochthonous (derived, detrital, washed in). The autochthonous organic matter predominantly comprises phytoplankton (algae, diatoms etc.), zooplankton, and bacteria. Allochthonous organic matters include terrestrial plant, spores and pollen and recycled (old) kerogen from earlier deposited sedimentary rocks.

The origin of petroleum involves three stages - diagenesis, catagenesis and metagenesis. **Diagenesis** involves low temperature processes, which involve hydrolysis of complex organic compounds, removal of functional groups, hydrogenation of double bonds, condensation of molecular fragments to form complex macromolecules. The end product of diagenesis is kerogen, which is a mixture of complex organic compounds that dominate organic matter in sediments. **Catagenesis** involves thermal cracking of kerogen and formation of the majority of crude oil. In the **metagenesis** stage, natural gas (mostly *methane*) is produced and residual carbon is left in the source rock.

5.1 Types of Kerogen: Kerogens are broadly divided into four types, I, II, III and IV on the basis of its H/C and O/C content. A single type or a mixture of types may be present in a hydrocarbon source rock. Table 4 lists these four basic kerogen types. Type I kerogen is rich in hydrogen and it is the best source of oil. It's H/C ratio and O/C ratio varies from 1.0 to 1.9 and 0.02 to 0.1 respectively. It is generally found in the sediments formed in a lake enviroment. Type II kerogen is also a good source of oil and it is the main kerogen type associated with marine organic matter. Its H/C and O/C varies from 0.8 to 1.5 and 0.02 to 0.2 resepectively. Type III kerogen is mainly responsible for gas formation and produces less oil. Its H/C and O/C varies from 1.0 to 0.5 and 0.03 to 0.3

resepectively. It is mainly derived from continental land plants. Type IV kerogen is carbon-rich, remains inert during the catagenesis stage. It's H/C ratio is always less than 0.5. It is also known as inert kerogen.

Macerals of coal may also be considered as kerogens. On the basis of their H/C and O/C ratios the maceral may be classified into different kerogen types. The H/C ratio of vitrinite macerals correponds to type III kerogen, while the internite macerals correspond to type IV kerogen (Table 4). Coal macerals may also belong to type I (spronite, alginite, resinite) and type II (cutinite). If a coal is predominatly consists of type I kerogen it may be a good source of oil, e.g. boghead coal and canal coal. The oil generating kerogens (type I and type II) predominantly consists of straight chains and branched chains, with a few aromatic fractions, which form oil because of thermal cracking (Fig.10). Poly-aromatic fractions dominate gas generating kerogens. Because of paucity of straight and bracnched chains it forms less amount of oil. A kerogen does not crack through the centre of the polyaromatic, condensed portion.

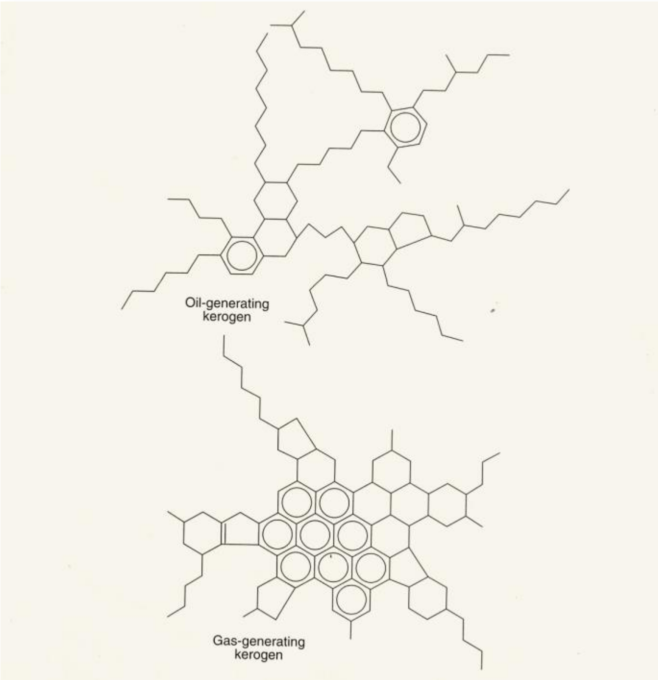


Fig. 10 Schematic structures of oil and gas generating kerogens. Note dominance of straight and branched chains in oil generating kerogens (after Hunt, 1997).

Tabel 4: Types of kerogen and their hydrocarbon potential.

Enviroment	Kerogen Type	Equivalent coal maceral	Origin	Hydrocabon Potential
Lacustrine	I	Sporinite, alginite	algae	Oil and gas
Marine	II	cutinite	Marine phytoplankton and zooplankton, bacteria	Oil and gas
Fluvial	III	vitrinite	Fibrous and woody plant fragments and structureless colloidal humic matter	Mainly gas, some oil
	IV	inertinite	Oxidised, recycled woody debris	none

5.2 Maturation of Kerogen and formation of Petroleum: Petroleum originates from organic matter following two separate pathways (Fig. 11). Approximately 10 to 20% of petroleum is directly formed from hydrocarbons synthesized by living organisms or from their molecules, which are readily converted to hydrocarbons (Hunt, 1997). This pathway involves an accumulation of hydrocarbons formed by minor bacterial activity and chemical reactions at low temperatures. Most of these early formed hydrocarbons contain more than 15 carbon atoms in their structure. The second pathway involves the thermal breakdown (maturation) of kerogen in the course of catagensis. With increasing burial depth and temperature, the organic matter progressively cracks to liquid petroleum through the intermediate stage of bitumen.

5.3 Oil Window: The temperature range of oil formation (and corresponding depth) is referred to as 'oil window'. The temperature requirement depends on the age of the rock. A Mesozoic rock requires less temperature than a Cenozoic rock. As the most oil source rock is formed during the Mesozoic, all temperature data provide in the following discussion is valid for a Mesozoic source rock. Again, temperature requirement for oil and gas generation depends on the type of kerogen. Type II variety of kerogen, containing sulphur (i.e. type IIS) requires lower temperature range compared to type I kerogen. Oil generation in the appropriately mature source rock initiates at a temperature of about 60°C for a Mesozoic source rock and continues until at a temperature of 150°C. This range of temperature is called as 'oil window' (Fig. 12). In areas of higher geothermal gradient, the oil window exists at a shallower depth and the depth range is less. For a Cenozoic source rock, the oil window temperature is slightly higher (90 to 200°C) than its Mesozoic counterpart.

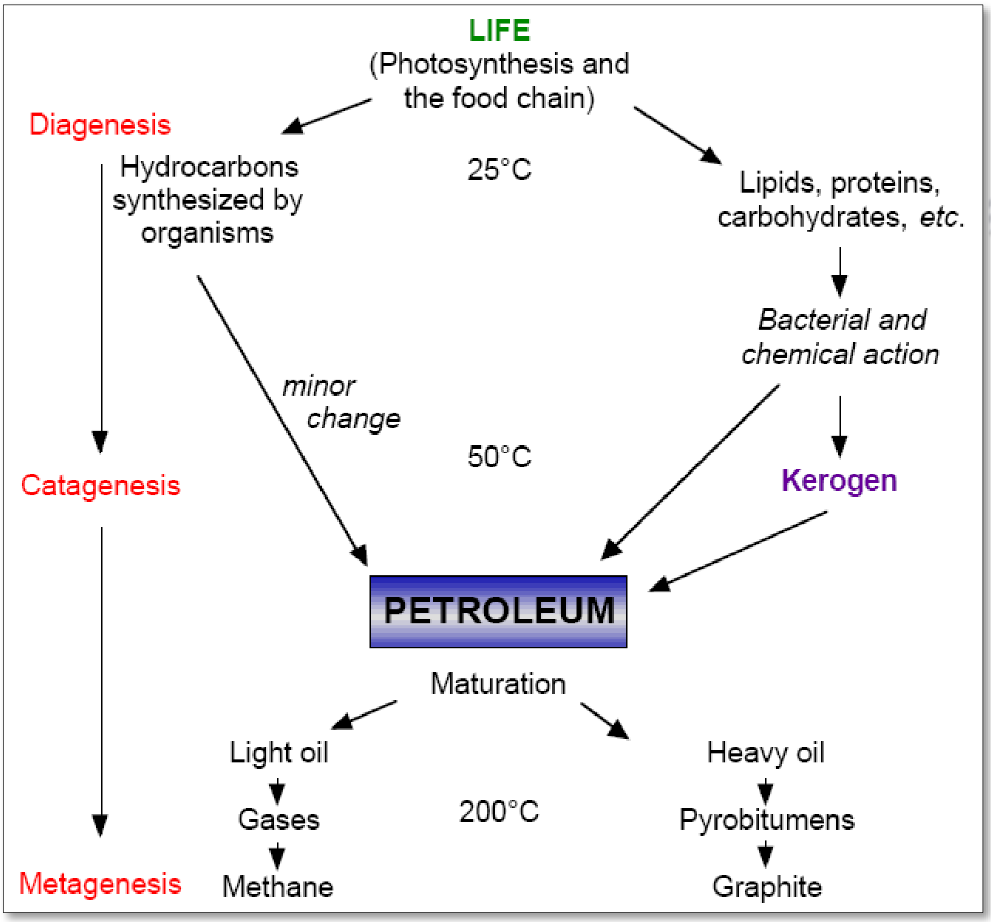


Fig. 11 Orgin and evolution of hydrocarbon through different stages (modified after Hunt, 1997).

5.4 Formation of Petroleum in different depth zones in the subsurface: The Figure below shows the formation of different types of hydrocarbons in different temperature/depth zones, which may be summarized as follows:

Diagenesis: Bacteriogenic methane and a lesser amount of heavy crude oil are produced at this stage. Biogenic methane production is very high close to the surface because of the activity of methanogenic bacteria. Methane production decreases with depth.

Catagenesis: Heavy oil and gas forms at the shallower part, followed by the formation of medium and light oil and gas. Condensate and wet gas forms at greater depth. The kerogen is converted into a carbon-rich residue at the end of catagensis.

Metagenesis: Dry gas is formed at this high temperature. Both kerogen and crude oil is converted to a carbon-rich residuum at this stage.

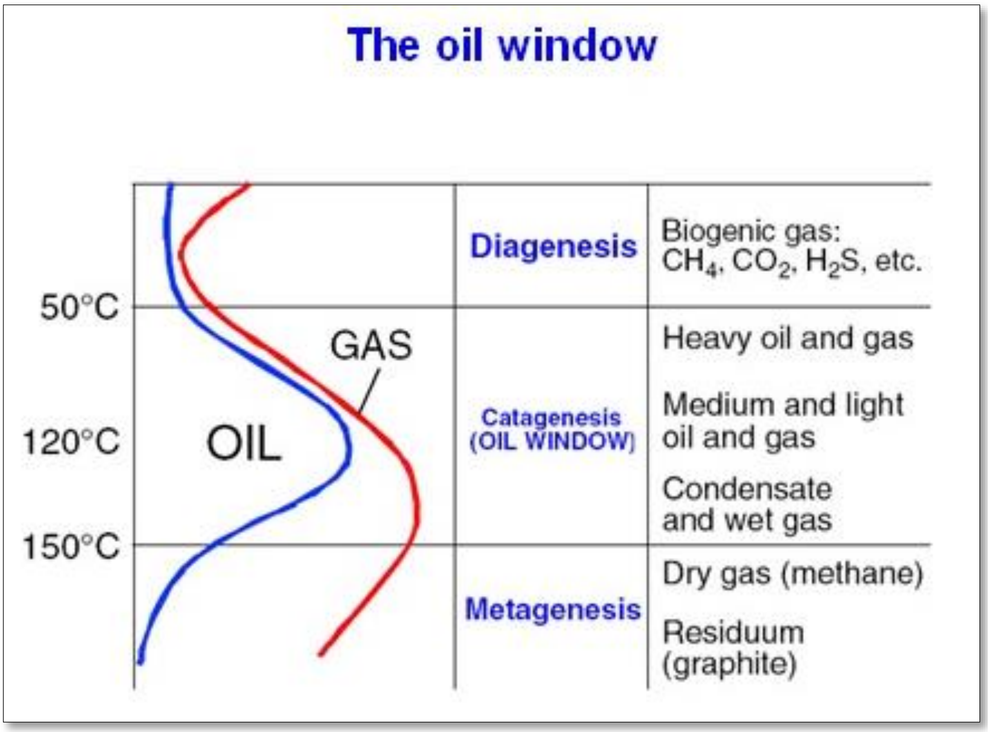


Fig. 12 Oil window and the formation of different types of petroleum (modified after Tissot and Welte, 1984).

5.5 Van-Krevelen plot and kerogen maturation: With depth and time, kerogen matures. The maturation of kerogen and hydrocarbon production can be best studied using Van Krevelen diagram (Fig. 13) which is a cross plot between atomic H/C and O/C of kerogens. Further, Kerogen types I, II, III and IV can be distinguished in the Van-Krevelen plot. The arrows in Fig. 13 indicate the direction of maturation of kerogen. Ro in the figure indicates vitrinite reflectance, which accurately estimates of kerogen maturation. The vitirinite reflectance takes care of both time and temperature factors in kerogen maturation.

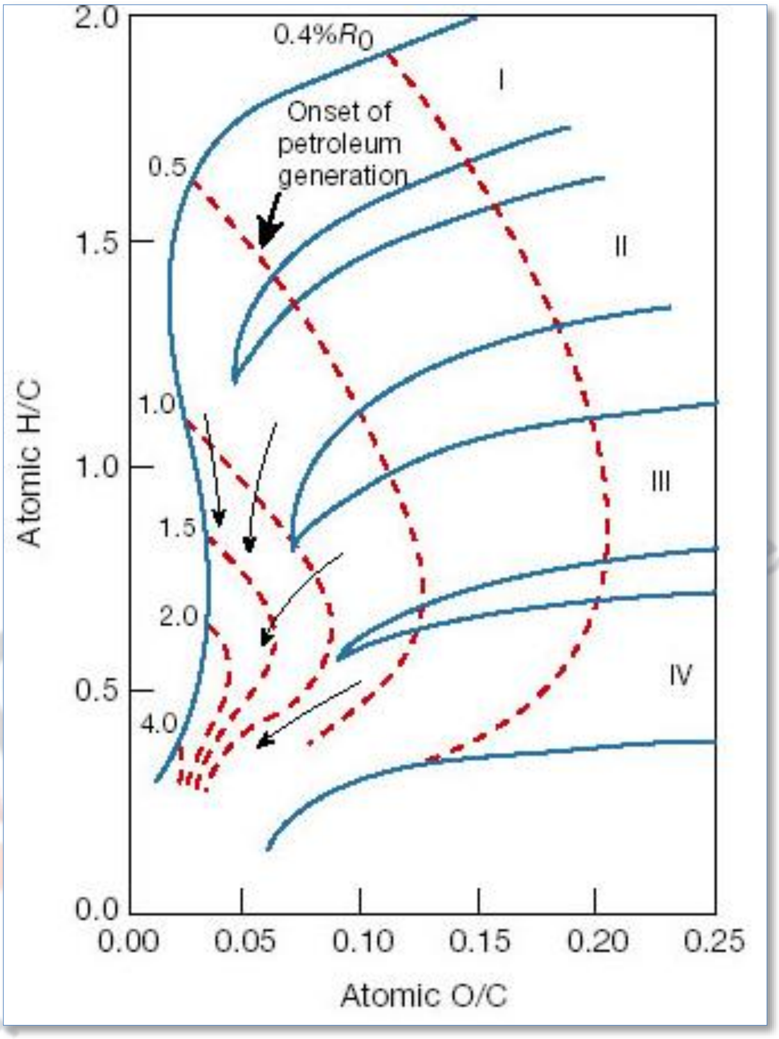


Fig. 13 Van Krevelen plot and kerogen maturation (modified after Hunt, 1997).

Figure 13 highlights some of the salient aspects of kerogen maturation which are mentioned below.

a) The reduction of H/C of kerogens indicates hydrocarbon generation. As the maximum reduction of H/C content is possible for type I kerogen, it forms most hydrocarbon.

b) The reduction of O/C of kerogensis associated with carbon dioxide formation. Type III and IV kerogens reduce their O/C content faster than their H/C content. These kerogens produce more carbon dioxide with very less or no oil.

c) Vitrinite reflectance values are superimposed in the figure to indicate the precise estimation of the oil window. Most oil is generated in the vitrinite reflectance range of 0.5 and 1.3. Most gas is formed at a slightly higher maturation range.

d) At higher temperature kerogen, composition merges and they are no more distinguishable into different types.

e) Vitirinte reflectance values more than 2 indicate inert kerogens, which are incapable to produce any oil.

6. Summary

Crude oil consists of a huge number of organic compounds belonging to alkanes, alkenes, cycloalkanes, aromatics and asphaltic compounds. Crude oil is a yellow to black color liquid with varied physical properties, which needs to be refined for any application. Based on its API value (the measure of its density) crude oil is divided into four types – extra heavy crude oil, heavy crude oil, medium crude oil and light crude oil. Thermal cracking of organic matters or kerogens produce crude oil. Kerogen is the precursor of all hydrocarbon compounds, which is divided into four types, Type I, Type II, Type III and Type IV. Type I and Type II generates most crude oil, while type II kerogen is known as gas generating kerogen. The Van Krevelen plot is a graphical plot of atomic H/C and O/C which demarcates the four types of kerogens along with the region of diagenesis, catagenesis and metagenesis.

Frequently Asked Questions-

Q1. What are the necessary conditions for the petroleum formation?

Ans: The necessary conditions for the formation of petroleum are a source rock with sufficient TOC (total organic carbon), an anoxic environment (to prevent oxidation of organic matters), the required temperature and depth and sufficient time.

Q2. What are the different states of petroleum?

Ans: Though in strict sense, petroleum is in liquid form but solid and gaseous forms also occur in nature. Solid forms include gibsonite, albertite, grahamite, tar sands, natural asphalt and oil sands. The liquid form is crude oil. Methane hydrates, swamp gas, coal bed methane, shale gas and natural gas forms in gaseous state.

Q3. How can you classify crude based on its API gravity?

Ans: Based on its API gravity crude may be divided into four types

i) Extra heavy crude – API<10^0
ii) Heavy crude – 10-22.3^0
iii) Medium crude –22.3-31.1^0
iv) Light crude – API>31.1^0

Q4. What are the different hydrocarbons present in petroleum?

Ans: The different hydrocarbons present in petroleum are alkanes, cycloalkanes, alkenes, aromatics and naptheno-aromatics.

Q5. What is oil window?

Ans: Oil generation in the initiates at a depth corresponding to a temperature of about 60°C and continues till 130°C for a Mesozoic source rock. This range of temperature and the depth interval is called as "oil window". This depth range may vary depending on the age of the source rock and the geothermal gradient.

Q6. What is Kerogen? What are the types of kerogen?

Ans: The naturally occurring solid, insoluble organic matter that occurs in source rocks and yield oil upon heating. Kerogen is the portion of naturally occurring organic matter that is non-extractable using organic solvent. Kerogen is of four types

i) Type I : algal kerogen
ii) Type II : herbaceous kerogen
iii) Type III : woody kerogen
iv) Type IV : oxidized kerogen

Multiple Choice Questions-

1. Which type of Kerogens do not produce hydrocarbon

(a) Type II
(b) Type III
(c) Type IV

Ans: c

2. Which is the best source rock

(a) Sandstone
(b) Black Shale
(c) Sparitic Limestone

Ans: b

3. Which products are formed at the metagenesis stage

(a) Heavy Oil and Gas
(b) Dry Gas and Graphite
(c) Medium and Light Oil and Gas

Ans: b

4. Which hydrocarbon add smell to liquid petroleum

(a) Alkane
(b) Cyclo-alkanes
(c) Aromatics

Ans: c

5. What is the API gravity of extra heavy crude oil

(a) $<10^0$
(b) $10\text{-}20^0$
(c) $20\text{-}30^0$

Ans: a

6. What is the range of oil window for a Mesozoic source rock

(a) 60-130 ^{0}C
(b) 100-200 ^{0}C
(c) 150-250 ^{0}C

Ans: a

7. Van Krevelen diagram is a plot of

(a) H/C and O/C
(b) O/H and C/H
(c) None of these

Ans: a

8. Which type of Kerogen is found in Lake Environment

(a) Type I
(b) Type II
(c) Type III

Ans: a

Suggested Readings:

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