Lecture 8. The composition and properties of oil and oil products. Preparation of oil for processing. Primary methods of refining.

Petroleum (or crude oil) is a complex, naturally occurring liquid mixture containing mostly hydrocarbons, but containing also some compounds of oxygen, nitrogen and sulfur. It is often referred to as the “black gold.”

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

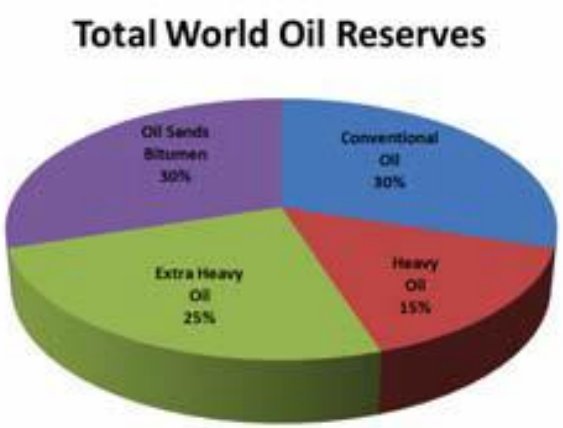
A fossil fuel, it is formed when large quantities of dead organisms, usually zooplankton and algae, are buried underneath sedimentary rock and undergo intense heat and pressure.

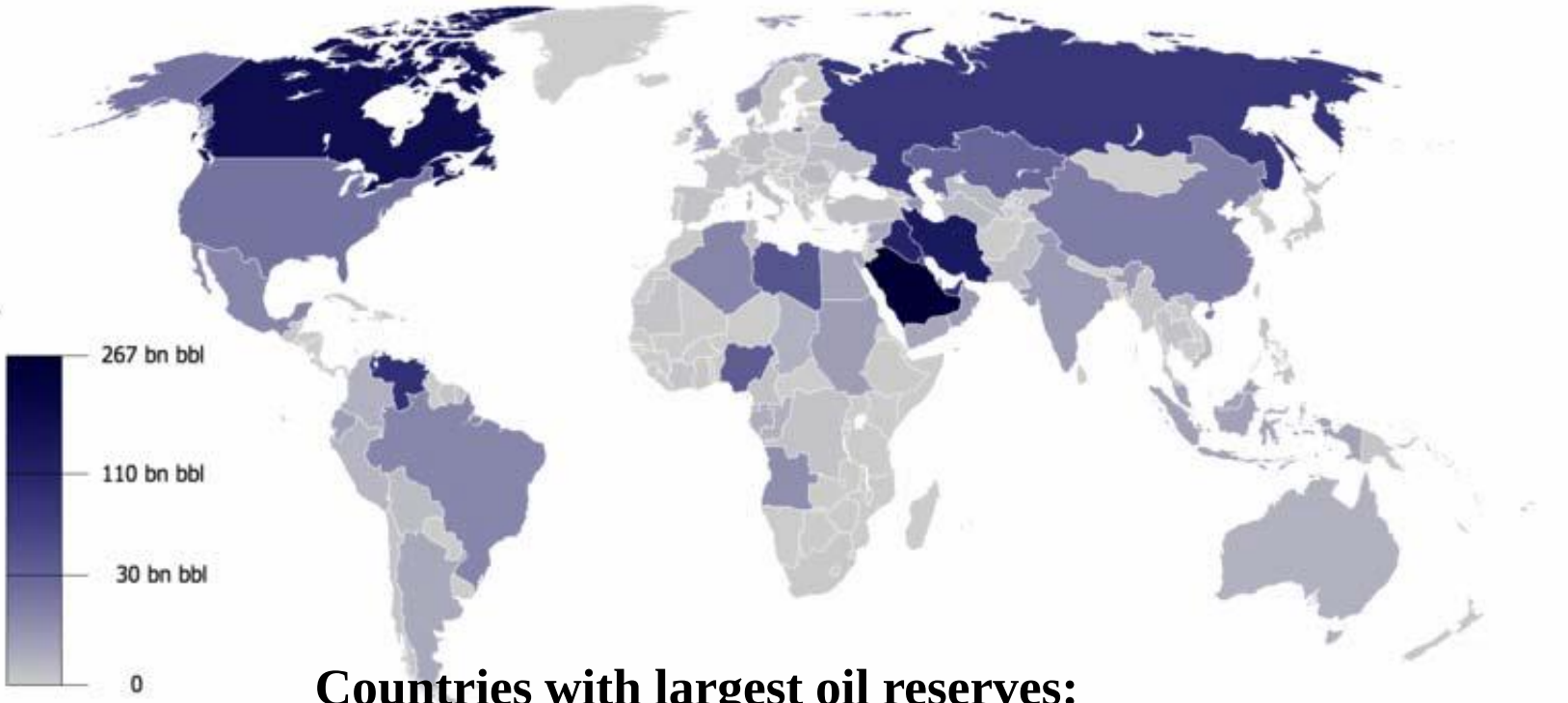
Petroleum is recovered mostly through oil drilling. This comes after the studies of structural geology (at the reservoir scale), sedimentary basin analysis, reservoir characterization (mainly in terms of porosity and permeable structures).

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.

Proven Oil Reserves





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.

Composition of Crude Oils

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%

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% to 60%
Naphthenes	49% to 60%
Aromatics	15% to 30%
Asphaltics	6% remainder

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.

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.

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.

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.

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).

CRUDE OIL CLASSIFICATION

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 oAPI light / 28 – 38 oAPI medium / 12 – 28 oAPI heavy

PROPERTIES OF CRUDE OILS

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

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

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.

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.

Ash Content

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

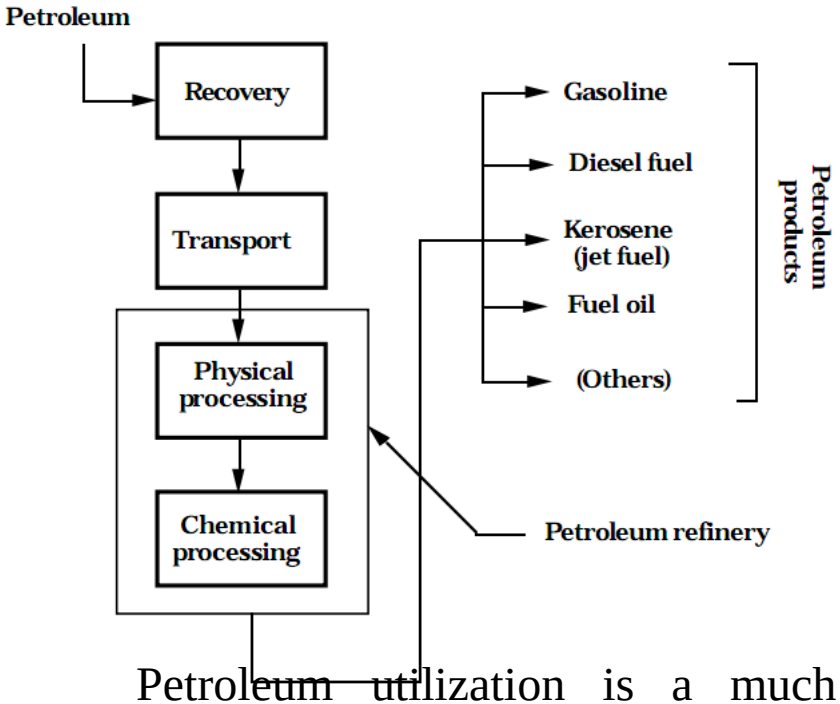
The ash left after completely burning an oil sample usually consists of stable metallic salts, metal oxides, and silicon oxide. The ash could be further analyzed for individual elements using spectroscopic techniques.

Sulfur Content

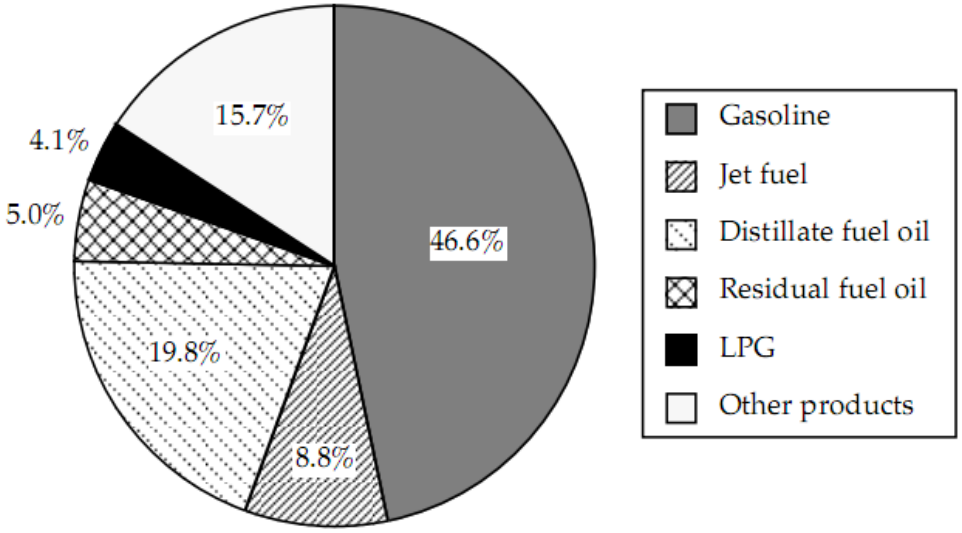
Pour Point

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.

Pathways to petroleum utilization



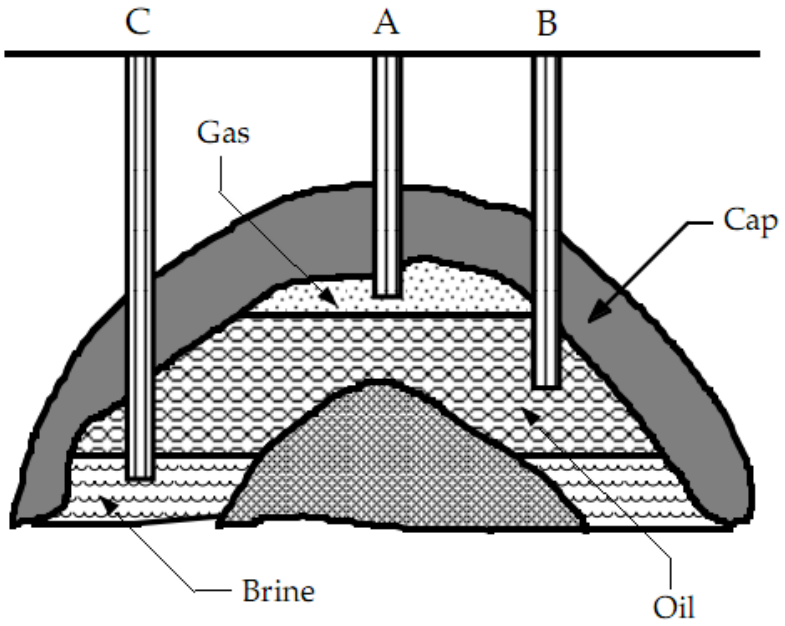
Distribution of products of petroleum refining



Petroleum utilization is a much more complex process than coal utilization. In particular, the preparation of petroleum before it is sold to the consumers is very extensive. The reason for this is that, despite their similar elemental composition, the chemical structure of different crude oils may be very different, as discussed above. Furthermore, a large number of different products is obtained from the petroleum refinery. Most of them are used as fuels. A small but very important fraction is used as the basis for the (petro)chemical industry which gives us such indispensable products as plastics, pharmaceuticals and textiles.

Oil Recovery (Drilling). After geologists of an oil company have located the general area in which petroleum is thought to occur, a well is drilled. Selecting the site for drilling requires detailed knowledge of the geologic features under the earth's surface. We can see from Figure that of the three wells shown, all of which are reasonably close to the oil pool, only well B would actually produce oil. Drilling is also done to determine the extent of the reserves.

Selection of a site for petroleum drilling

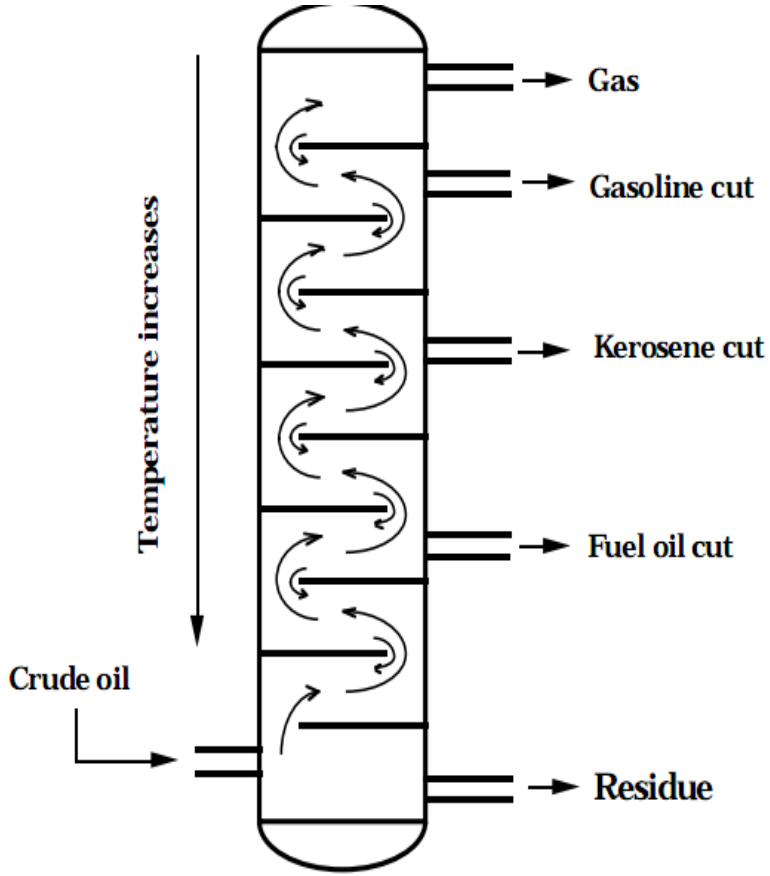


Transportation. Once the oil has been pumped out of the ground, it must then be transported to the users. Two major methods are used for petroleum transportation. First transportation method uses oil pipelines.

The second transportation method uses ships – oil tankers and the huge, ocean-crossing supertankers. The supertankers are very economical.

Petroleum Refining

The key step in refining is distillation. Distillation is the separation of materials based on differences in their volatility (as indicated by their boiling points). This operation is carried out in a distillation tower (or column) illustrated in Figure. Vapors from the heated crude oil rise and recondense continuously as they ascend within the column. The more volatile substances – those with the lower boiling points – become relatively enriched near the top of the column. Substances with very high boiling points are enriched near the bottom. At any given location in the column, there is a mixture of vapors corresponding to a liquid of particular composition and volatility.



Schematic representation of a distillation tower.

These vapors can be withdrawn from the column and condensed to form a liquid product. Such a liquid is still a mixture of many components, but in this case the components have fairly similar boiling points. The separation of crude oil by distillation is a physical process based on the fact that different chemical compounds have different boiling points.

Petroleum Products

Five broad categories of products are obtained by distillation of crude oil.

Gases are mainly propane and butane that were dissolved in the oil. They can be liquefied and sold as the useful fuel LPG (liquefied petroleum gas).

Gasoline produced by distillation of crude oil is called straight-run gasoline. This mixture boils in the range 25-150°C. The major chemical components of straight-run gasoline are straight-chain paraffins in the range of pentane to nonane.

Kerosene consists mainly of compounds with ten to twelve carbon atoms, boiling in the range of 170-300 °C.

Fuel oil boils at temperatures above 300°C and consists of molecules with twelve or more carbon atoms.

The residue is the material that doesn't boil at all in the distillation operation. In the petroleum business, it is often referred to as the resid. Special treatments of the resid can produce heavy fuel oils, asphalt, waxes and greases.

Gasoline is the most important product of a petroleum refinery. A good quality old-deep crude oil may yield 20% straight-run gasoline upon distillation. That is, every 100 barrels of crude oil distilled would provide 20 barrels of gasoline.