**Tikrit University**

**The College of Petroleum Processes Engineering**

**Petroleum Systems Control Engineering Department**

# Properties of Petroleum & Natural Gas

**Third Class**

**Lecture 4**

**By**

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# Composition of Petroleum

Petroleum occurs in nature in all three possible states solid, liquid and gas. The liquid petroleum is usually colored from dark brown to bluish black or black, exhibiting sometimes bloom or fluorescence. The semi-solid or solid petroleum is well known by the name pitch, usually black in color. Such kind of deposits ate assumed to form after the evaporation or migration of lighter fractions. The gaseous deposits of petroleum are known as natural gas deposits, where sometimes gasolines are also accompanied. Gas from condensate reservoirs contain a good portion of lighter fractions of a boiling point upto 30° C. Associated reservoirs contain gas mainly in dissolved form in liquid petroleum.

Although the composition of petroleum depends not, very much on the origin of formation, but certainly change with the time of formation, storage and different stratas through which it migrated. It is a homogeneous mixture of various hydrocarbons of saturates and ring-structures. The average ultimate composition of petroleum is mainly given in terms of constituents of hydrocarbons, namely carbon and hydrogen as follows:

Carbon 84—86%

Hydrogen 11—14%

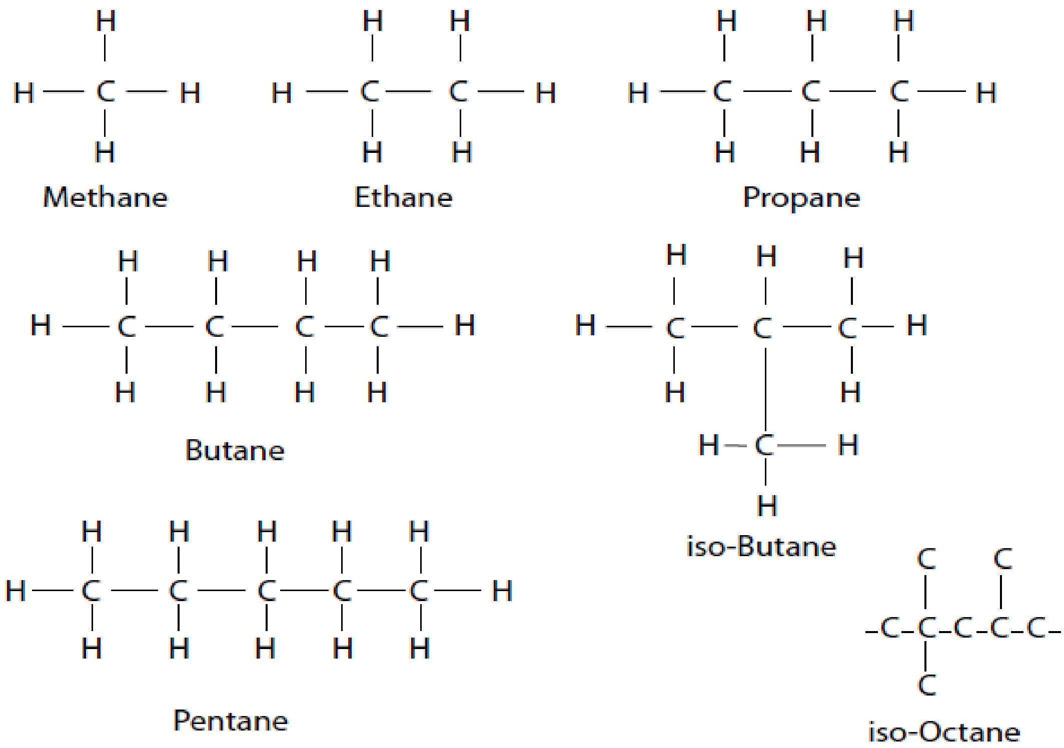
The other major elements of importance are sulfur, oxygen and nitrogen. These elements in hydrocarbons are usually treated as impurities because of their inherent properties like odor, color corrosiveness etc. Generally these three elements combined, do not exceed 5% on an average.

The bulk of petroleum is made up of hydrocarbons, of saturated compounds like paraffins, naphthenes and unsaturated cyclic compounds mainly aromatics.

The highest carbon atom present in the crude is C70. Further, except first few hydrocarbons, all other hydrocarbons exhibit isomerism. The general properties of these homologous series are discussed below :

## Paraffins

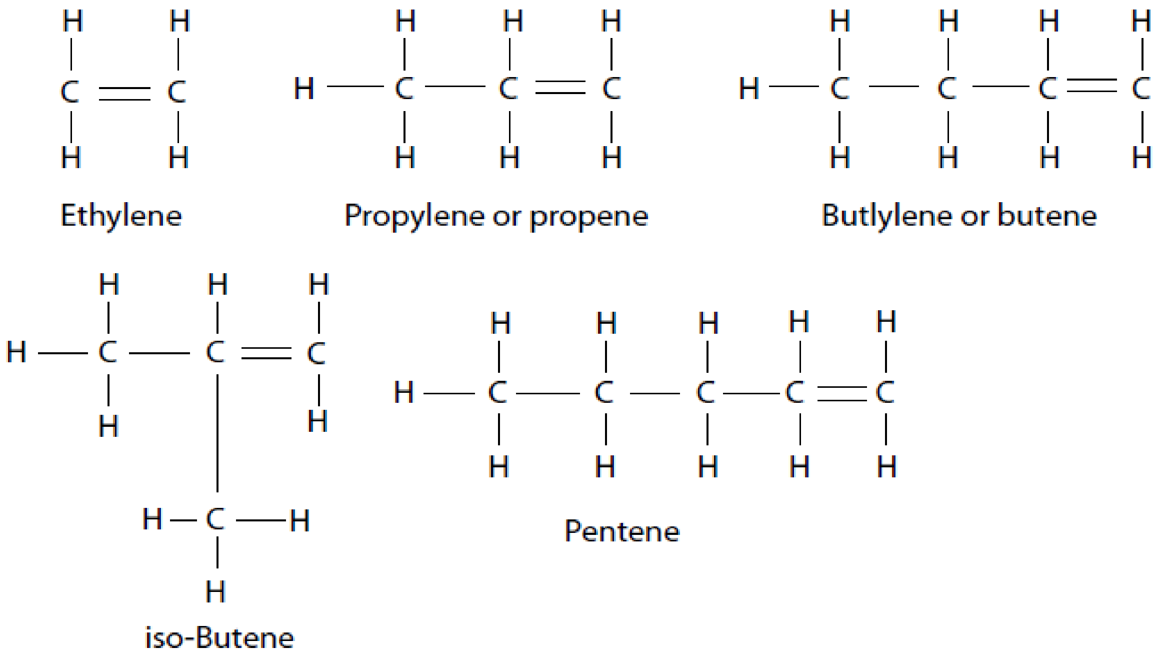
Paraffins refer to alkanes such as methane, ethane, propane, n and iso butane, n and iso pentane. These compounds are primarily obtained as a gas fraction from the crude distillation unit.




Paraffin Hydrocarbons

## Olefins

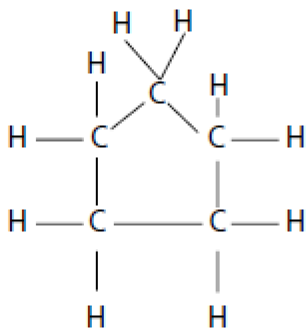
Alkenes such as ethylene, propylene and butylenes are highly chemically reactive.



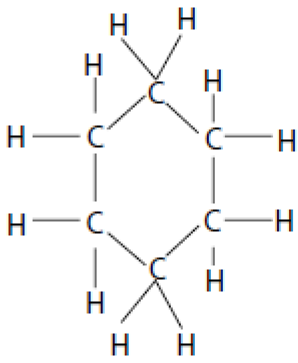

Olefin Hydrocarbons

## Naphthenes

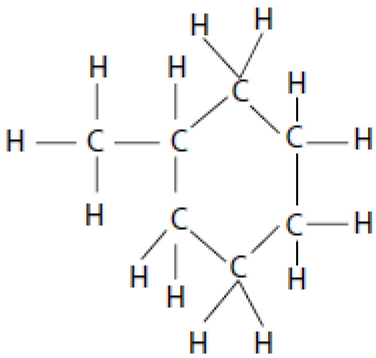
Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the crude oil. These compounds are not aromatic and hence do not contribute much to the octane number. Therefore, in the reforming reaction, these compounds are targeted to generate aromatics which have higher octane numbers than the naphthenes.



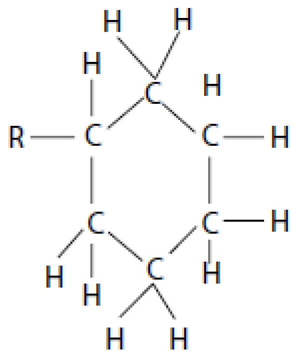
Cyclo-pentane



Cyclo-hexane



Methyl-cyclo-hexane

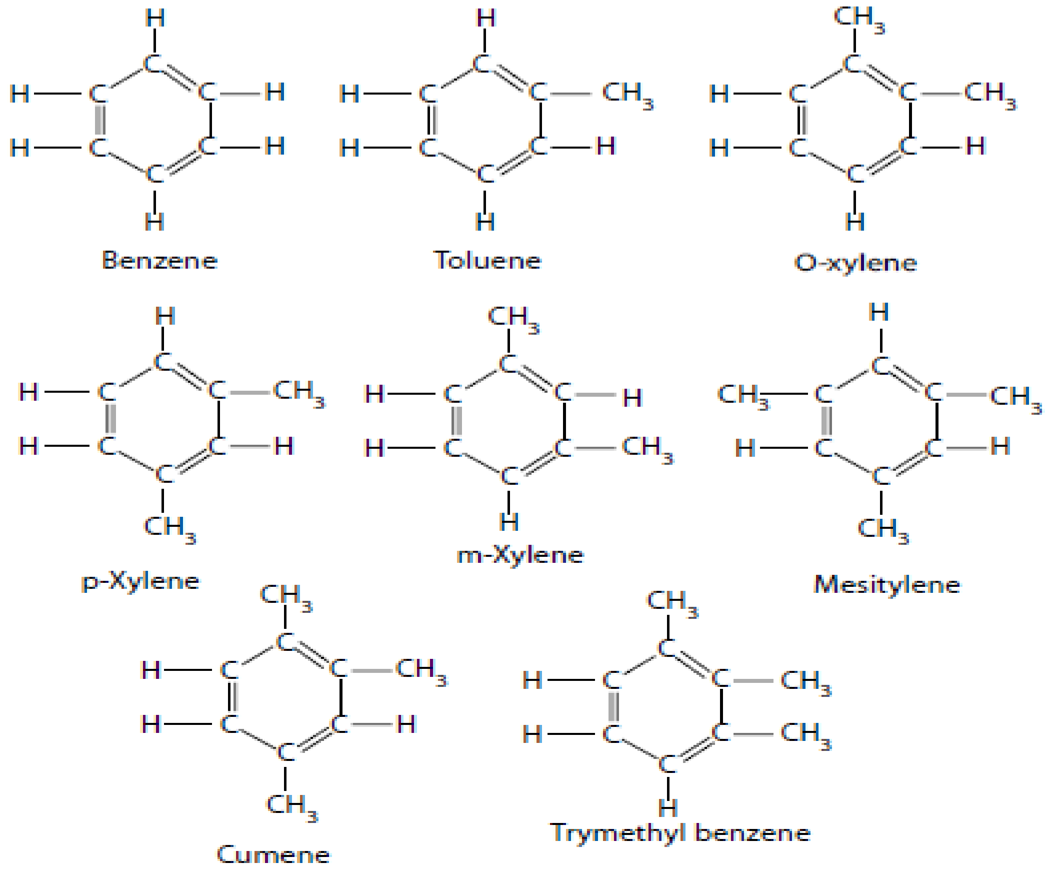


Alkyl sustituted cyclohexane
R is the alkyl radical methyl, ethyl, etc

Naphthene hydrocarbons

## Aromatics

Aromatics such as benzene, toluene o/m/p-xylene are also available in the crude oil. These contribute towards higher octane number products and the target is to maximize their quantity in a refinery process.




Aromatic hydrocarbons

## Organic Sulphur Compounds

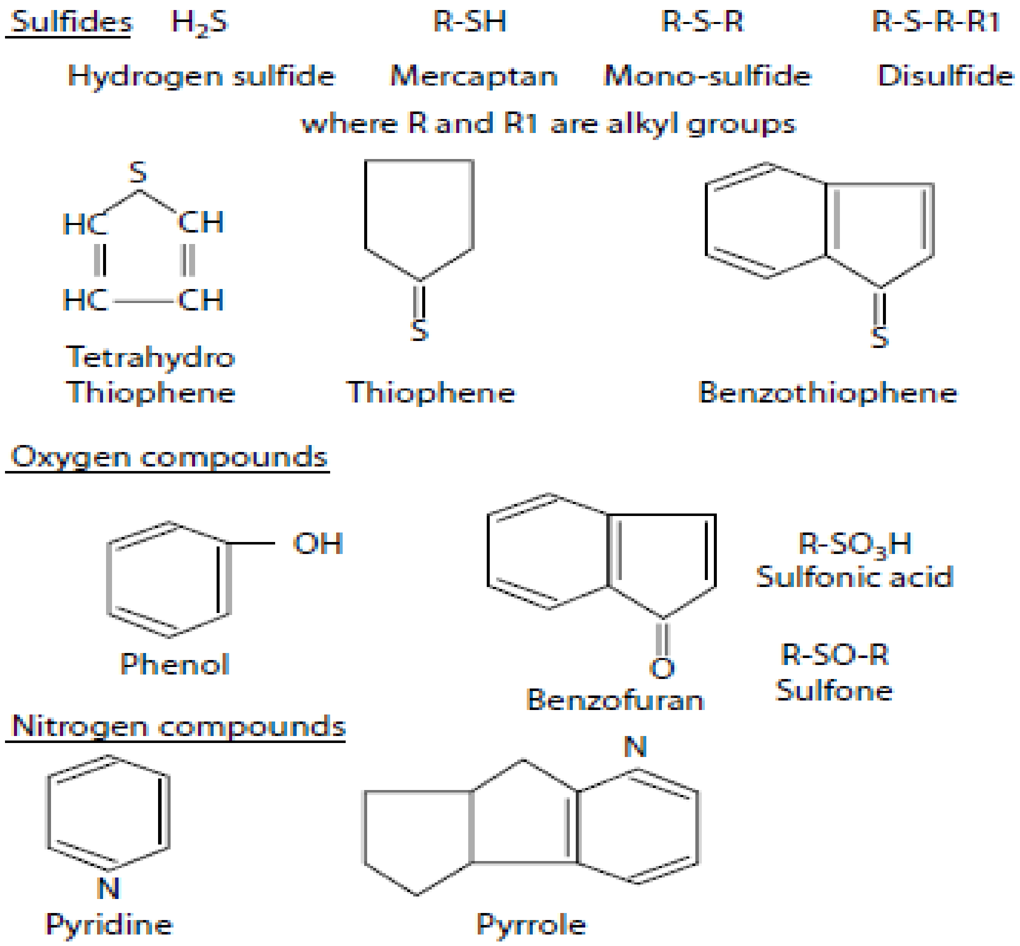
Not all compounds in the crude are hydrocarbons consisting of hydrogen and carbon only. Organic sulphur compounds such as thiophene, pyridine also exist in the crude oil. The basic difficulty of these organic sulphur compounds is the additional hydrogen requirements in the hydrotreaters to meet the euro III standards.

## Oxygen containing compounds

Crude oil may contain oxygen containing compounds, such as naphthenic acids, phenols, and cresols, which are responsible for corrosive activities. These compounds do not exist 2 % by weight in the crude oil. Oxygen also acts as a poison for many catalysts. This can be removed by catalytic hydrogenation. Excess oxygen compounds may even lead to explosion.

## Nitrogen containing compounds

Nitrogen compounds usually found in the heavier parts of the crude oil. These are responsible for colour and colour instability and poisoning of certain catalysts. Nitrogen in petroleum fuels causes the generation of oxides of nitrogen (NOx), which are also strong pollutants of the atmosphere. Nitrogen can be eliminated from petroleum products by catalytic hydrogenation. Like sulfur, nitrogen in the heavier parts of petroleum cannot be removed without severe cracking or hydrogenation reactions.



## Resins

Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Their molecular weights vary between 500 – 1500. These compounds also contain sulphur, nitrogen, oxygen, vanadium and nickel.

## Asphaltenes

Asphaltenes are polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffinic and naphthenic chains. A crude with high quantities of resins and asphaltenes (heavy crude) is usually targeted for coke production.

## Metallic compounds

Metallic compounds of vanadium, nickel, lead, arsenic, etc., are also found in crude oil. Vanadium and nickel are found in the form of organo-metallic compounds mostly in the heavier fractions of crude oil where the metal atoms are distributed within the compound in a complex form called porphyrins. Petroleum fuels containing these metallic compounds may damage the burners, lines, and walls of the combustion chambers.

# Classification of Crude Oil

Classification of crude oil refers to natural and type of crude oil (**type of hydrocarbons in crude oil**) by simplified tests. Four mainly methods are used

## A- Watson or UOP characterization factor (Kw):

Watson characterization factor (Kw) can be calculated from the following equation:

$$K_w = \frac{\sqrt[3]{MeABP}}{Sp.Gr\ @\ 60°F} \quad .... 1$$

Kw = Watson characterization factor

**MeABP** = mean average boiling point temperature in Rankin = **VABP - Δ**

**VABP** = volume average boiling point temperatures in °F.

VABP can be calculated as the average of the five boiling temperatures at 10, 30, 50, 70 and 90 percent distilled.

**Sp.Gr**. 60/60°F = Specific Gravity at 15°C (60 °F) = **density crude oil @ 60°F / density of water @ 60°F**

$$Sp.Gr\ @\ 60°F = \frac{141.5}{API+131.5} \quad .... 2$$

Crude oil classifications by Watson characterization factor as follows:

**1- Kw = 12.15 – 13 paraffinic (or light) based crude oil**

**2- Kw = 11.1 – 12.0 mixed (or intermediate) based crude oil**

**3- Kw = 10 – 11.0 naphthenic (asphaltic or heavy) based crude oil**

## B- (API gravity)

API = American Petroleum Institute

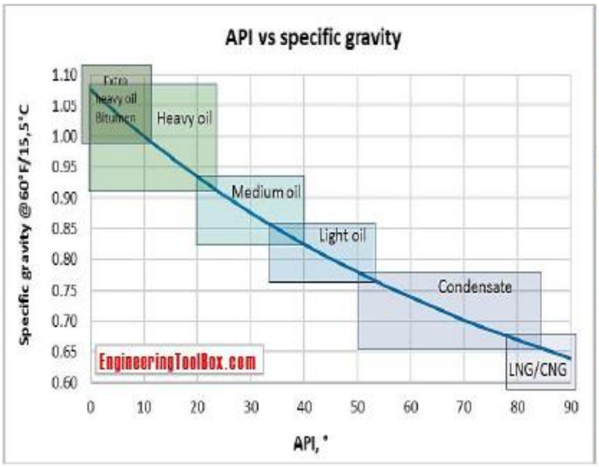
$$API = \frac{141.5}{Sp.Gr.@\ 60°F} - 131.5 \quad .... 3$$

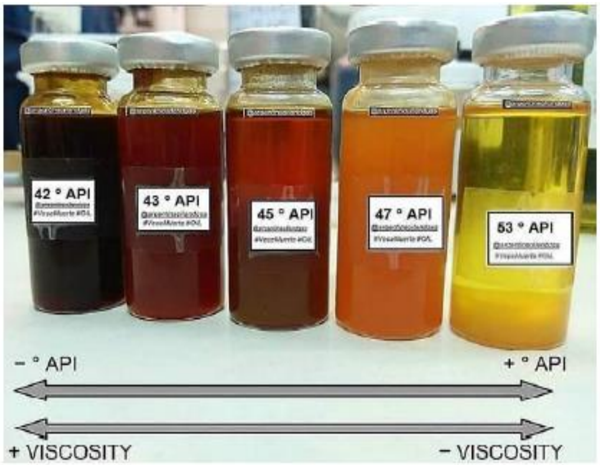
**At atmospheric (1 atm),** the crude oil classification will be as follows:

**1- API gravity > 40 paraffinic (or light) based crude oil**

**2- API gravity = 33 - 40 mixed (or intermediate) based crude oil**

**3- API gravity < 33 naphthenic (asphaltic or heavy) based crude oil**




## C- Correlation Index (C.I)

This method based on the percentages of various hydrocarbons types in the crude oil which are classified into paraffinic or aromatic according to following

$$C.I = 473.7\ SG\ at\ 60F - 456.8 + \frac{48680}{ABP\ °K} \quad ....4$$

ABP: average boiling point in Kelvin

The crude oil can be classified as follow as:

**1. C.I. = 0 (normal paraffinic based crude oil)**

**2. C.I = 0-15 (predominance of n-paraffinic crude oil)**

**3. C.I = 15 – 50 (paraffinic and aromatic mixture)**

**4. C.I > 50 (predominance of aromatic crude oil)**

**5. C.I = 100 benzene (Aromatic)**

## D- Classification by Viscosity-Gravity Constant

The viscosity gravity constant is of particular value in indicating a predominantly paraffinic or cyclic composition. **The lower the index number**, **the more paraffinic the stock**; for example, napthenic lubricating oil distillates have VGC = 0.876 while raffinate obtained by solvent distillation of lubricating oil distillate has VGC ~ 0.840

$$VGC = \frac{10\ Sp.Gr - 1.0752\ \log(v_{38} - 38)}{10 - \log(v - 38)} \quad ....5$$

**V** is the saybolt viscosity at 38° C (100°F). For oils so heavy that low-temperature viscosity is difficult to measure, an alternative formula has been proposed in which the **99°C (210°F) saybolt viscosity is used**.

$$VGC = \frac{Sp.Gr - 0.24 - 0.022\ \log(v_{99} - 35.5)}{0.755} \quad ....6$$

The Saybolt universal viscosity (SUS) is the time in seconds required for the flow of 60 ml of petroleum from a container, at a constant temperature, through a calibrated orifice.

**VGC:**

**1) 0.70-0.79 paraffinic hydrocarbon.**

**2) 0.80-0.90 naphthenic base.**

**3) 0.91-1.31 aromatic base.**

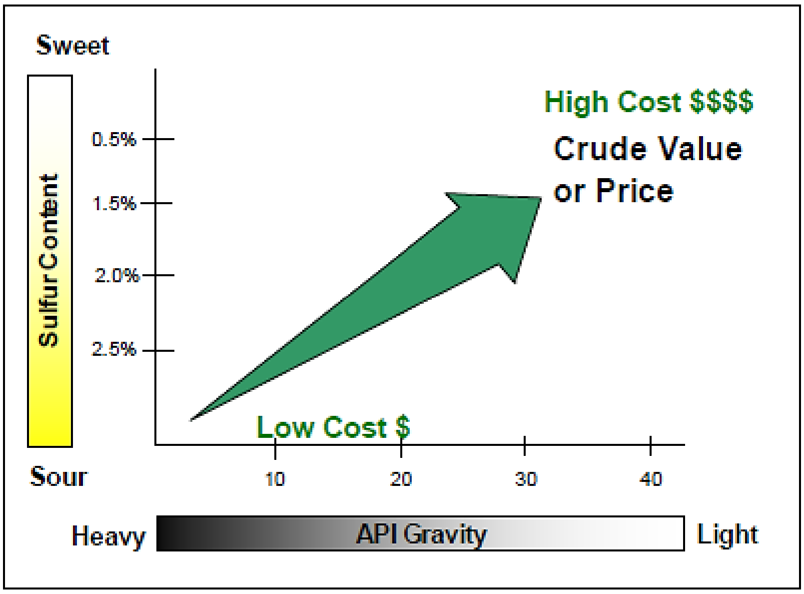
C varies for paraffinic hydrocarbons from 0.74 0.75, for naphthenic from 0.89 to 0.94, and for aromatics from0.95 to 1.13

## E - Sulfur Content

• If crude has **less than 0.5%** sulfur content, then it will be considered as **sweet crude oil.**

• **If crude has greater than 2.5% sulfur, then it will be sour crude oil.**

• **Crude with sulfur content between these two end points is called intermediate.**




## F- Technological Classification of Petroleum

According to technological classification, the oil can be classified as:

• **Low sulfur oil** containing not more than 0.5% of the sulfur, whereby the gasoline fraction contains less than 0.1% sulfur and diesel fraction less than 0.2%.

• **High sulfur oil** containing over 2% of sulfur.

• **Low paraffinic oil** containing less than 1.5% of paraffins. This type of oil can be used for production of jet and winter diesel fuels without deparaffinization.

• **Medium paraffinic oil** containing over 1.5% and fewer than 6% of paraffins. This type of oil can be used for production of jet and summer diesel fuels without deparaffinization.

• **High paraffinic oil** containing over 6% of paraffins. This type of oil can be used for production of diesel and jet fuels only after deparaffinization.