

Lecture Two

Properties of Natural Gas

Treated natural gas consists mainly of methane , the properties of both gases (natural gas and methane) are nearly similar . However , natural gas is not pure methane , and its properties are modified by the presence of impurities , such as N_2 and CO_2 and small amounts of unrecovered heavier hydrocarbons . An important property of natural gas is its heating value . Relatively high amounts of nitrogen and / or carbon dioxide reduce the heating value of the gas. Pure methane has a heating value of 1,009 Btu/ft³ . This value is reduced to approximately 900 Btu/ft³ if the gas contains about 10% N_2 and CO_2 . (The heating value of either nitrogen or carbon dioxide is zero) . On the other hand , the heating value of natural gas could exceed methane's due to the presence of higher – molecular weight hydrocarbons , which have higher heating values . For example , ethane's heating value is 1,800 Btu/ft³ , compared to 1,009 Btu/ft³ for methane . Heating values of hydrocarbons normally present in natural gas are shown in Table 1-4 . Natural gas is usually sold according to its heating values . The heating value of a product gas is a function of the constituents present in the mixture . In the natural gas trade , a heating value of one million Btu is approximately equivalent to 1,000 ft³ of natural gas .

Table 1-4

Heating values of methane and heavier hydrocarbons present in natural gas

Hydrocarbon	Formula	Heating value Btu/ft ³
Methane	CH ₄	1,009
Ethane	C ₂ H ₆	1,800
Propane	C ₃ H ₈	2,300
Isobutane	C ₄ H ₁₀	3,253
n-Butane	C ₄ H ₁₀	3,262
Isopentane	C ₅ H ₁₂	4,000
n-Pentane	C ₅ H ₁₂	4,010
n-Hexane	C ₆ H ₁₄	4,750
n-Heptane	C ₇ H ₁₆	5,502

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.

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).

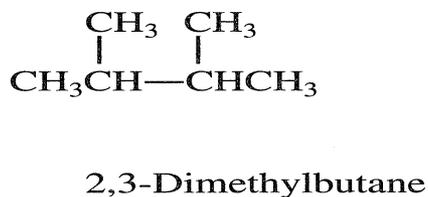
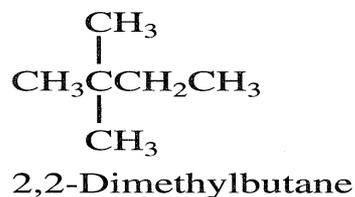
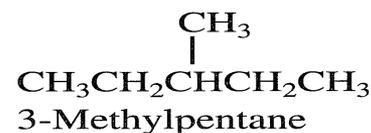
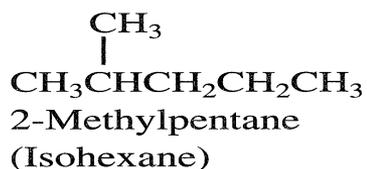
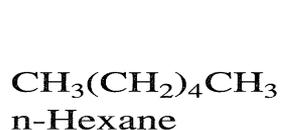
Hydrocarbon Compounds

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. The following is a brief description of the different hydrocarbon classes found in all 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.

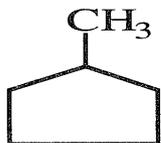
Normal alkanes (n-alkanes, n-paraffins) are straight-chain hydrocarbons having no branches. Branched alkanes are saturated hydrocarbons with an alkyl substituent or a side branch from the main chain. A branched alkane with the same number of carbons and hydrogens as a n-alkane is called an isomer. For 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:



An isoparaffin is an isomer having a methyl group branching from carbon number 2 of the main chain. 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.

Cycloparaffins (Naphthenes)

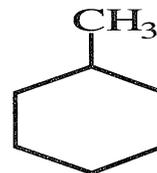
Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils. Their ratio, however, depends on the crude type. The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds. They are normally present in the light and the heavy naphtha fractions. Cyclohexanes, substituted cyclopentanes, and substituted cyclohexanes are important precursors for aromatic hydrocarbons.



Methylcyclopentane



Cyclohexane



Methylcyclohexane

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).

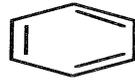
Heavier petroleum fractions such as kerosine and gas oil may contain two or more cyclohexane rings fused through two vicinal carbons.

Aromatic Compounds

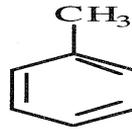
Lower members of aromatic compounds are present in small amounts in crude oils and light petroleum fractions. The simplest mononuclear aromatic compound is benzene (C_6H_6). Toluene (C_7H_8) and xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oils. Benzene, 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.

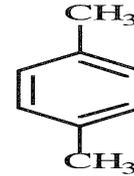
Binuclear aromatic hydrocarbons are found in heavier fractions than naphtha. Trinuclear and polynuclear aromatic hydrocarbons, in combination with heterocyclic compounds, are major constituents of heavy crudes and crude residues. Asphaltenes are a complex mixture of aromatic and heterocyclic compounds. The nature and structure of some of these compounds have been investigated. The following are representative examples of some aromatic compounds found in crude oils: Only a few aromatic-cycloparaffin compounds have been isolated and identified. Tetralin is an example of this class.



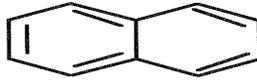
Benzene



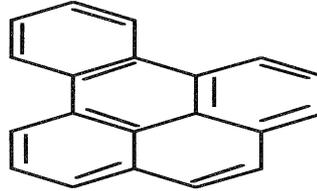
Toluene



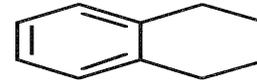
p-Xylene



Naphthalene



1,2-Benzopyrene



Tetralin

Non-hydrocarbon Compounds

Various types of non-hydrocarbon compounds occur in crude oils and refinery streams. The most important are the organic sulfur, nitrogen, and oxygen compounds. Traces of metallic compounds are also found in all crudes. The presence of these impurities is harmful and may cause problems to certain catalytic processes. Fuels having high sulfur and nitrogen levels cause pollution problems in addition to the corrosive nature of their oxidization products.

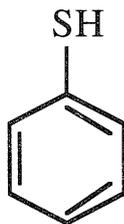
Sulfur Compounds

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. Examples of some sulfur compounds from the two types are:

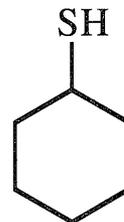
Acidic Sulfur Compounds



Methyl mercaptan



Phenyl mercaptan

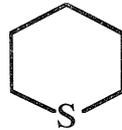


Cyclohexylthiol

Non-acidic Sulfur Compounds



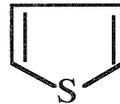
Dimethyl sulfide



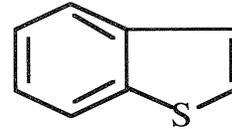
Thiocyclohexane



Dimethyldisulfide



Thiophene

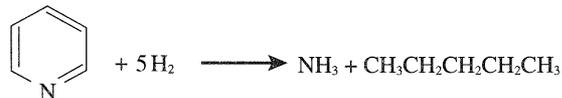


Benzothiophene

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.

Nitrogen Compounds

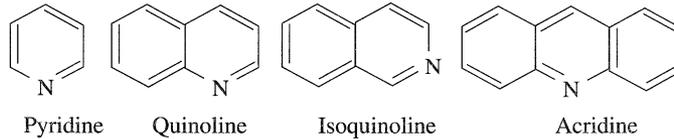
Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C₅H₅N) and pyrrole (C₄H₅N), or in a complex structure as in porphyrin. The nitrogen content in most crudes is very low and does not exceed 0.1 wt%. In some heavy crudes, however, the nitrogen content may 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:



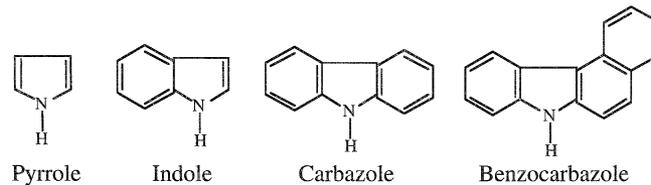
Nitrogen compounds in crudes may generally be classified into basic and non-basic categories. Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic compounds have a pyrrole structure. Both pyridine and pyrrole are stable compounds due to their aromatic nature.

The following are examples of organic nitrogen compounds.

Basic Nitrogen Compounds



Non-Basic Nitrogen Compounds



Separation of nitrogen compounds is difficult, and the compounds are susceptible to alteration and loss during handling. However, the basic low molecular weight compounds may be extracted with dilute mineral acids.

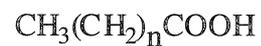
Oxygen Compounds

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.

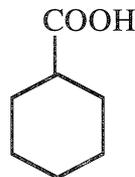
Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solutions. The total acid content of most crudes is generally low, but may reach as much as 3%, as in some California crudes.

Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds. They are of no commercial value. The following shows some of the oxygen compounds commonly found in crude oils:

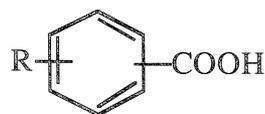
Acidic Oxygen Compounds



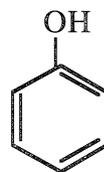
An aliphatic carboxylic acid



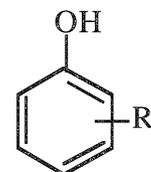
Cyclohexane
carboxylic acid



Aromatic acids



Phenol



Cresylic acid

Non-Acidic Oxygen Compounds



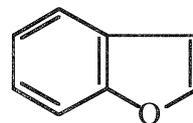
Esters



Furan



Amides



Benzofuran



Ketone

Metallic Compounds

Many metals occur in crude oils. Some of the more abundant are sodium, calcium, magnesium, aluminium, iron, vanadium, and nickel. They are present either as inorganic salts, such as sodium and magnesium chlorides, or in the form of organometallic compounds, such as those of nickel and vanadium (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.

COAL, OIL SHALE, TAR SAND, AND GAS HYDRATES

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. The following briefly discusses these alternative energy and chemical sources.

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.

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.

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 even large tar deposits. The oil sands resources in Western Canada sedimentary basin is the largest in the world.

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.