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Petroleum Refining and Petrochemical Processes

Crude oil: composition, classification;
Coal; Oil Shale; Tar Sand; Gas Hydrates

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Petroleum - Crude oil

Petroleum (L. *petroleum*, from Greek: Πέτρα (rock) + Latin: oleum (oil)) is a naturally occurring flammable liquid consisting of a **complex mixture of hydrocarbons of various molecular weights and other liquid organic compounds**, that are found in geologic formations beneath the Earth's surface.

The name Petroleum covers both naturally occurring unprocessed crude oils and petroleum products that are made up of refined crude oil.

A **fossil fuel**, it is formed when large quantities of dead organisms, usually zooplankton and algae, are buried underneath sedimentary rock and undergo intense heat and pressure.

Petroleum is recovered mostly through oil drilling. This comes after the studies of structural geology (at the reservoir scale), sedimentary basin analysis, reservoir characterization (mainly in terms of porosity and permeable structures).

It is refined and separated, most easily by boiling point, into a large number of consumer products, from petrol (or gasoline) and kerosene to asphalt and chemical reagents used to make plastics and pharmaceuticals.

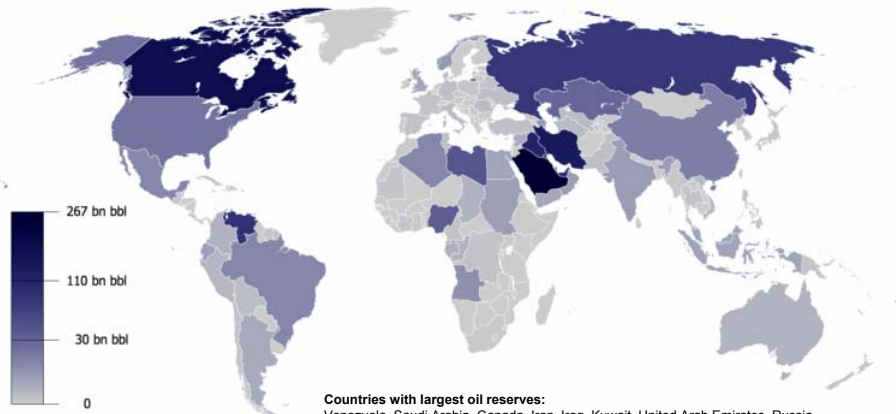
Petroleum is used in manufacturing a wide variety of materials, and it is estimated that the world consumes about 88 million barrels each day.



Pumpjack pumping an oil well

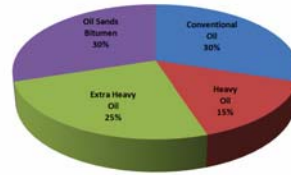
Petroleum - Crude oil

Proven Oil Reserves
[CIA Factbook, 2009]



Countries with largest oil reserves:
Venezuela, Saudi Arabia, Canada, Iran, Iraq, Kuwait, United Arab Emirates, Russia,
Kazakhstan, Libya, Nigeria, Qatar, China, United States, Angola, Algeria, Brazil

Total World Oil Reserves



Composition of Crude Oils

Crude oil (petroleum) is a naturally occurring brown to black flammable liquid.

Crude oils are principally found in oil reservoirs associated with sedimentary rocks beneath the earth's surface. Although exactly how crude oils originated is not established, it is generally agreed that crude oils derived from marine animal and plant debris subjected to high temperatures and pressures. It is also suspected that the transformation may have been catalyzed by rock constituents.

Regardless of their origins, all crude oils are mainly constituted of **hydrocarbons** mixed with variable amounts of **sulfur, nitrogen, and oxygen compounds**.

Metals in the forms of **inorganic salts** or **organometallic compounds** are present in the crude mixture in trace amounts.

The ratio of the different constituents in crude oils, however, vary appreciably from one reservoir to another.

Normally, crude oils are not used directly as fuels or as feedstocks for the production of chemicals. This is due to the complex nature of the crude oil mixture and the presence of some impurities that are corrosive or poisonous to processing catalysts.

Crude oils are refined to separate the mixture into simpler fractions that can be used as fuels, lubricants, or as intermediate feedstock to the petrochemical industries.

A general knowledge of this composite mixture is essential for establishing a processing strategy.

Petroleum - Crude oil

Composition

The hydrocarbons in crude oil are mostly **alkanes (paraffins)**, **cycloalkanes (naphthenes)** and **various aromatic hydrocarbons** while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium.

The exact molecular composition varies widely from formation to formation but the proportion of chemical elements vary over fairly narrow limits as follows:

Composition by weight

| Element | Percent range |
|---------|---------------|
|---------|---------------|

| | |
|----------|--------------|
| Carbon | 83 to 87% |
| Hydrogen | 10 to 14% |
| Nitrogen | 0.1 to 2% |
| Oxygen | 0.05 to 1.5% |
| Sulfur | 0.05 to 6.0% |
| Metals | < 0.1% |

Petroleum - Crude oil

Composition

Four different types of hydrocarbon molecules appear in crude oil.

The relative percentage of each varies from oil to oil, determining the properties of each oil.

Composition by weight

| Hydrocarbon | Average | Range |
|-------------|---------|-----------|
| Paraffins | 30% | 15 to 60% |
| Naphthenes | 49% | 30 to 60% |
| Aromatics | 15% | 3 to 30% |
| Asphaltics | 6% | remainder |

Petroleum is used mostly, by volume, for producing **fuel oil** and **petrol**, both important "primary energy" sources. 84 vol. % of the hydrocarbons present in petroleum is converted into energy-rich fuels (petroleum-based fuels), including **petrol, diesel, jet, heating, and other fuel oils, and liquefied petroleum gas.**

The lighter grades of crude oil produce the best yields of these products, but as the world's reserves of light and medium oil are depleted, oil refineries are increasingly having to process heavy oil and bitumen, and use more complex and expensive methods to produce the products required. Because heavier crude oils have too much carbon and not enough hydrogen, these processes generally involve removing carbon from or adding hydrogen to the molecules, and using fluid catalytic cracking to convert the longer, more complex molecules in the oil to the shorter, simpler ones in the fuels.

Petroleum - Crude oil

Composition

In its strictest sense, petroleum includes only crude oil, but in common usage it includes all liquid, gaseous, and solid hydrocarbons. Under surface pressure and temperature conditions, lighter hydrocarbons methane, ethane, propane and butane occur as gases, while pentane and heavier ones are in the form of liquids or solids. However, in an underground oil reservoir the proportions of gas, liquid, and solid depend on subsurface conditions and on the phase diagram of the petroleum mixture.

An oil well produces predominantly crude oil, with some natural gas dissolved in it. Because the pressure is lower at the surface than underground, some of the gas will come out of solution and be recovered (or burned) as associated gas or solution gas.

A gas well produces predominantly natural gas. However, because the underground temperature and pressure are higher than at the surface, the gas may contain heavier hydrocarbons such as pentane, hexane, and heptane in the gaseous state. At surface conditions these will condense out of the gas to form natural gas condensate, often shortened to condensate. Condensate resembles petrol in appearance and is similar in composition to some volatile light crude oils.

The proportion of light hydrocarbons in the petroleum mixture varies greatly among different oil fields, ranging from as much as 97 percent by weight in the lighter oils to as little as 50 percent in the heavier oils and bitumens.



Natural gas flares in the Zubair oil field in southern Iraq /

The World Bank: Global **gas flaring** has remained largely stable over the past twelve years, in the range of 150 to 170 billion cubic meters. Flaring adds about 400 million tons of carbon dioxide into the atmosphere each year.

Composition of Crude Oils

The crude oil mixture is composed of the following groups:

1. **Hydrocarbon compounds** (compounds made of carbon and hydrogen).
2. **Non-hydrocarbon compounds.**
3. **Organometallic compounds and inorganic salts (metallic compounds).**

Hydrocarbon Compounds

The principal constituents of most crude oils are hydrocarbon compounds.

All hydrocarbon classes are present in the crude mixture, except alkenes and alkynes.

This may indicate that crude oils originated under a reducing atmosphere.

Composition of Crude Oils

Alkanes (Paraffins)

Alkanes are saturated hydrocarbons having the general formula C_nH_{2n+2} .

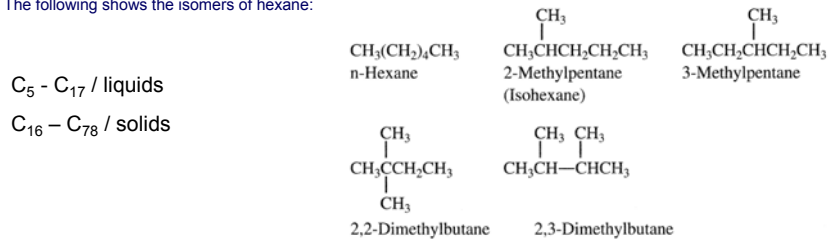
The simplest alkane, methane (CH_4), is the principal constituent of natural gas.

Methane, ethane, propane, and butane are gaseous hydrocarbons at ambient temperatures and atmospheric pressure. They are usually found associated with crude oils in a dissolved state.

Normal alkanes (n-alkanes, n-paraffins) are straight-chain hydrocarbons having no branches. Branched alkanes are saturated hydrocarbons with an alkyl substituent or a side branch from the main chain.

A branched alkane with the same number of carbons and hydrogens as an n-alkane is called an isomer.

For example, butane (C_4H_{10}) has two isomers, n-butane and 2-methyl propane (isobutane). As the molecular weight of the hydrocarbon increases, the number of isomers also increases. Pentane (C_5H_{12}) has three isomers; hexane (C_6H_{14}) has five. The following shows the isomers of hexane:



$C_5 - C_{17}$ / liquids

$C_{16} - C_{78}$ / solids

Crude oils contain many short, medium, and long-chain normal and branched paraffins.

A naphtha fraction (obtained as a light liquid stream from crude fractionation) with a narrow boiling range may contain a limited but still large number of isomers.

Petroleum

Composition - Chemistry

Petroleum is a mixture of a very large number of different hydrocarbons; the most commonly found molecules are alkanes (linear or branched), cycloalkanes, aromatic hydrocarbons, or more complicated chemicals like asphaltenes.

Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties, like color and viscosity.

ALKANES / PARAFFINS

The **alkanes (paraffins)**, are saturated hydrocarbons with straight (normal) or branched (iso) chains which contain only carbon and hydrogen and have the general formula C_nH_{2n+2} .

They generally have from 5 to 40 carbon atoms per molecule, although trace amounts of shorter or longer molecules may be present in the mixture.

- the alkanes from pentane (C_5H_{12}) to octane (C_8H_{18}) are refined into **petrol**, the ones from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) into diesel fuel, kerosene and jet fuel.

- alkanes with more than 16 carbon atoms can be refined into **fuel oil** and **lubricating oil**.

- at the heavier end of the range, paraffin wax is an alkane with approximately 25 carbon atoms, while asphalt has 35 and up, although these are usually cracked by modern refineries into more valuable products.

- the shortest molecules, those with four or fewer carbon atoms, are in a gaseous state at room temperature. They are the petroleum gases.

Depending on demand and the cost of recovery, these gases are either flared off, sold as liquified petroleum gas under pressure, or used to power the refinery's own burners.

During the winter, butane (C_4H_{10}), is blended into the petrol pool at high rates, because its high vapor pressure assists with cold starts.

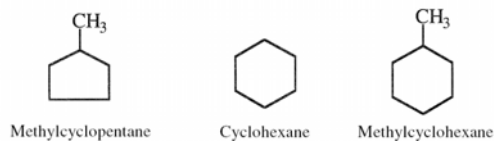
Composition of Crude Oils

Cycloparaffins (Naphthenes)

Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils. Their ratio, however, depends on the crude type. The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds.

They are normally present in the light and the heavy naphtha fractions.

Cyclohexanes, substituted cyclopentanes, and substituted cyclohexanes are important precursors for aromatic hydrocarbons.



The examples shown here are for three naphthenes of special importance.

If a naphtha fraction contains these compounds, the first two can be converted to benzene, and the last compound can dehydrogenate to toluene during processing. Dimethylcyclohexanes are also important precursors for xylenes (see "Xylenes" later in this section). Heavier petroleum fractions such as kerosine and gas oil may contain two or more cyclohexane rings fused through two vicinal carbons.

Petroleum

Composition - Chemistry

CYCLOALKANES / NAPHTHENES

The **cycloalkanes (naphthenes)**, are saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula C_nH_{2n} .

Cycloalkanes have similar properties to alkanes but have higher boiling points.

Composition of Crude Oils

Aromatic Compounds

Lower members of aromatic compounds are present in small amounts in crude oils and light petroleum fractions.

The simplest mononuclear aromatic compound is benzene (C_6H_6). Toluene (C_7H_8) and xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oils.

Benzene, toluene, and xylenes (BTX) are important petrochemical intermediates as well as valuable gasoline components.

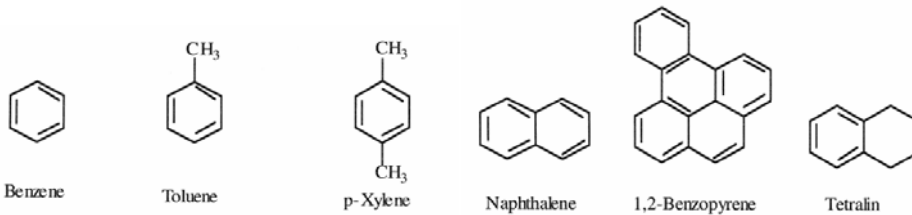
Separating BTX aromatics from crude oil distillates is not feasible because they are present in low concentrations. Enriching a naphtha fraction with these aromatics is possible through a catalytic reforming process.

Binuclear aromatic hydrocarbons are found in heavier fractions than naphtha.

Trinuclear and polynuclear aromatic hydrocarbons, in combination with heterocyclic compounds, are major constituents of heavy crudes and crude residues.

Asphaltenes are a complex mixture of aromatic and heterocyclic compounds.

The following are representative examples of some aromatic compounds found in crude oils:



Petroleum

Composition - Chemistry

AROMATIC HYDROCARBONS

The **aromatic hydrocarbons** are unsaturated hydrocarbons which have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula C_nH_n .

They tend to burn with a sooty flame, and many have a sweet aroma. Some are carcinogenic.

Composition of Crude Oils

Sulfur Compounds

Sulfur in crude oils is mainly present in the form of organosulfur compounds.

Hydrogen sulfide is the only important inorganic sulfur compound found in crude oil.

Its presence, however, is harmful because of its corrosive nature.

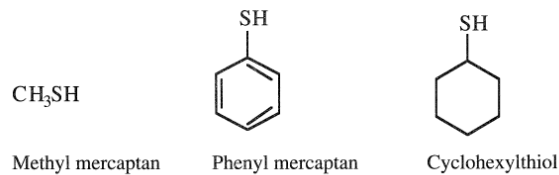
Organosulfur compounds may generally be classified as acidic and non-acidic.

Acidic sulfur compounds are the thiols (mercaptans).

Thiophene, sulfides, and disulfides are examples of non-acidic sulfur compounds found in crude fractions.

Extensive research has been carried out to identify some sulfur compounds in a narrow light petroleum fraction. Examples (1) of some sulfur compounds from the two types are:

Acidic Sulfur Compounds

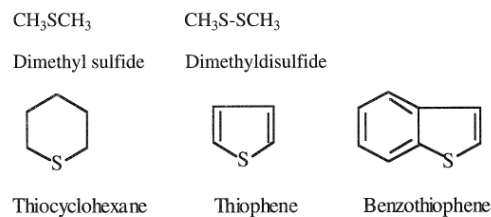


Composition of Crude Oils

Sulfur Compounds

Examples (2) of some sulfur compounds from the two types are:

Non-acidic Sulfur Compounds



Sour crudes contain a high percentage of hydrogen sulfide.

Because many organic sulfur compounds are not thermally stable, hydrogen sulfide is often produced during crude processing. High-sulfur crudes are less desirable because treating the different refinery streams for acidic hydrogen sulfide increases production costs.

Most sulfur compounds can be removed from petroleum streams through hydrotreatment processes, where hydrogen sulfide is produced and the corresponding hydrocarbon released. Hydrogen sulfide is then absorbed in a suitable absorbent and recovered as sulfur.

Composition of Crude Oils

Nitrogen Compounds

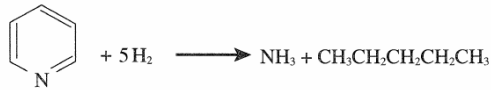
Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C_5H_5N) and pyrrole (C_4H_5N), or in a complex structure as in porphyrin. The nitrogen content in most crudes is very low and does not exceed 0.1 wt%. In some heavy crudes, however, the nitrogen content may reach up to 0.9 wt %.

Nitrogen compounds are more thermally stable than sulfur compounds and accordingly are concentrated in heavier petroleum fractions and residues.

Light petroleum streams may contain trace amounts of nitrogen compounds, which should be removed because they poison many processing catalysts.

During hydrotreatment of petroleum fractions, nitrogen compounds are hydrodenitrogenated to ammonia and the corresponding hydrocarbon.

For example, pyridine is denitrogenated to ammonia and pentane:



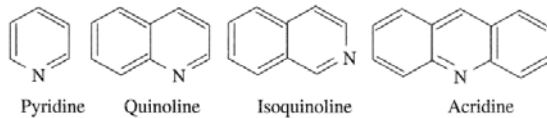
Composition of Crude Oils

Nitrogen Compounds

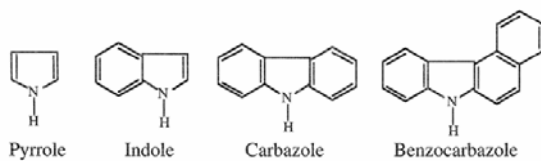
Nitrogen compounds in crudes may generally be classified into basic and non-basic categories. Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic compounds have a pyrrole structure.

Both pyridine and pyrrole are stable compounds due to their aromatic nature.

Basic Nitrogen Compounds



Non-Basic Nitrogen Compounds



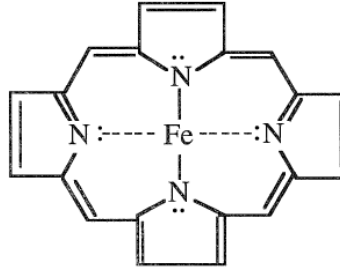
Composition of Crude Oils

Porphyrins are non-basic nitrogen compounds.

The porphyrin ring system is composed of four pyrrole rings joined by =CH- groups.

The entire ring system is aromatic. Many metal ions can replace the pyrrole hydrogens and form chelates. The chelate is planar around the metal ion and resonance results in four equivalent bonds from the nitrogen atoms to the metal.

Almost all crude oils and bitumens contain detectable amounts of vanadyl and nickel porphyrins. The following shows a porphyrin structure:



Composition of Crude Oils

Oxygen Compounds

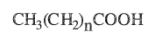
Oxygen compounds in crude oils are more complex than the sulfur types. However, their presence in petroleum streams is not poisonous to processing catalysts.

Many of the oxygen compounds found in crude oils are weakly acidic. They are carboxylic acids, cresylic acid, phenol, and naphthenic acid. Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain.

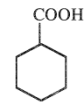
Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solutions. The total acid content of most crudes is generally low, but may reach as much as 3%, as in some California crudes.

Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds. They are of no commercial value.

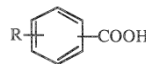
Acidic Oxygen Compounds



An aliphatic carboxylic acid



Cyclohexane carboxylic acid



Aromatic acids



Phenol



Cresylic acid

Non-Acidic Oxygen Compounds



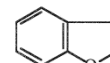
Esters



Furan



Amides



Benzofuran



Ketone

Composition of Crude Oils

Metallic Compounds

Many metals occur in crude oils.

Some of the more abundant are sodium (Na), calcium (Ca), magnesium (Mg), aluminium (Al), iron (Fe), vanadium (V), and nickel (Ni).

They are present either as **inorganic salts**, such as sodium and magnesium chlorides, or in the form of **organometallic compounds**, such as those of Ni and V (as in porphyrins).

Calcium and magnesium can form salts or soaps with carboxylic acids. These compounds act as emulsifiers, and their presence is undesirable.

Although metals in crudes are found in trace amounts, their presence is harmful and should be removed. When crude oil is processed, sodium and magnesium chlorides produce hydrochloric acid, which is very corrosive.

Desalting crude oils is a necessary step to reduce these salts.

Vanadium and nickel are poisons to many catalysts and should be reduced to very low levels. Most of the vanadium and nickel compounds are concentrated in the heavy residues.

Solvent extraction processes are used to reduce the concentration of heavy metals in petroleum residues.

CRUDE OIL CLASSIFICATION

Appreciable property differences appear between crude oils as a result of the variable ratios of the crude oil components. For a refiner dealing with crudes of different origins, a simple criterion may be established to group crudes with similar characteristics.

Crude oils can be arbitrarily classified into three or four groups depending on the relative ratio of the hydrocarbon classes that predominates in the mixture.

The following describes three types of crudes:

1. **Paraffinic** - the ratio of paraffinic hydrocarbons is high compared to aromatics and naphthenes.
2. **Naphthenic** - the ratios of naphthenic and aromatic hydrocarbons are relatively higher than in paraffinic crudes.
3. **Asphaltic** - contain relatively a large amount of polynuclear aromatics, a high asphaltene content, and relatively less paraffins than paraffinic crudes.

General characteristics

- Content of impurities: water, sediment, salts, metals, nitrogen
- Sulfur: 0.1 – 0.5 wt.% sweet / 0.5 – 0.8 wt.% semi-sweet / 0.8 – 5 wt.% sour
- Density: 38 – 45 °API light / 28 – 38 °API medium / 12 – 28 °API heavy

Properties of crude oils vary considerably according to their types.

Table: the analyses of some crudes from different origins.

| Typical analysis of some crude oils | | | | |
|-------------------------------------|----------------------|------------------|---------------|-----------------|
| | Arab Extra Light* | Alameen Egypt | Arab Heavy | Bakr-9 Egypt |
| Gravity, °API | 38.5 | 33.4 | 28.0 | 20.9 |
| Carbon residue (wt %) | 2.0 | 5.1 | 6.8 | 11.7 |
| Sulfur content (wt %) | 1.1 | 0.86 | 2.8 | 3.8 |
| Nitrogen content (wt %) | 0.04 | 0.12 | 0.15 | — |
| Ash content (wt %) | 0.002 | 0.004 | 0.012 | 0.04 |
| Iron (ppm) | 0.4 | 0.0 | 1.0 | — |
| Nickel (ppm) | 0.6 | 0.0 | 9.0 | 108 |
| Vanadium (ppm) | 2.2 | 15 | 40.0 | 150 |
| Pour point (°F) | ≈Zero | 35 | -11.0 | 55 |
| Paraffin wax content (wt %) | — | 3.3 | — | — |

* Ali, M. F et al., *Hydrocarbon Processing*, Vol. 64, No. 2, 1985 p. 83.

PROPERTIES OF CRUDE OILS

Crude oils differ appreciably in their properties according to origin and the ratio of the different components in the mixture.

Lighter crudes generally yield more valuable light and middle distillates and are sold at higher prices. Crudes containing a high percent of impurities, such as sulfur compounds, are less desirable than low-sulfur crudes because of their corrosivity and the extra treating cost.

Corrosivity of crude oils is a function of many parameters among which are the type of sulfur compounds and their decomposition temperatures, the total acid number, the type of carboxylic and naphthenic acids in the crude and their decomposition temperatures. It was found that naphthenic acids begin to decompose at 600 °F. Refinery experience has shown that above 750 °F there is no naphthenic acid corrosion.

For a refiner, it is necessary to establish certain criteria to relate one crude to another to be able to assess crude quality and choose the best processing scheme.

The following are some of the important tests used to determine the properties of crude oils.

Density, Specific Gravity and API Gravity

Density is defined as the mass of unit volume of a material at a specific temperature.

A more useful unit used by the petroleum industry is specific gravity, which is the ratio of the weight of a given volume of a material to the weight of the same volume of water measured at the same temperature.

Specific gravity is used to calculate the mass of crude oils and its products.

Usually, crude oils and their liquid products are first measured on a volume basis, then changed to the corresponding masses using the specific gravity.

The API (American Petroleum Institute) gravity is another way to express the relative masses of crude oils. The API gravity could be calculated mathematically using the following equation:

$$^{\circ}\text{API} = \frac{141.5}{\text{Sp.gr. } 60/60^{\circ}} - 131.5$$

A low API gravity indicates a heavier crude oil or a petroleum product, while a higher API gravity means a lighter crude or product.

Specific gravities of crude oils roughly range from 0.82 for lighter crudes to over 1.0 for heavier crudes (41 - 10 °API scale).

Salt Content

The salt content expressed in milligrams of sodium chloride per liter oil (or in pounds/barrel) indicates the amount of salt dissolved in water. Water in crudes is mainly present in an emulsified form. A high salt content in a crude oil presents serious corrosion problems during the refining process. In addition, high salt content is a major cause of plugging heat exchangers and heater pipes. A salt content higher than 10 lb/1,000 barrels (expressed as NaCl) requires desalting.

Sulfur Content

Pour Point

The pour point of a crude oil or product is the lowest temperature at which an oil is observed to flow under the conditions of the test. Pour point data indicates the amount of long-chain paraffins (petroleum wax) found in a crude oil. Paraffinic crudes usually have higher wax content than other crude types. Handling and transporting crude oils and heavy fuels is difficult at temperatures below their pour points. Often, chemical additives known as pour point depressants are used to improve the flow properties of the fuel.

Long-chain n-paraffins ranging from 16–60 carbon atoms in particular, are responsible for near-ambient temperature precipitation.

In middle distillates, less than 1% wax can be sufficient to cause solidification of the fuel.

Ash Content

This test indicates the amount of metallic constituents in a crude oil.

The ash left after completely burning an oil sample usually consists of stable metallic salts, metal oxides, and silicon oxide. The ash could be further analyzed for individual elements using spectroscopic techniques.

COAL, OIL SHALE, TAR SAND, GAS HYDRATES - alternative energy and chemical sources

Coal, oil shale, and tar sand are carbonaceous materials that can serve as future energy and chemical sources when oil and gas are consumed.

The H/C ratio of these materials is lower than in most crude oils. As solids or semi-solids, they are not easy to handle or to use as fuels, compared to crude oils. In addition, most of these materials have high sulfur and/or nitrogen contents, which require extensive processing. Changing these materials into hydrocarbon liquids or gaseous fuels is possible but expensive.

COAL

Coal is a natural combustible rock composed of an organic heterogeneous substance contaminated with variable amounts of inorganic compounds. Most coal reserves are concentrated in North America, Europe, and China.

Coal is classified into different ranks according to the degree of chemical change that occurred during the decomposition of plant remains in the prehistoric period. In general, coals with a high heating value and a high fixed carbon content are considered to have been subjected to more severe changes than those with lower heating values and fixed carbon contents. For example, peat, which is considered a young coal, has a low fixed carbon content and a low heating value.

Important coal ranks are anthracite (which has been subjected to the most chemical change and is mostly carbon), bituminous coal, sub-bituminous coal, and lignite.

During the late seventies and early eighties, when oil prices rose after the 1973 war, extensive research was done to change coal to liquid hydrocarbons. However, coal-derived hydrocarbons were more expensive than crude oils.

Another way to use coal is through gasification to a fuel gas mixture of CO and H₂ (medium Btu gas).

This gas mixture could be used as a fuel or as a synthesis gas mixture for the production of fuels and chemicals via a Fischer Tropsch synthesis route. This process is operative in South Africa for the production of hydrocarbon fuels.

Typical element analysis of some coals compared with a crude oil²³

| | Weight % | | | | | H/C mol ratio |
|-----------------|----------|------|-----|-----|------|---------------|
| | C | H | S | N | O | |
| Crude oil | 84.6 | 12.8 | 1.5 | 0.4 | 0.5 | 1.82 |
| Peat | 56.8 | 5.6 | 0.3 | 2.7 | 34.6 | 1.18 |
| Lignite | 68.8 | 4.9 | 0.7 | 1.1 | 24.5 | 0.86 |
| Bituminous Coal | 81.8 | 5.6 | 1.5 | 1.4 | 9.7 | 0.82 |
| Anthracite | 91.7 | 3.5 | — | — | 2.7 | 0.46 |

OIL SHALE

Oil shale is a low-permeable rock made of inorganic material interspersed with a high-molecular weight organic substance called "Kerogen." Heating the shale rock produces an oily substance with a complex structure.

The composition of oil shales differs greatly from one shale to another. For example, the amount of oil obtained from one ton of eastern U.S. shale deposit is only 10 gallons, compared to 30 gallons from western U.S. shale deposits.

Retorting is a process used to convert the shale to a high molecular weight oily material. In this process, crushed shale is heated to high temperatures to pyrolyze Kerogen. The product oil is a viscous, high molecular weight material.

Further processing is required to change the oil into a liquid fuel.

Major obstacles to large-scale production are the disposal of the spent shale and the vast earth-moving operations.

Typical analysis of shale oil

| Test | Result |
|------------------------|--------|
| Gravity | 19.7 |
| Nitrogen, wt % | 2.18 |
| Conradson Carbon, wt % | 4.5 |
| Sulfur, wt % | 0.74 |
| Ash, wt % | 0.06 |

TAR SAND

Tar sands (oil sands) are large deposits of sand saturated with bitumen and water. Tar sand deposits are commonly found at or near the earth's surface entrapped in large sedimentary basins. Large accumulations of tar sand deposits are few.

About 98% of all world tar sand is found in seven large tar deposits.

The oil sands resources in Western Canada sedimentary basin is the largest in the world. In 1997, it produced 99% of Canada's crude oil. It is estimated to hold 1.7–2.5 trillion barrels of bitumen in place. This makes it one of the largest hydrocarbon deposits in the world.

Tar sand is difficult to handle. During summer, it is soft and sticky, and during the winter it changes to a hard, solid material. Recovering the bitumen is not easy, and the deposits are either strip mined if they are near the surface, or recovered in situ if they are in deeper beds. The bitumen could be extracted by using hot water and steam and adding some alkali to disperse it. The produced bitumen is a very thick material having a density of approximately 1.05 g/cm³. It is then subjected to a cracking process to produce distillate fuels and coke. The distillates are hydro-treated to saturate olefinic components.

GAS HYDRATES

Gas hydrates are an ice-like material which is constituted of methane molecules encaged in a cluster of water molecules and held together by hydrogen bonds.

This material occurs in large underground deposits found beneath the ocean floor on continental margins and in places north of the arctic circle such as Siberia.

It is estimated that gas hydrate deposits contain twice as much carbon as all other fossil fuels on earth.

This source, if proven feasible for recovery, could be a future energy as well as chemical source for petrochemicals.

Due to its physical nature (a solid material only under high pressure and low temperature), it cannot be processed by conventional methods used for natural gas and crude oils.

One approach is by dissociating this cluster into methane and water by injecting a warmer fluid such as sea water. Another approach is by drilling into the deposit.

This reduces the pressure and frees methane from water. However, the environmental effects of such drilling must still be evaluated.

Classification

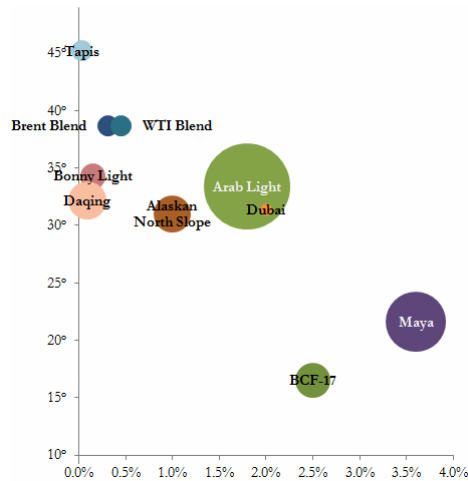
The [petroleum industry](#) generally classifies crude oil by the geographic location it is produced in (e.g. [West Texas Intermediate](#), [Brent](#), or [Oman](#)), its [API gravity](#) (an oil industry measure of density), and its sulfur content.

Crude oil may be considered [light](#) if it has low density or [heavy](#) if it has high density; and it may be referred to as [sweet](#) if it contains relatively little sulfur or [sour](#) if it contains substantial amounts of sulfur.

The geographic location is important because it affects transportation costs to the refinery. *Light* crude oil is more desirable than *heavy* oil since it produces a higher yield of petrol, while *sweet* oil commands a higher price than *sour* oil because it has fewer environmental problems and requires less refining to meet sulfur standards imposed on fuels in consuming countries.

Each crude oil has unique molecular characteristics which are understood by the use of [crude oil assay analysis](#) in petroleum laboratories.

Some marker crudes with their S content (horizontal) and API gravity (vertical) and relative production quantity.



Petroleum industry

The petroleum industry is involved in the global processes of exploration, extraction, refining, transporting (with oil tankers and pipelines), and marketing petroleum and petroleum products.

The largest volume products of the industry are fuel oil and petrol. Petroleum is also the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics.

The industry is usually divided into three major components: upstream, midstream and downstream. Midstream operations are usually included in the downstream category.

Oil accounts for a large percentage of the world's energy consumption, ranging from a low of 32 percent for Europe and Asia, up to a high of 53 percent for the Middle East, South and Central America (44%), Africa (41%), and North America (40%).

The world at large consumes 30 billion barrels (4.8 km³) of oil per year, and the top oil consumers largely consist of developed nations. In fact, 24 percent of the oil consumed in 2004 went to the United States alone, though by 2007 this had dropped to 21 per cent of world oil consumed.

Uses

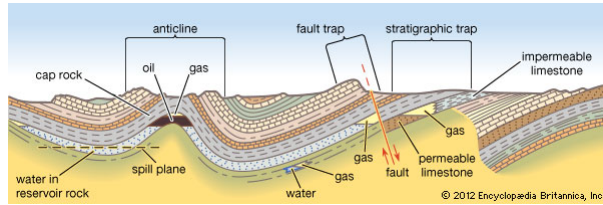
The chemical structure of petroleum is heterogeneous, composed of hydrocarbon chains of different lengths. Because of this, petroleum may be taken to oil refineries and the hydrocarbon chemicals separated by distillation and treated by other chemical processes, to be used for a variety of purposes.

The most common distillation fractions of petroleum are fuels.

Fuels include (by increasing boiling temperature range):

(common fractions of petroleum as fuels)

| Fraction | Boiling Range / °C |
|--------------------------------------|---------------------------|
| <u>Liquefied petroleum gas</u> (LPG) | -40 to -1 |
| <u>Petrol</u> | -1 to 110 |
| <u>Jet fuel</u> | 150 to 205 |
| <u>Kerosene</u> | 205 to 260 |
| <u>Fuel oil</u> | 205 to 290 |
| <u>Diesel fuel</u> | 260 to 315 |



Principal types of petroleum traps