Chemistry of Petrochemical Processes

ChE 464

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Book

Chemistry of Petrochemical Processes

Second Edition

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Grading

- Presence: 10 %
- Major Exams = 2 x 15% = 30 %
- Quizzes: 2 x 10% = 20 %
- Final Exam= 40 %

Chapter One

Primary raw materials for petrochemicals

Primary raw Materials for Petrochemicals

a- Natural gas

b- Crude oil

Secondary raw Materials for Petrochemicals

-Obtained from natural gas or crude oil by different processing schemes

- It can be:

  -Light hydrocarbon compounds (Methane or Ethane)

  - Heavy hydrocarbon mixtures (naphtha or gas oil (crude oil fractions)

  - Complex carbonaceous raw materials

Natural Gas

Naturally occurring light hydrocarbons (gases) + some non hydrocarbon compounds.

Types

- Non-associated → dry well → no oil
- associated → on top or dissolved in crude oil

Composition:

In principal methane

+ C_2— C_7 hydrocarbons in very small amounts

Table 1-1

Composition of non-associated and associated natural gases[1]

	Non-associated gas		Associated gas	
Component	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	—	—

The amount of higher hydrocarbons changes considerably with the field

In non-associated gas fields → high % of methane

In associated gas fields → high % of $C_2 – C_7$

Non-hydrocarbons: weak acids e.g. H_2S & CO_2

Inert gases, e.g. N_2, He and Ar

Some natural gas reservoirs contain enough He for commercial production.

$C_2 – C_7$ → important fuels produced in the liquid form

e.g. ethane used as a feedstock for steam cracking to ethylene

Propane + butane → sold as liquified petroleum gas (LPG)

Natural gas treatment process

Disadavantages of acid gases:

- H_2S is poisonous and corrosive
- CO_2 reduces the heat value of the fuel and solidifies under transportation conditions (high pressure and low temperature).

Therefore, removal of these harmful gases is necessary

Acid gas treatment (Removal)

1- Physical absorption using a selective absortion solvent

2- Physical adsorption by solid adsorbent

3- Chemical absorption (Chemisorption)

Physical Absorption

Known Processes:

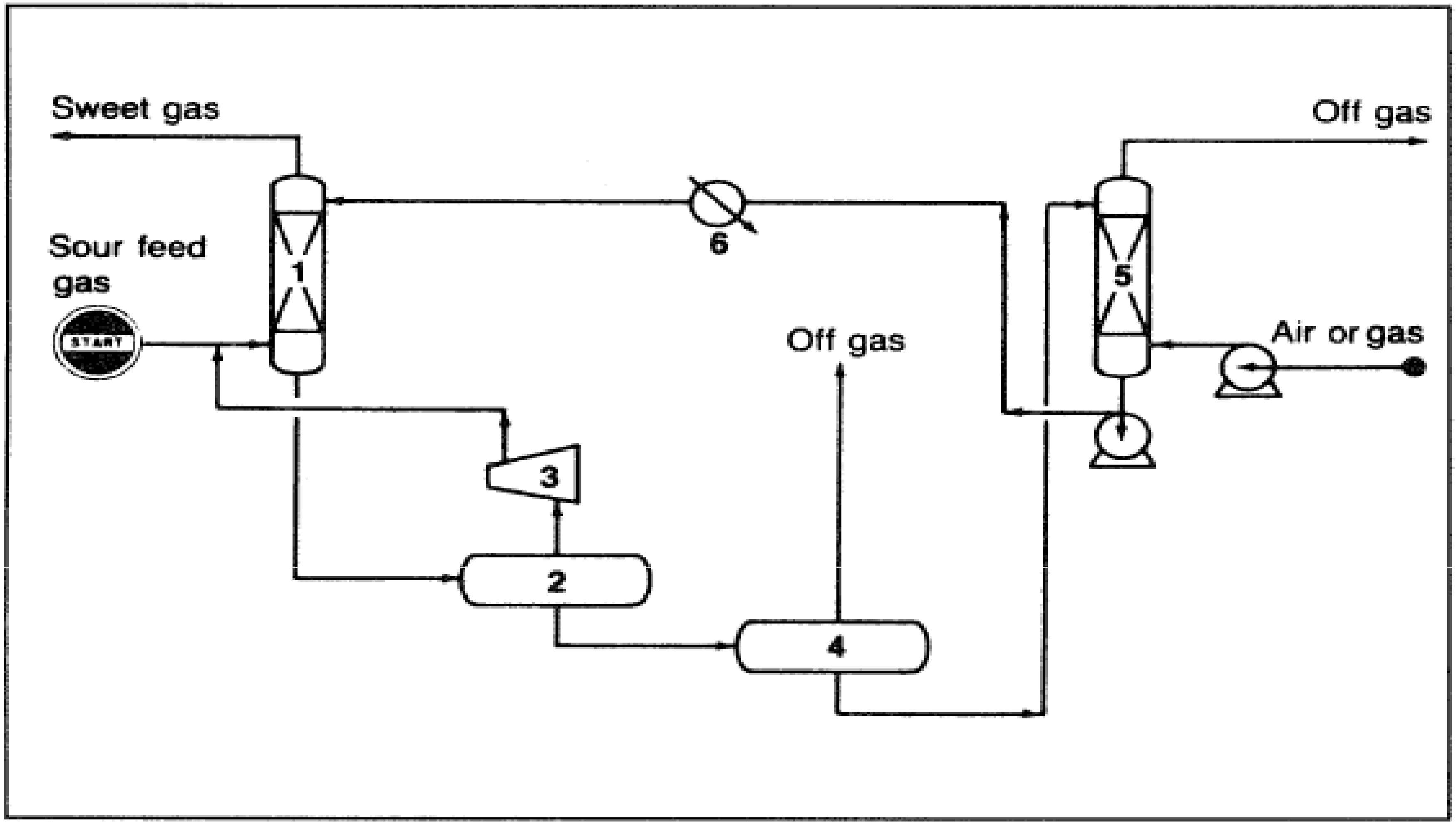
A- Selexol   B- Sulfinol   C- Rectisol

Characteristics:

- No reaction occurs between the acid gas and solvent
- Using a solvent which selectively absorb the acid gas

Selexol:

- Raw natural gas passes counter-currently to the descending solvent.
- When the solvent becomes saturated with the acid gases, the oressure is reduced , H_2S and CO_2 are desorbed
- The solvent is recycled to the absortion Tower



The selexol process for acid gas removal

(1) Absorber (2) flash drum (3) compressor

(4) low-pressure drum (5) stripper (6) cooler

Physical Adsorption

Molecular sieves zeolites are used as adsorbents:

Adsorb large amounts of gases and water

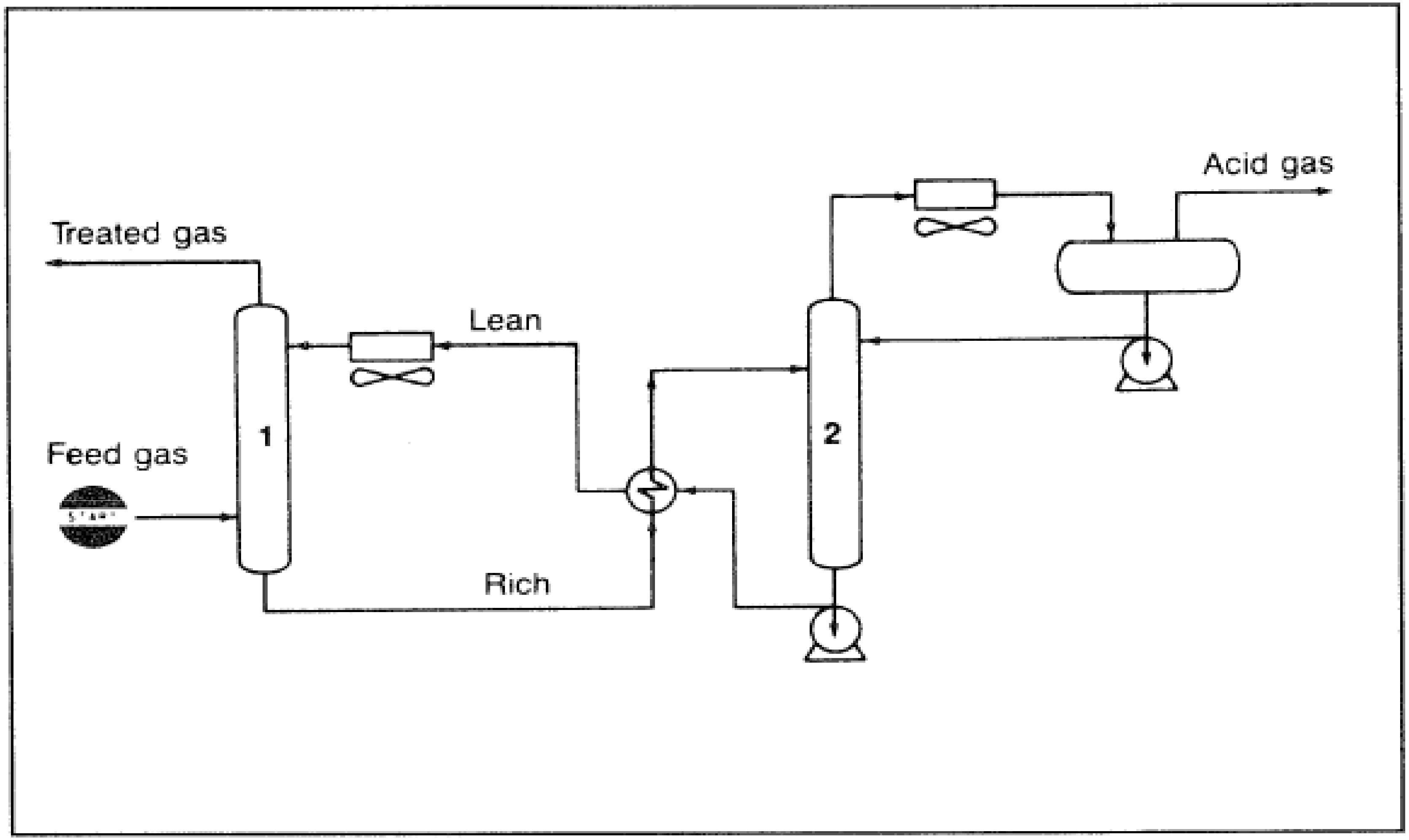
Zeolite molecular sieves are microporous aluminosilicate compounds able to make adsorption of moleules, some hydrophilic types such as 13X are capable of absorpting water molecules.

More than one adsorption beds are used for alternate adsorption and regenration (by hot dry fuel gas)

Only used when the amount of acid gasses are low

Chemical Adsorption

- Used in case of large amounts of acid gases
- A solution of weak base is used (monoethanol amine)
- The acid gases are removed via the formation of weak bonds with the base solution.
- These bonds can easily be destroyed and the base solution can easily be regenerated.
- Mono- and diethanol amines are normally used. With which natural gas reacts to form carbonates and sulphides.
- Diethanol amine is favored due to its low corrosion rates
- Diglycolamine is another amine solvent used in the econamine process shown below.



The econamine process: (1) absorption tower

(2) Regeneration tower

In this process:

- Acid gases are absorbed in an absorber containing an aqueous solution of diglycolamine (DGA), and the heated saturated acid gas solution is pumped to the regenerator.

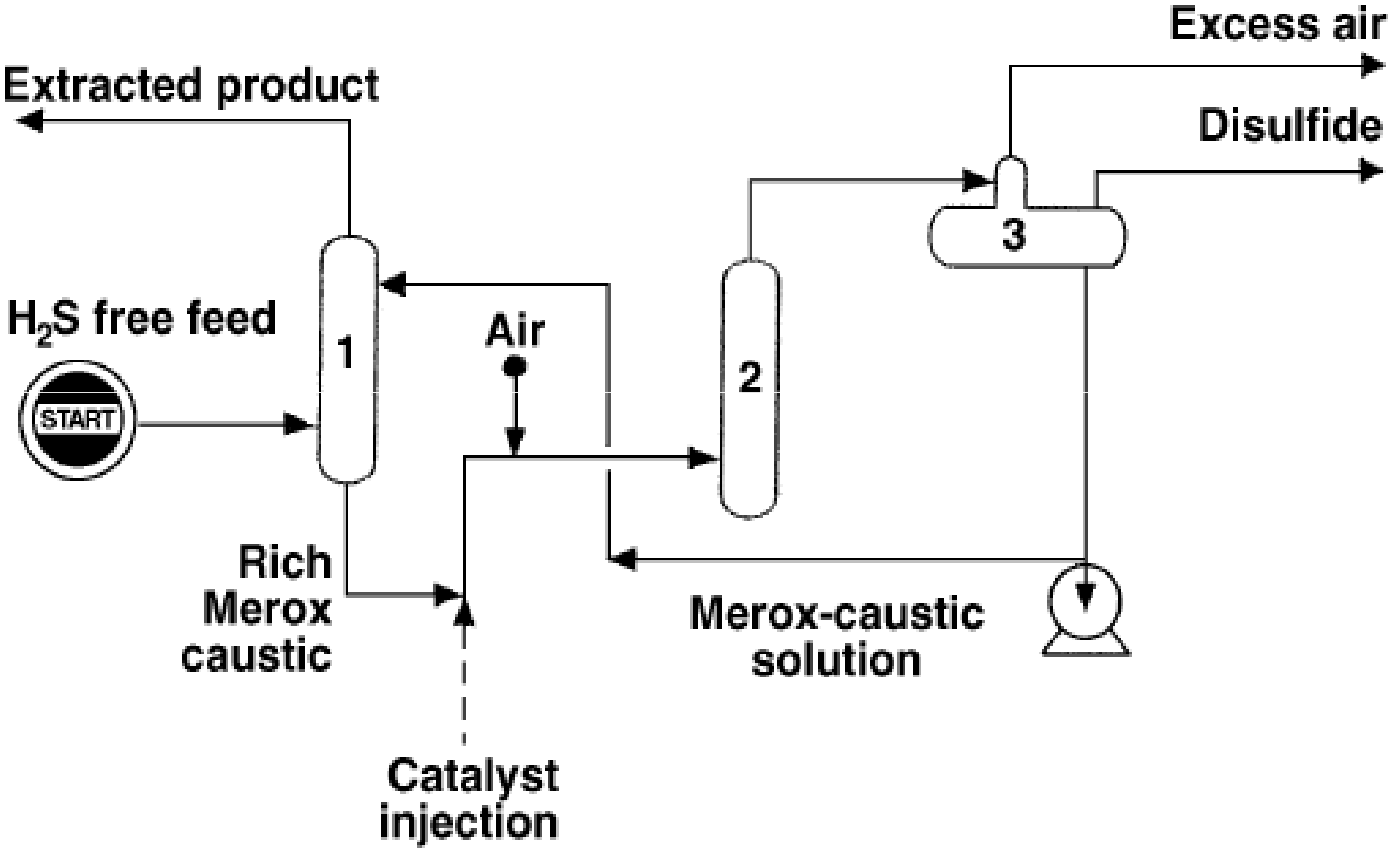
- Diglycolamine solution has low freezing point and can be used in areas with cold climates.

- Solutions of strong bases are not frequently used as they form stable salts that is not easily separated.

$$CO_2 + 2\,NaOH \rightarrow Na_2CO_3 + H_2O$$

$$H_2S + 2\,NaOH \rightarrow Na_2S + 2\,H_2O$$

However, strong caustic solution is used to remove mercaptans (R—SH) from the gas and liquid streams in **The Merox Process**



The Merox process:[5] (1) extractor, (2) oxidation reactor.

- A caustic solution containing cobalt catalyst is used to convert mercaptans (RSH) to RSSR (disulphide).

- Air is used to oxidize the mercaptans to disulphides. (R-S-S-R)

- The caustic solution is then recycled for regeneration.

- It is mainly used for treatment of refinery gas streams.

Water Removal

Moisture cause corrosion and form hydrates.

Water + hydrocarbons → hydrates (white compounds)

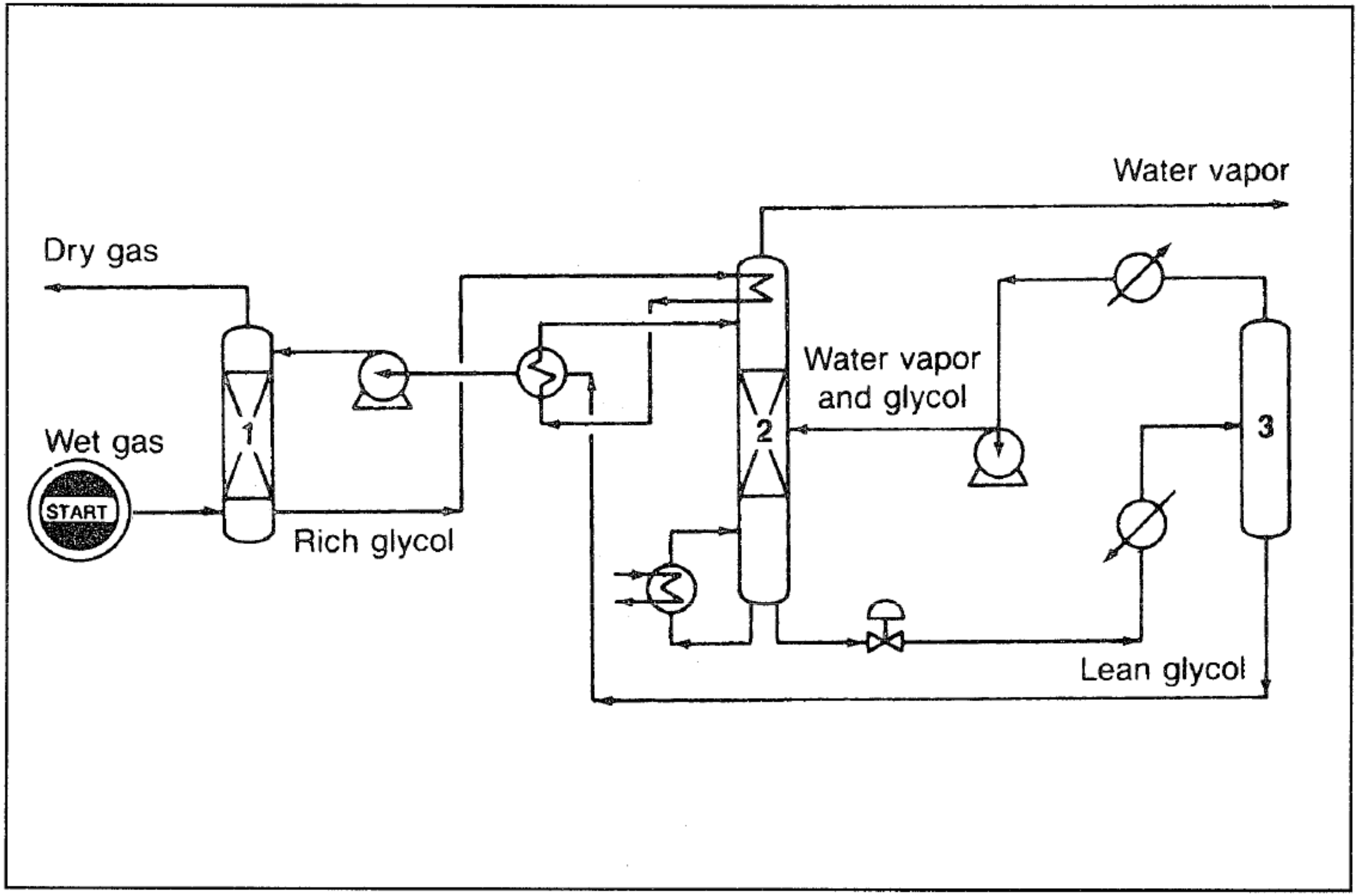
(conditions: high pressures and low temperatures during transportation)

Disadvantages

Reduce the pipeline efficiency

Prevention: treatment with glycols such as:

Ethylene glycol (EG), Di EG (DEG) and Tri EG (TEG)



Flow diagram of the Dehydrate process[8]: (1) absorption column, (2) glycol sill, (3) vacuum drum.

Alternative ways:

1- Injection of methanol: Lowering of the hydrate formation temperature below ambient.

2- Employing of solid adsorbents such as molecular sieves.

Condensable hydrocarbon recovery

C_2-- C_7 hydrocarbons are valuable fuels.

It can be recovered by weak oil extraction.

By cooling 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.

The condensed hydrocarbons or natural gas liquids (NGL) are stripped from the rich solvent, which is recycled.

NATURAL GAS LIQUIDS (NGL)

Natural gas liquids (condensable hydrocarbons): heavier than methane in the natural gas.

High in associated gas.

Fractionated to separate them into:

1. An ethane-rich stream, which is used for producing ethylene.

2. Liquefied petroleum gas (LPG), which is a propane-butane mixture.

3. Natural gasoline (NG) is mainly constituted of C5 + hydrocarbons and is added to gasoline to raise its vapor pressure.

NGL contain significant amounts of cyclohexane, a precursor for nylon 6

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 recently developed instead.

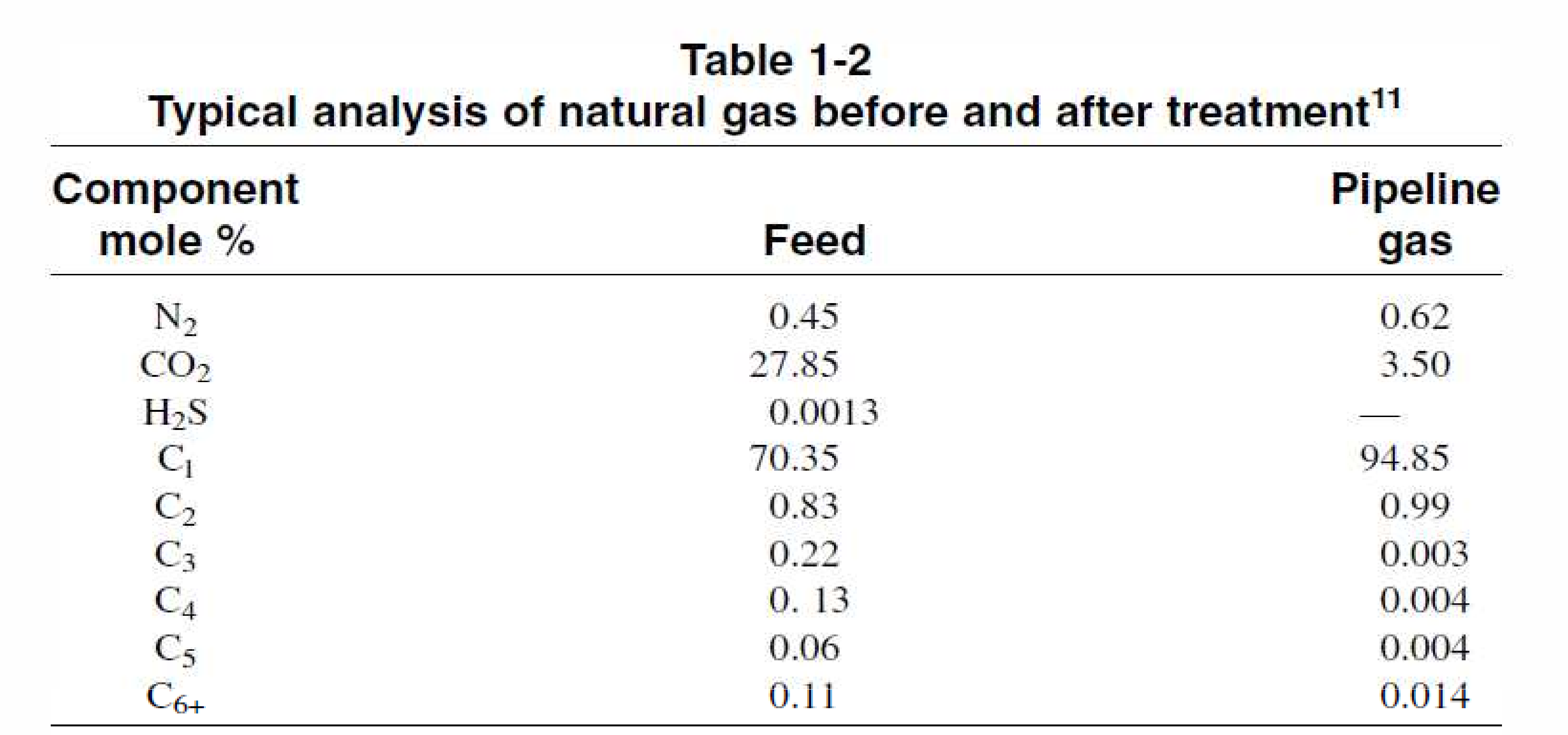


Table 1-2
Typical analysis of natural gas before and after treatment[11]

Component mole %	Feed	Pipeline gas
N_2	0.45	0.62
CO_2	27.85	3.50
H_2S	0.0013	—
C_1	70.35	94.85
C_2	0.83	0.99
C_3	0.22	0.003
C_4	0. 13	0.004
C_5	0.06	0.004
C_{6+}	0.11	0.014

1- Another way to recover NGL is through cryogenic cooling to very low temperatures (–150 to –180°F), by adiabatic expansion of the inlet gas.

2- First, remove water and acid gases, then cooled via heat exchange and refrigeration. Further cooling of the gas is accomplished through turbo expanders, and the gas is sent to a demethanizer to separate methane from NGL.

3-Improved NGL recovery could be achieved through better control strategies and use of on-line gas chromatographic analysis.

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 recently developed by Phillips Petroleum Co. to separate cyclohexane

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 and carbon dioxide and hydrogen sulfide to less than 100 and 50 ppm, respectively.

Two methods are generally used to liquefy natural gas: the expander cycle and mechanical refrigeration. 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 temperature of methane is reached. Figure 1-5 is a flow diagram for the expander cycle for liquefying natural gas

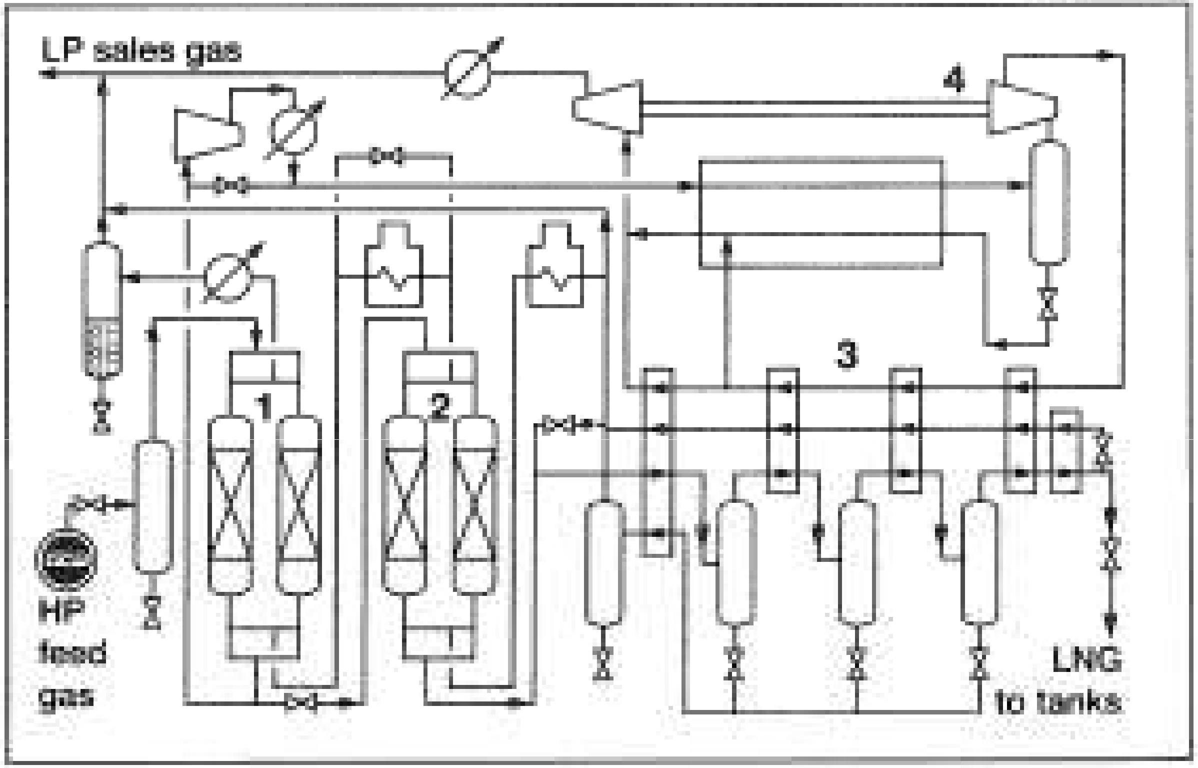


Figure 1-5. Flow diagram of the expander cycle for liquefying natural gas:[15] (1) pretreatment (mol.sieve), (2) heat exchanger, (3) turboexpander.

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. Figure 1-6 shows the MCR natural gas liquefaction process.

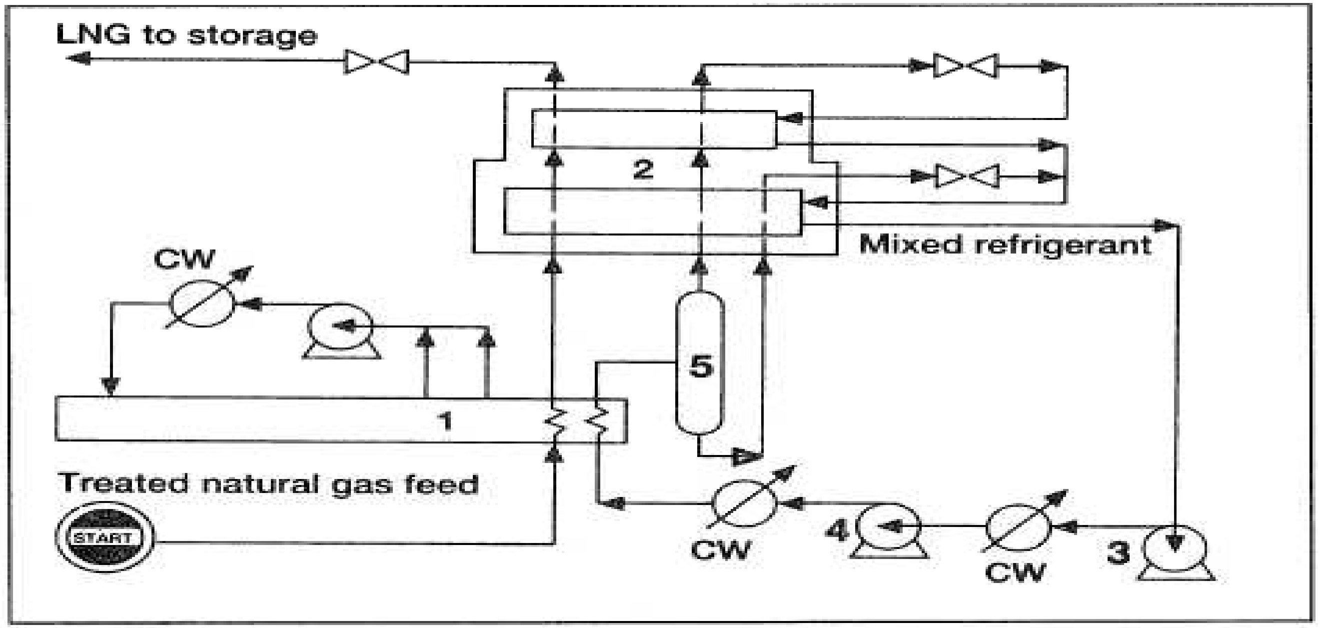


Figure 1-6. The MCR process for liquefying natural gas:[15] (1) coolers, (2) heat exchangers, (3,4) two stage compressors, (5) liquid-vapor phase separator.

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 N2 and CO2 and small amounts of unrecovered heavier hydrocarbons.

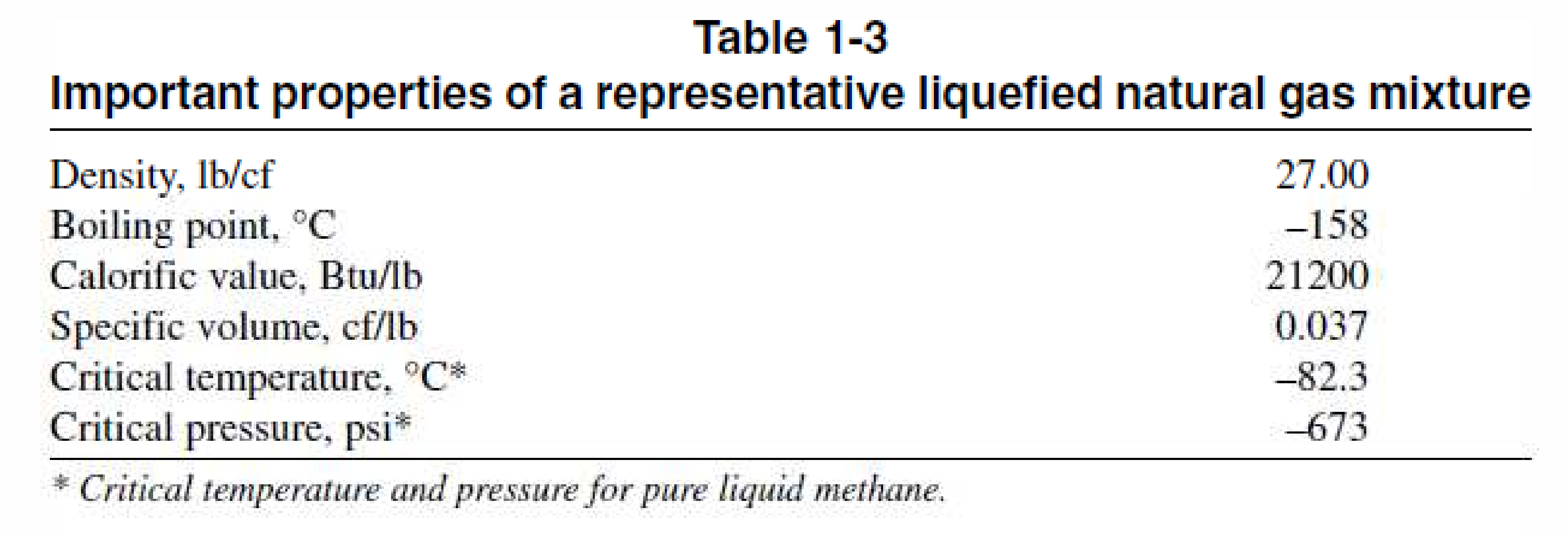


Table 1-3

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.*

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 ethane has a heating value of 1,009 Btu/ft3. This value is reduced to approximately 900 Btu/ft3 if the gas contains about 10% N2 and CO2. (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_2H_6	1,800
Propane	C_3H_8	2,300
Isobutane	C_4H_{10}	3,253
n-Butane	C_4H_{10}	3,262
Isopentane	C_5H_{12}	4,000
n-Pentane	C_5H_{12}	4,010
n-Hexane	C_6H_{14}	4,750
n-Heptane	C_7H_{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.

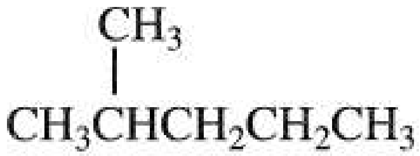
Alkanes (Paraffins)

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 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_5C_{12}) has three isomers; hexane (C_6H_{14}) has five. The following shows the isomers of hexane:

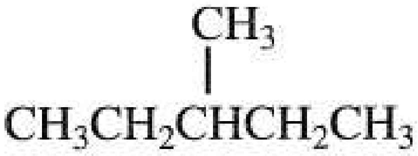
$CH_3(CH_2)_4CH_3$

n-Hexane



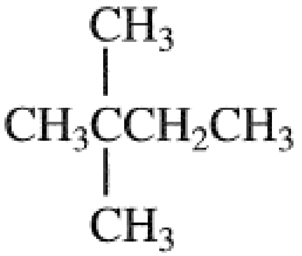
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$

2-Methylpentane
(Isohexane)



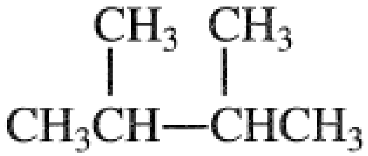
$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$

3-Methylpentane



$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2CH_3$

2,2-Dimethylbutane



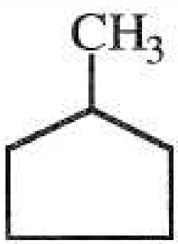
$CH_3\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}HCH_3$

2,3-Dimethylbutane

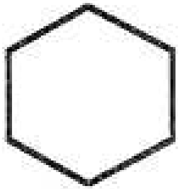
An isoparaffin is an isomer having a methyl group branching from carbon number 2 of the main chain. Crude oils contain many short, medium, and long-chain normal and branched paraffins. A naphtha fraction (obtained as a light liquid stream from crude fractionation) with a narrow boiling range may contain a limited but still large number of isomers.

Cycloparaffins (Naphthenes)

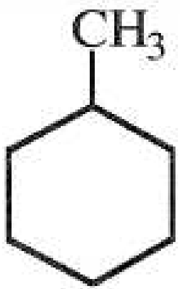
Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils. Their ratio, however, depends on the crude type. The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds. They are normally present in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



Methylcyclopentane

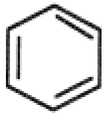


Cyclohexane

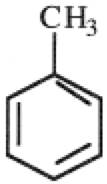


Methylcyclohexane

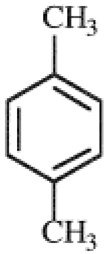
Aromatic Compounds



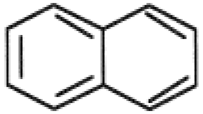
Benzene



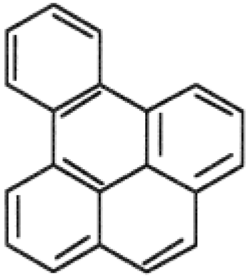
Toluene



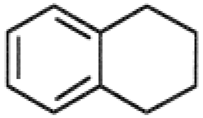
p-Xylene



Naphthalene



1,2-Benzopyrene



Tetralin

Only a few aromatic-cycloparaffin compounds have been isolated and identified. Tetralin is an example of this class.

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.

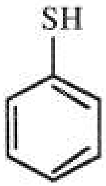
Sulfur Compounds

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. Extensive research has been carried out to identify some sulfur compounds in a narrow light petroleum fraction.[17] Examples of some sulfur compounds from the two types are:

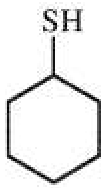
Acidic Sulfur Compounds

CH_3SH

Methyl mercaptan



Phenyl mercaptan



Cyclohexylthiol

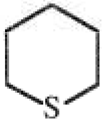
Non-acidic Sulfur Compounds

CH_3SCH_3

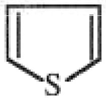
Dimethyl sulfide

$CH_3S\text{-}SCH_3$

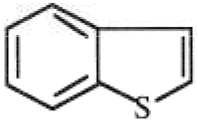
Dimethyldisulfide



Thiocyclohexane



Thiophene



Benzothiophene

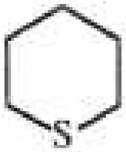
Non-acidic Sulfur Compounds

CH_3SCH_3

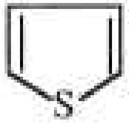
Dimethyl sulfide

$CH_3S\text{-}SCH_3$

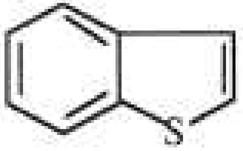
Dimethyldisulfide



Thiocyclohexane



Thiophene



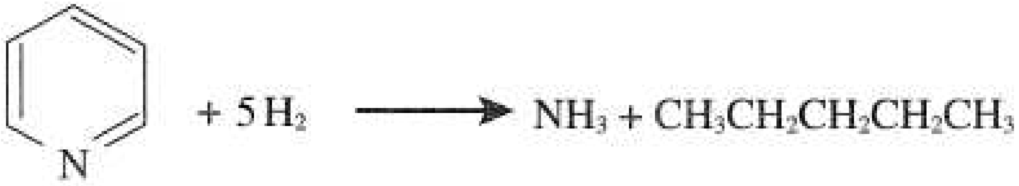
Benzothiophene

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 (Chapter 4).

Nitrogen Compounds

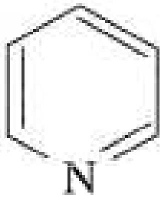
Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C_5H_5N) and pyrrole (C_4H_5N), or in a complex structure as in porphyrin. The nitrogen content in most crudes is very low and does not exceed 0.1 wt%. In some heavy crudes, however, the nitrogen content may reach up to 0.9 wt %.[18] 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:



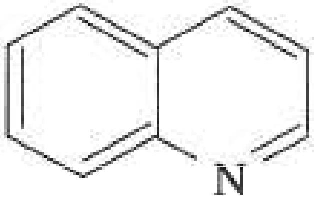
Nitrogen compounds in crudes may generally be classified into basic and non-basic categories. Basic nitrogen compounds are mainly those having a pyridine ring, and the non-basic compounds have a pyrrole structure. Both pyridine and pyrrole are stable compounds due to their aromatic nature.

The following are examples of organic nitrogen compounds.

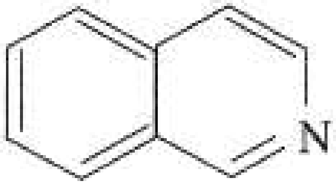
Basic Nitrogen Compounds



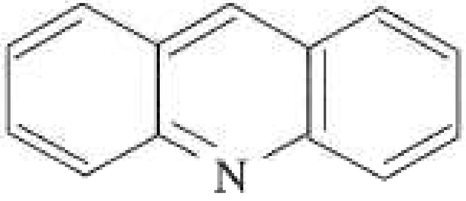
Pyridine



Quinoline

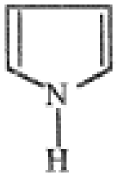


Isoquinoline

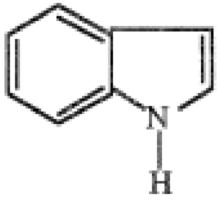


Acridine

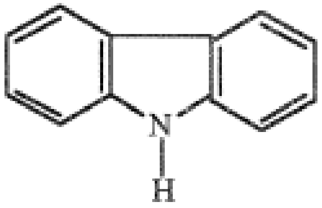
Non-Basic Nitrogen Compounds



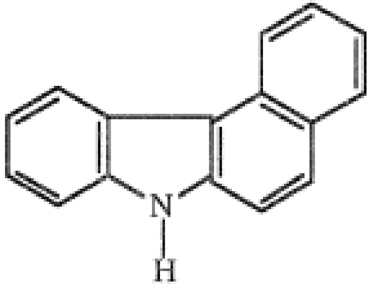
Pyrrole



Indole

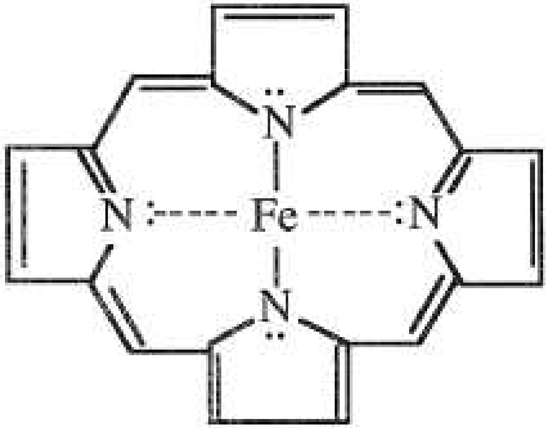


Carbazole



Benzocarbazole

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



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.

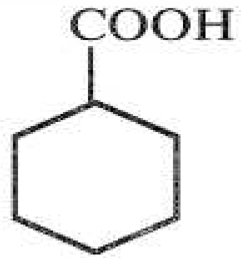
Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solutions. The total acid content of most crudes is generally low, but may reach as much as 3%, as in some California crudes.

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:

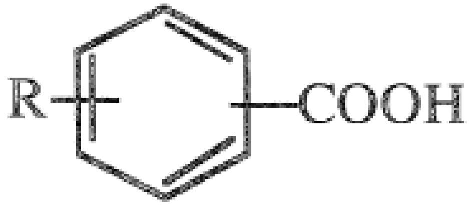
Acidic Oxygen Compounds

$CH_3(CH_2)_nCOOH$

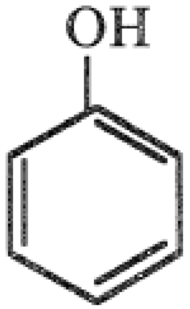
An aliphatic carboxylic acid



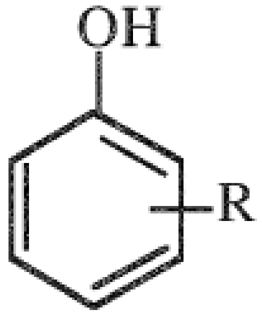
Cyclohexane carboxylic acid



Aromatic acids



Phenol



Cresylic acid