

# CHAPTER 1

## Primary Raw Materials for Petrochemicals

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## INTRODUCTION

- Secondary raw materials, or intermediates, are obtained from natural and crude oils through different processing schemes.
- The intermediate may be light hydrocarbon compounds such as methane and other heavier hydrocarbon mixtures such as naphtha or gas oil.
- Both naphtha and gas oil are crude oil fractions with different boiling ranges.

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## INTRODUCTION

- Coal, oil shale, and tar sand are complex carbonaceous raw materials possible future energy and chemical sources.
- However, they must undergo lengthy and extensive processing before they yield fuels and chemicals similar to those produced from crude oils (substitute natural (SNG) and synthetic crude from coal, tar sand and oil shale).

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## NATURAL GAS

### (Non-associated and Associated Natural Gases)

- Natural gas is naturally occurring mixture of light hydrocarbons accompanied by some non-hydrocarbon compounds.
- Non-associated natural gas is found in reservoirs containing no oil (dry wells).
- Associated gas on the other hand, is present in contact with and/or dissolved crude oil and is co-produced with it.

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## NATURAL GAS

### (Non-associated and Associated Natural Gases)

- The principal component of most natural gases is methane.
- Higher molecular weight paraffinic hydrocarbons are usually present in smaller amounts with the natural gas mixture, and their ratios vary considerably from one gas field to another.
- Non-associated gas normally contains a higher methane ratio than associated gas, while the latter contains a higher ratio of heavier hydrocarbons.

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## NATURAL GAS

### (Non-associated and Associated Natural Gases)

Table 1-1. Composition of non-associated and associated natural gases

Component	Non-associated gas		Associated gas	
	Salt Lake US	Kliffside US	Abqaiq Saudi Arabia	North Sea UK
Methane	95.0	65.8	62.2	85.9
Ethane	0.8	3.8	15.1	8.1
Propane	0.2	1.7	6.6	2.7
Butanes	-	0.8	2.4	0.9
Pentane and Heavier	-	0.5	1.1	0.3
Hydrogen sulfide	-	-	2.8	-
Carbon dioxide	3.6	-	9.2	1.6
Nitrogen	0.4	25.6	-	0.5
Helium	-	1.8	-	-

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## NATURAL GAS

### (Non-associated and Associated Natural Gases)

- The non-hydrocarbon constituents in natural gas vary appreciably from one gas field to another.
- Some of these compounds are weak acids such as hydrogen sulfide and carbon dioxide.
- Others are inert, such as nitrogen, helium and argon.
- Some natural gas reservoirs contain enough helium for commercial production.

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## NATURAL GAS

### (Non-associated and Associated Natural Gases)

- Higher molecular weight hydrocarbons present in natural gases are important fuels as well as chemical feedstocks and are normally recovered as natural gas liquids.
- For example, ethane may be separated for use as a feedstock for steam cracking for the production of ethylene.
- Propane and butane are recovered from natural gas and sold as liquefied petroleum gas (LPG). Before natural gas is used it must be processed or treated to remove the impurities and to recover the heavier hydrocarbons (heavier than methane).

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## NATURAL GAS TREATMENT PROCESSES

- Raw natural gases contain variable amounts of carbon dioxide, hydrogen sulfide, and water vapor.
- The presence of hydrogen sulfide in natural gas for domestic consumption cannot be tolerated because it is poisonous. It also corrodes metallic equipment.
- Carbon dioxide is undesirable, because it reduces the heating value of the gas and solidifies under the higher pressure and low temperatures used for transporting natural gas.
- For obtaining a sweet, dry natural gas, acid gases must be removed and water vapor reduced.
- In addition, natural gas with appreciable amounts of heavy hydrocarbons should be treated for their recovery as natural gas liquids.

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**NATURAL GAS TREATMENT PROCESSES**  
**Acid Gas Treatment**

- Acid gases can be reduced or removed by one or more of the following methods:
  - Physical absorption using a selective absorption solvent.
  - Physical adsorption using a solid adsorbent.
  - Chemical absorption where a solvent (a chemical) capable of reacting reversibly with the acid gases is used.

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**NATURAL GAS TREATMENT PROCESSES**  
**Acid Gas Treatment - *Physical Absorption***

- Important processes commercially used are the Selexol, the Sulfinol, and the Rectisol processes.
- In these processes, no chemical reaction occurs between the acid gas and the solvent.
- The solvent, or absorbent, is a liquid that selectively absorbs the acid gases and leaves out the hydrocarbons.

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**NATURAL GAS TREATMENT PROCESSES**  
**Acid Gas Treatment - *Physical Absorption***

- In the Selexol process for example, the solvent is dimethyl ether of polyethylene glycol.
- Raw natural gas passes countercurrent to the descending solvent.
- When the solvent becomes saturated with the acid gases, the pressure is reduced, and hydrogen sulfide and carbon dioxide are desorbed.
- The solvent is then recycled to the absorption tower.

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## NATURAL GAS TREATMENT PROCESSES

### Acid Gas Treatment - *Physical Absorption*

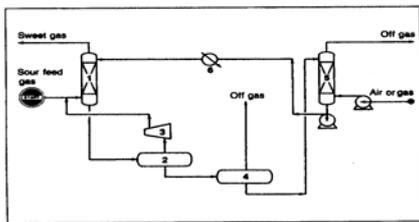


Figure 1-1. The Selexol process for acid gas removal. (1) absorber, (2) flash Drum, (3) compressor, (4) low-pressure drum, (5) stripper, (6) cooler.

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## NATURAL GAS TREATMENT PROCESSES

### Acid Gas Treatment - *Chemical Absorption*

- These processes are characterized by a high capability of absorbing large amounts of acid gases.
- They use a solution of a relatively weak base, such as monoethanolamine. The acid gas forms a weak bond with the base which can be regenerated easily.
- Mono- and diethanolamines are frequently used for this purpose. The amine concentration normally ranges between 15 and 30%.
- Natural gas is passed through the amine solution where sulfides, carbonates, and bicarbonates reformed.

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## NATURAL GAS TREATMENT PROCESSES

### Acid Gas Treatment - *Chemical Absorption*

- Diethanolamine is a favored absorbent due to its lower corrosion rate, smaller amine loss potential, fewer utility requirements, and minimal reclaiming needs.
- Diethanolamine also reacts reversibly with 75% of carbonyl sulfides (COS), while the mono- reacts irreversibly with 95% of the COS and forms a degradation product that must be disposed of.
- Diglycolamine (DGA), is another amine solvent used in the Econamine process.

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## NATURAL GAS TREATMENT PROCESSES

### Acid Gas Treatment - *Chemical Absorption*

- Absorption of acid gases occurs in an absorber containing an aqueous solution of DGA, and the heated rich solution (saturated with acid gases) is pumped to The regenerator.
- Diglycolamine solutions are characterized by low freezing points, which make them suitable for use in cold climates.

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## NATURAL GAS TREATMENT PROCESSES

### Acid Gas Treatment - *Chemical Absorption*

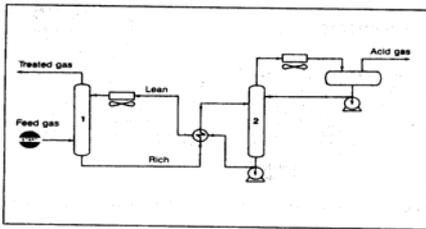


Figure 1-2. The Econamine processes: (1) absorption tower, (2) regeneration tower.

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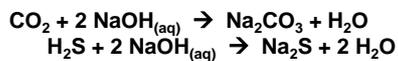
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## NATURAL GAS TREATMENT PROCESSES

### Acid Gas Treatment - *Chemical Absorption*

- Strong basic solutions are effective solvents for acid gases.
- However, these solutions are not normally used for treating large volumes of natural gas because the acid gases form stable salts, which are not easily regenerated.
- For example, carbon dioxide and hydrogen sulfide react with aqueous sodium hydroxide to yield sodium carbonate and sodium sulfide, respectively.



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## NATURAL GAS TREATMENT PROCESSES

### Acid Gas Treatment - *Chemical Absorption*

- However, a strong caustic solution is used to remove mercaptans from gas and liquid streams.
- In the Merox Process, for example, a caustic solvent containing a catalyst such as cobalt, which is capable of converting mercaptans (RSH) to caustic insoluble disulfides (RSSR), is used for streams rich in mercaptans after removal of H<sub>2</sub>S.
- Air is used to oxidize the mercaptans to disulfides. The caustic solution is then recycled for regeneration.
- The Merox process is mainly used for treatment of refinery gas streams.

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## NATURAL GAS TREATMENT PROCESSES

### Acid Gas Treatment - *Chemical Absorption*

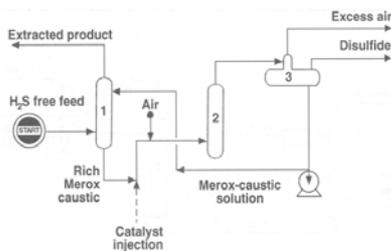


Figure 1-3. The Merox process: (1) extractor, (2) oxidation reactor.

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## NATURAL GAS TREATMENT PROCESSES

### Water Removal

- Moisture must be removed from natural gas to reduce corrosion problems and to prevent hydrate formation.
- Hydrates are solid white compounds formed from a physical-chemical reaction between hydrocarbons and water under the high pressures and low temperatures used to transport natural gas via pipeline.
- Hydrates reduce pipeline efficiency.

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## NATURAL GAS TREATMENT PROCESSES

### Water Removal

- To prevent hydrate formation, natural gas may be treated with glycols, which dissolve water efficiently.
- Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) are typical solvents for water removal.
- Triethylene glycol is preferable vapor phase processes because of its low vapor pressure, which results in less glycol loss.
- Predicting the interaction between TEG and water vapor in natural gas over a broad range allows the designs for ultra-low dew point applications to be made.

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## NATURAL GAS TREATMENT PROCESSES

### Water Removal

- The Dehydrate process where EG, DEG, or TEG could be used as an absorbent.
- Flow passage direct the gas and liquid flows countercurrent to each other.

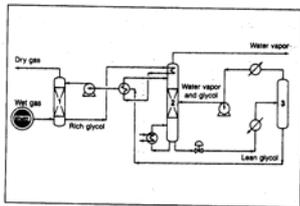


Figure 1-4. Flow diagram of the Dehydrate process: (1) absorption column, (2) glycol still, (3) vacuum drum.

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## NATURAL GAS TREATMENT PROCESSES

### Water Removal

- Another way to dehydrate natural gas is by injecting methanol into gas lines to lower the hydrate-formation temperature below ambient.
- Water can also be reduced or removed from natural gas by using solid adsorbents such as molecular sieves or silica gel.

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**NATURAL GAS TREATMENT PROCESSES**  
**Condensable Hydrocarbon Recovery**

- Hydrocarbons heavier than methane that are present in natural gases are valuable raw materials and important fuels.
- They can be recovered by lean oil extraction. The first step in this scheme is to cool the treated gas by exchange with liquid propane.
- The cooled gas is then washed with a cold hydrocarbon liquid, which dissolves most of the condensable hydrocarbons.
- The uncondensed gas is dry natural gas and is composed mainly of methane with small amounts of ethane and heavier hydrocarbons .

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**NATURAL GAS TREATMENT PROCESSES**  
**Condensable Hydrocarbon Recovery**

- The condensed hydrocarbons or natural gas liquids (NGL) are stripped from the rich solvent, which is recycled.
- Table 1-2 compares the analysis of natural gas before and after treatment.
- Dry natural gas may then be used either as a fuel or as a chemical feedstock.
- Another way to recover NGL is through cryogenic cooling to very low temperature (-150 to -180°F), which are achieved primarily through adiabatic expansion of the inlet gas.

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**NATURAL GAS TREATMENT PROCESSES**  
**Condensable Hydrocarbon Recovery**

Table 1-2  
 Typical analysis of natural gas before and after treatment<sup>11</sup>

Component Mole%	Feed	Pipeline gas
N <sub>2</sub>	0.45	0.62
CO <sub>2</sub>	27.85	3.50
H <sub>2</sub> S	0.0013	-
C <sub>1</sub>	70.35	94.85
C <sub>2</sub>	0.83	0.99
C <sub>3</sub>	0.22	0.003
C <sub>4</sub>	0.13	0.004
C <sub>5</sub>	0.06	0.004
C <sub>6+</sub>	0.11	0.014

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## NATURAL GAS LIQUIDS (NGL)

- Natural gas liquids (condensable hydrocarbons) are those hydrocarbons heavier than methane that are recovered from natural gas.
- The amount of NGL depends mainly on the percentage of the heavier hydrocarbons present in the gas and on the efficiency of the process used to recover them.
- (A high percentage is normally expected from associated gas.)

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## NATURAL GAS LIQUIDS (NGL)

- Natural gas liquids are normally fractionated to separate them into three streams:
  1. An ethane-rich stream, which is used for producing ethylene.
  2. Liquefied petroleum gas (LPG), which is a propane-butane mixture. It is mainly used as a fuel or a chemical feedstock. Liquefied petroleum gas is evolving into an important feedstock for olefin production. The world (LPG) market for chemicals grew from 23.1 million tons consumed in 1988 to 36.0 million tons in 2000.
  3. Natural gasoline (NG) is mainly constituted of C5+ hydrocarbons and is added to gasoline to raise its vapor pressure. Natural gasoline is usually sold according to its vapor pressure.

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## NATURAL GAS LIQUIDS (NGL)

- Natural gas liquids may contain significant amounts of cyclohexane, a precursor for nylon 6 (Chapter 10).
- Recovery of cyclohexane from NGL by conventional distillation is difficult and not economical because heptane isomers are also present which boil at temperatures nearly identical to that of cyclohexane.
- An extractive distillation process has been developed by Phillips Petroleum Co. to separate cyclohexane.

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## NATURAL GAS LIQUIDS (NGL)

### Liquefied Natural Gas (LNG)

- After the recovery of natural gas liquids, sweet dry natural gas may be liquefied for transportation through cryogenic tankers.
- Further treatment may be required to reduce the water vapor below 10 ppm.
- Two methods are generally used to liquefy natural gas: the expander cycle and mechanical refrigeration.

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## NATURAL GAS LIQUIDS (NGL)

### Liquefied Natural Gas (LNG)

- In the expander cycle, part of the gas is expanded from a high transmission pressure to a lower pressure. This lowers the temperature of the gas.
- Through heat exchange, the cold gas cools the incoming gas, which in a similar way cools more incoming gas until the liquefaction temperatures of methane is reached.

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## NATURAL GAS LIQUIDS (NGL)

### Liquefied Natural Gas (LNG)

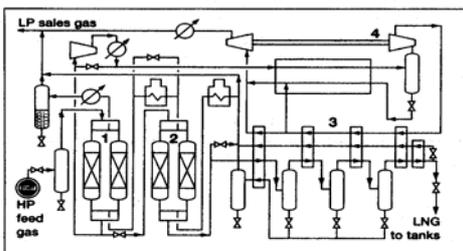


Figure 1-5. Flow diagram of the expander cycle for liquefying natural gas. (1) pretreatment (mol. sieve), (2) heat exchanger, (3) turbo expander.

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## NATURAL GAS LIQUIDS (NGL)

### Liquefied Natural Gas (LNG)

- In mechanical refrigeration, a multicomponent refrigerant consisting of nitrogen, methane, ethane, and propane is used through a cascade cycle.
- When these liquids evaporate, the heat required is obtained from natural gas which loses energy/temperature till it is liquefied.
- The refrigerant gases are recompressed and recycled.

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## NATURAL GAS LIQUIDS (NGL)

### Liquefied Natural Gas (LNG)

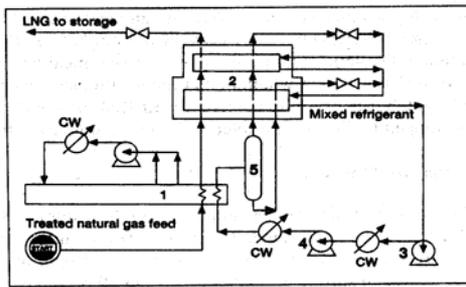


Figure 1-6. The MCR process for liquefying natural gas: (1) coolers, (2) heat Exchangers, (3,4) two stage compressors, (5) liquid-vapor phase separator.

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## 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.

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## PROPERTIES OF NATURAL GAS

Table 1-3

Important properties of a representative liquefied natural gas mixture

Density, lb/cf	27.00
Boiling point, °C	-158
Calorific value, Btu/lb	21200
Specific volume, cf/lb	0.037
Critical temperature, °C*	-82.3
Critical pressure, psi*	-673

\*Critical temperature and pressure for pure liquid methane.

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## PROPERTIES OF NATURAL GAS

- 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/ft<sup>3</sup>. This value is reduced to approximately 900 Btu/ft<sup>3</sup> if the gas contains about 10% N<sub>2</sub> and CO<sub>2</sub>.
- (The heating value of either nitrogen or carbon dioxide is zero.)

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## PROPERTIES OF NATURAL GAS

- 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/ft<sup>3</sup>, compared to 1,009 Btu/ft<sup>3</sup> for methane.
- 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 ft<sup>3</sup> of natural gas.

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## PROPERTIES OF NATURAL GAS

**Table 1-4**  
Heating values of methane and heavier hydrocarbons  
Present in natural gas

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

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## CRUDE OILS

- Crude oil (petroleum) is a naturally occurring brown to black flammable liquid.
- Crude oils are principally found in oils 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.

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## CRUDE OILS

- 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.

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## CRUDE OILS

### 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 com-pounds).

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### COMPOSITION OF CRUDE OILS

#### Hydrocarbon Compounds - 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.

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### COMPOSITION OF CRUDE OILS

#### Hydrocarbon Compounds - Alkanes (Paraffins)

- 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:

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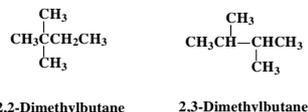
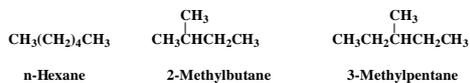
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**COMPOSITION OF CRUDE OILS**  
**Hydrocarbon Compounds - Alkanes (Paraffins)**



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**COMPOSITION OF CRUDE OILS**  
**Hydrocarbon Compounds - Alkanes (Paraffins)**

- 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.

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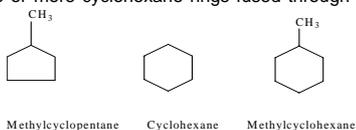
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**COMPOSITION OF CRUDE OILS**  
**Hydrocarbon Compounds - Cycloparaffins (Naphthenes)**

- Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils.
- 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.
- Heavier petroleum fractions such as kerosine and gas oil may contain two or more cyclohexane rings fused through two vicinal carbons.




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## COMPOSITION OF CRUDE OILS

### Hydrocarbon Compounds – 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<sub>6</sub>H<sub>6</sub>).
- Toluene (C<sub>7</sub>H<sub>8</sub>) and xylene (C<sub>8</sub>H<sub>10</sub>) 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.

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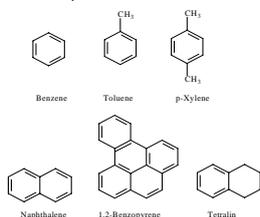
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## COMPOSITION OF CRUDE OILS

### Hydrocarbon Compounds – Aromatic Compounds

- 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.



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## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - 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.

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## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - 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.

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## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - Sulfur Compounds

#### ■ Acidic Sulfur Compounds



Methyl mercaptan



Phenyl mercaptan



Cyclohexylthiol

#### ■ Non-Acidic Sulfur Compounds



Dimethyl sulfide



Dimethyldisulfide



Thiocyclohexane



Thiophene



Benzothiophene

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## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - Nitrogen Compounds

- Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) and pyrrole ( $\text{C}_4\text{H}_5\text{N}$ ), 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, 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.

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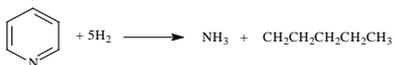
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## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - Nitrogen Compounds

- 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 crude oil may generally be classified into basic and non-basic categories.

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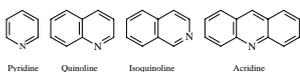
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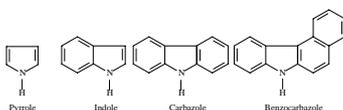
## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - Nitrogen Compounds

#### Basic Nitrogen Compounds



#### Non-Basic Nitrogen Compounds



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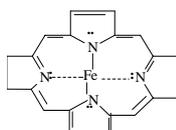
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## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - Nitrogen Compounds

- Porphyryns 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.



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## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - 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.

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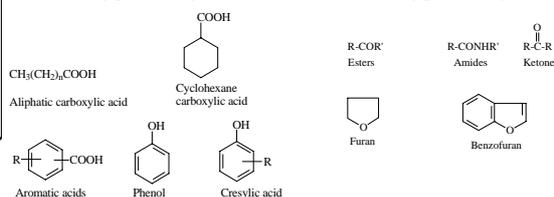
## COMPOSITION OF CRUDE OILS

### Non-hydrocarbon Compounds - Oxygen Compounds

- 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

#### Non-Acidic Oxygen Compounds



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## COMPOSITION OF CRUDE OILS

### Metallic Compounds

- Many metals occur in crude oils. Some of the more abundant are sodium, calcium, magnesium, aluminum, 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.

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## COMPOSITION OF CRUDE OILS

### Metallic Compounds

- 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.

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## COMPOSITION OF CRUDE OILS

### 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.

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## COMPOSITION OF CRUDE OILS

### PROPERTIES OF CRUDE OILS

- 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.

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## COMPOSITION 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.

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## COMPOSITION OF CRUDE OILS

### Density, Specific Gravity and API Gravity

- The API (American Petroleum Institute) gravity is another way to express the relative masses of crude oils.

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

- 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<sup>o</sup>API scale).

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## COMPOSITION OF CRUDE OILS

### Density, Specific Gravity and API Gravity

#### 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.
- 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 MCI) requires desalting .

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## COMPOSITION OF CRUDE OILS

Density, Specific Gravity and API Gravity

### Sulfur Content

- The sulfur content in crudes is important because the amount of sulfur indicates the type of treatment required for the distillates.
- To determine sulfur content, a weighed crude sample (or fraction) is burned in an air stream.
- All sulfur compounds are oxidized to sulfur dioxide, which is further oxidized to sulfur trioxide and finally titrated with a standard alkali.

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## COMPOSITION OF CRUDE OILS

Density, Specific Gravity and API Gravity

### Sulfur Content

- Identifying sulfur compounds in crude oils and their products is of little use to a refiner because all sulfur compounds can easily be hydrodesulfurized to hydrogen sulfide and the, corresponding hydrocarbon.
- The sulfur content of crudes, however, is important and is usually considered when determining commercial values.

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## COMPOSITION OF CRUDE OILS

Density, Specific Gravity and API Gravity

### 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.

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## COMPOSITION OF CRUDE OILS

Density, Specific Gravity and API Gravity

### Pour Point

- Handling and transporting crude oils and heavy fuels is difficult at temperatures below their pour points.
- 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.

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## COMPOSITION OF CRUDE OILS

Density, Specific Gravity and API Gravity

### 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.

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## CLASSIFICATION OF CRUDE OILS

### Three types of crudes:

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

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## CLASSIFICATION OF CRUDE OILS

- A correlation index is a useful criterion for indicating the crude class or type.
- The following relationship between the mid-boiling point in Kelvin degrees (°K) and the specific gravity of a crude oil or a fraction yields the correlation index (**Bureau of Mines Correlation index**).

$$\text{BMCI} = 48,640 / K + (473.6d - 456.8)$$

K = mid-boiling point in Kelvin degrees (Mid-boiling point is the temperature at which 50 vol % of the crude is distilled.)

d = specific gravity at 60/60°F

- **A zero value has been assumed for n-paraffins, 100 for aromatics. A low BMCI value indicates a higher paraffin concentration in a petroleum fraction.**

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## CLASSIFICATION OF CRUDE OILS

- Another relationship used to indicate the crude type is the Watson characterization factor. The factor also relates the mid-boiling point of the crude or a fraction to the specific gravity.

$$\text{Watson characterization factor} = \frac{T^{1/3}}{d}$$

where T = mid-boiling point in °R (°R is the absolute °F, and equals °F + 460)

- A value higher than 10 indicates a predominance of paraffins while a value around 10 means a predominance of aromatics.

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