DKK 3343

Gas Technology & Petroleum Refining

- **Instructor**: Engr. Mohd. Kamaruddin Abd. Hamid

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- **Meeting Time:** 1630-1930 Saturday
1130-1530 Sunday

Venue: P402, UTM City Campus, Jalan Semarak
Kuala Lumpur

Instructor's Background….

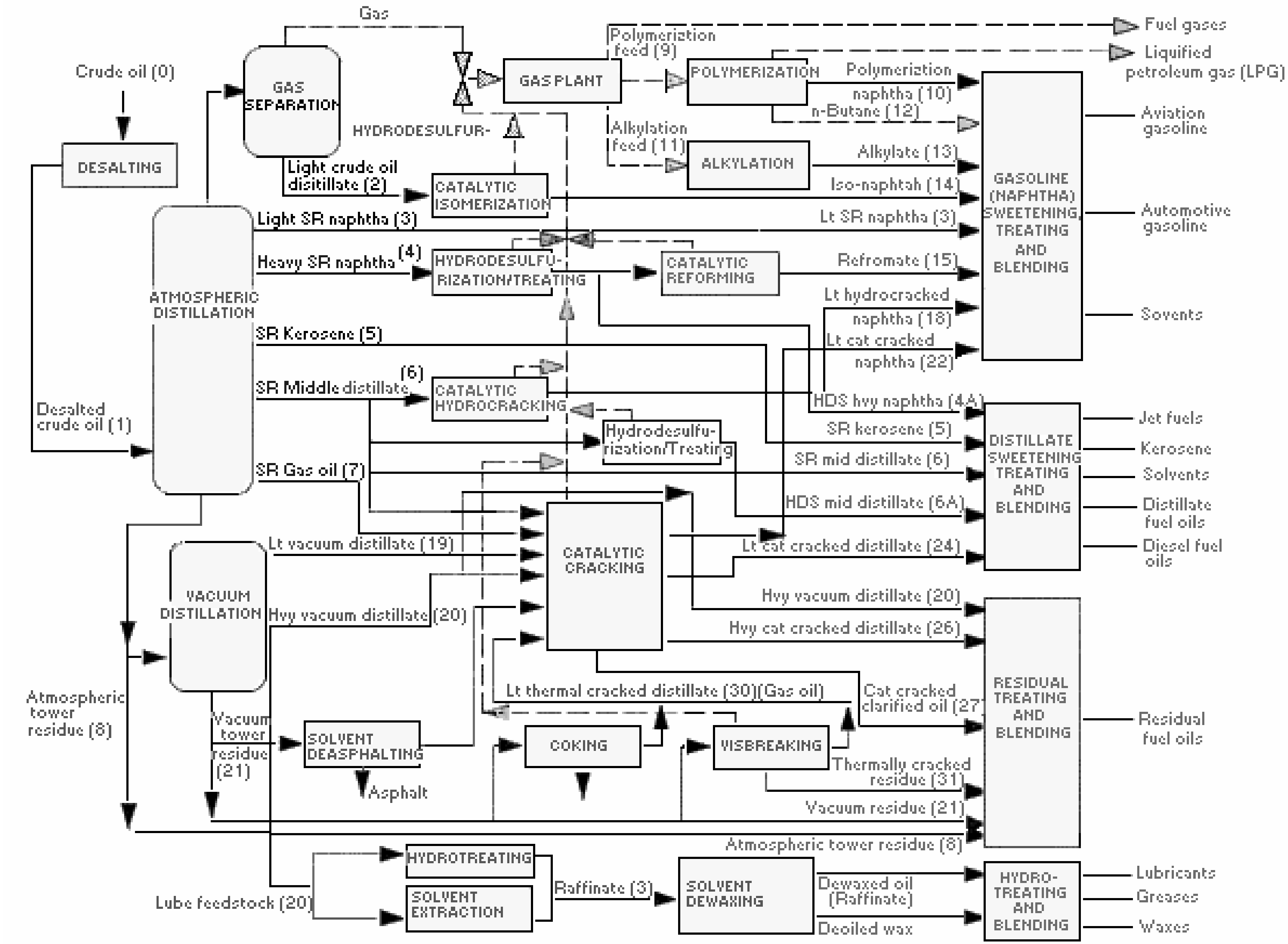
Education

- B.Eng. (Chemical with Honors): Universiti Teknologi Malaysia (2001)
- M.Eng. (Chemical): Universiti Teknologi Malaysia (2003)

Specialization

- Process Modelling, Simulation and Control; Neural Network Modelling, Fault Detection and Diagnosis

Course Synopsis

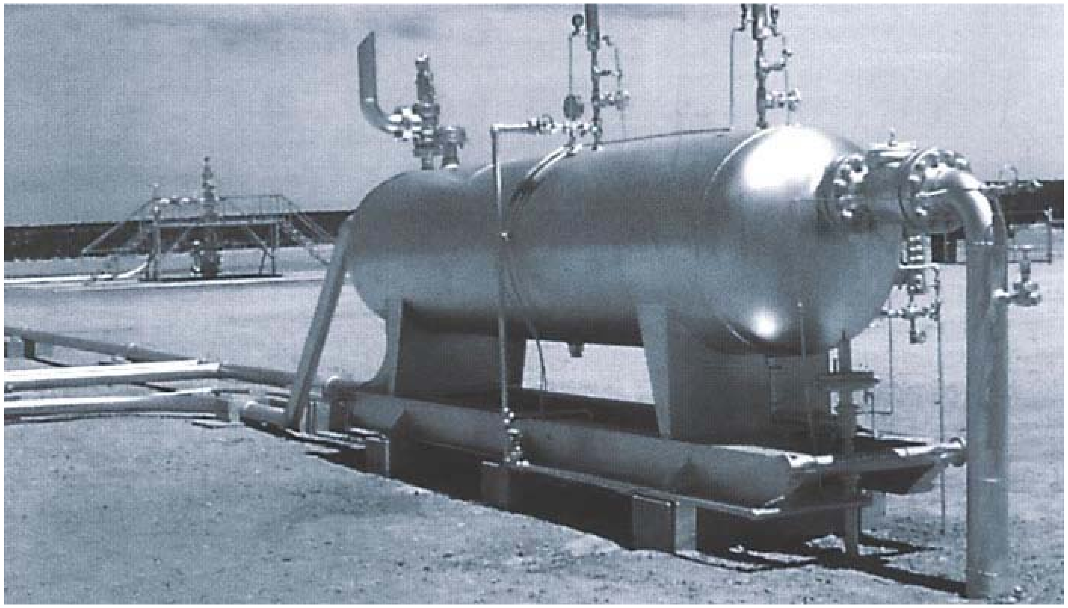


Course Syllabus
Part I: Background

1. Oil and Gas: From Formation to Production
2. Crude Oils, Hydrocarbons, and Refinery Products
3. Basic Refinery Process: Description and History

Course Syllabus
Part II: Separation of Produced Fluids

1. Two-Phase Gas-Oil Separation
2. Three-Phase Oil-Water-Gas Separation



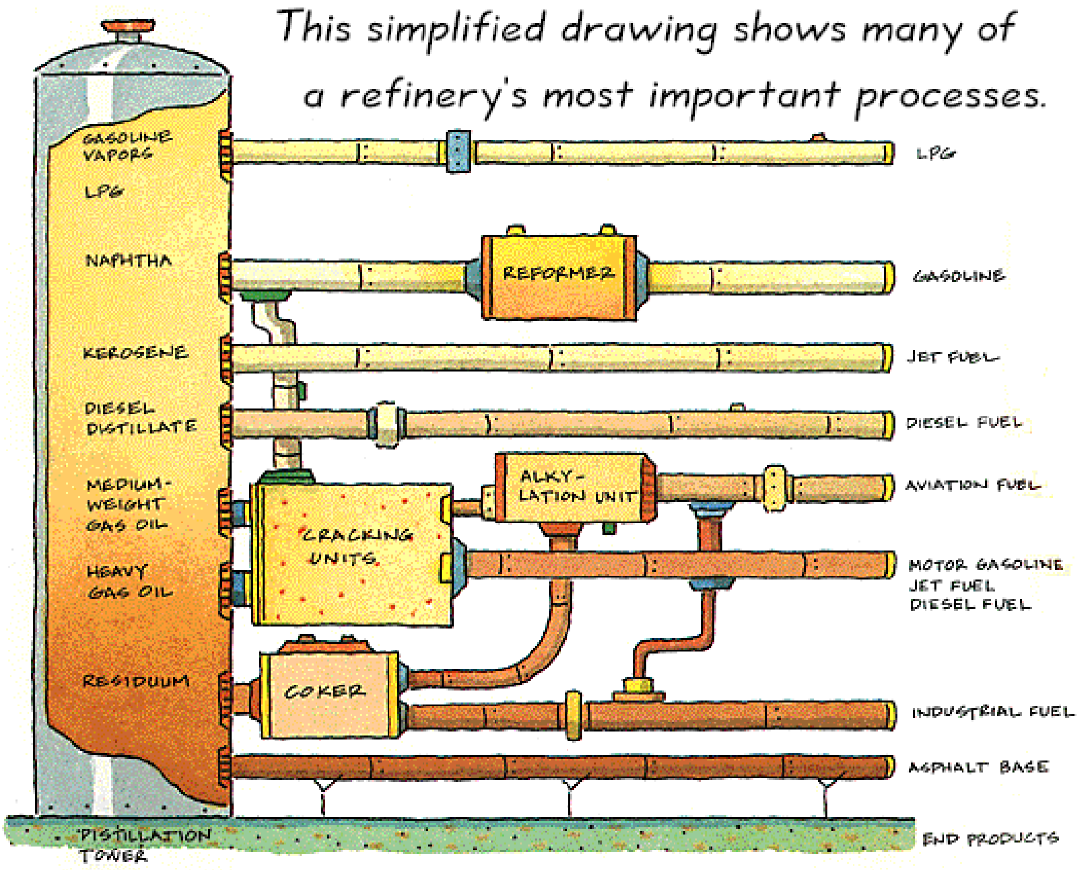
Course Syllabus
Part III: Treatment of Crude Oil

1. Emulsion Treatment and Dehydration of Crude Oil
2. Desalting of Crude Oil
3. Crude Oil Stabilization and Sweetening

Course Syllabus
Part IV: Field Processing and Treatment of Natural Gas

1. Overview of Gas Field Processing
2. Sour Gas Treating
3. Gas Dehydration
4. Recovery, Separation, and Fractionation of Natural Gas Liquids

Course Syllabus
Part V: Petroleum Refinery Process



This simplified drawing shows many of a refinery's most important processes.

1. Crude Oil Processing
2. Residual Oil Processing
3. Heavy Distillate Processing
4. Light Distillate Processing
5. Light Hydrocarbon Processing
6. Oxygenates
7. Treating and Other Auxiliary Processes
8. Product Blending

Reference Texts

1. Robert A. Meyers, *Handbook of Petroleum Refining Processes (3rd Edition)*, McGraw Hill, 2004.
2. Robert E. Maples, *Petroleum Refinery Process Economics (2nd Edition)*, PennWell Corp., 2000.
3. H.K. Abdel-Aal, Mohamed Aggour, M.A. Fahim, *Petroleum and Gas Field Processing*, Marcel Dekker, 2003.
4. Ozren Ocic, *Oil Refineries in the 21st Century*, John Wiley, 2005.

Teaching Methodology & Assessment

Process Control & Safety

- ❑ Teaching Methodology:
  - ✓ Lectures
  - ✓ Cooperative Learning
  - ✓ Group Project

- ❑ Assessment:
  - ✓ Test 1 : 15%
  - ✓ Test 2 : 15%
  - ✓ Final Test : 30%
  - ✓ Project : 30%
  - ✓ Attendance & Participation: 10%

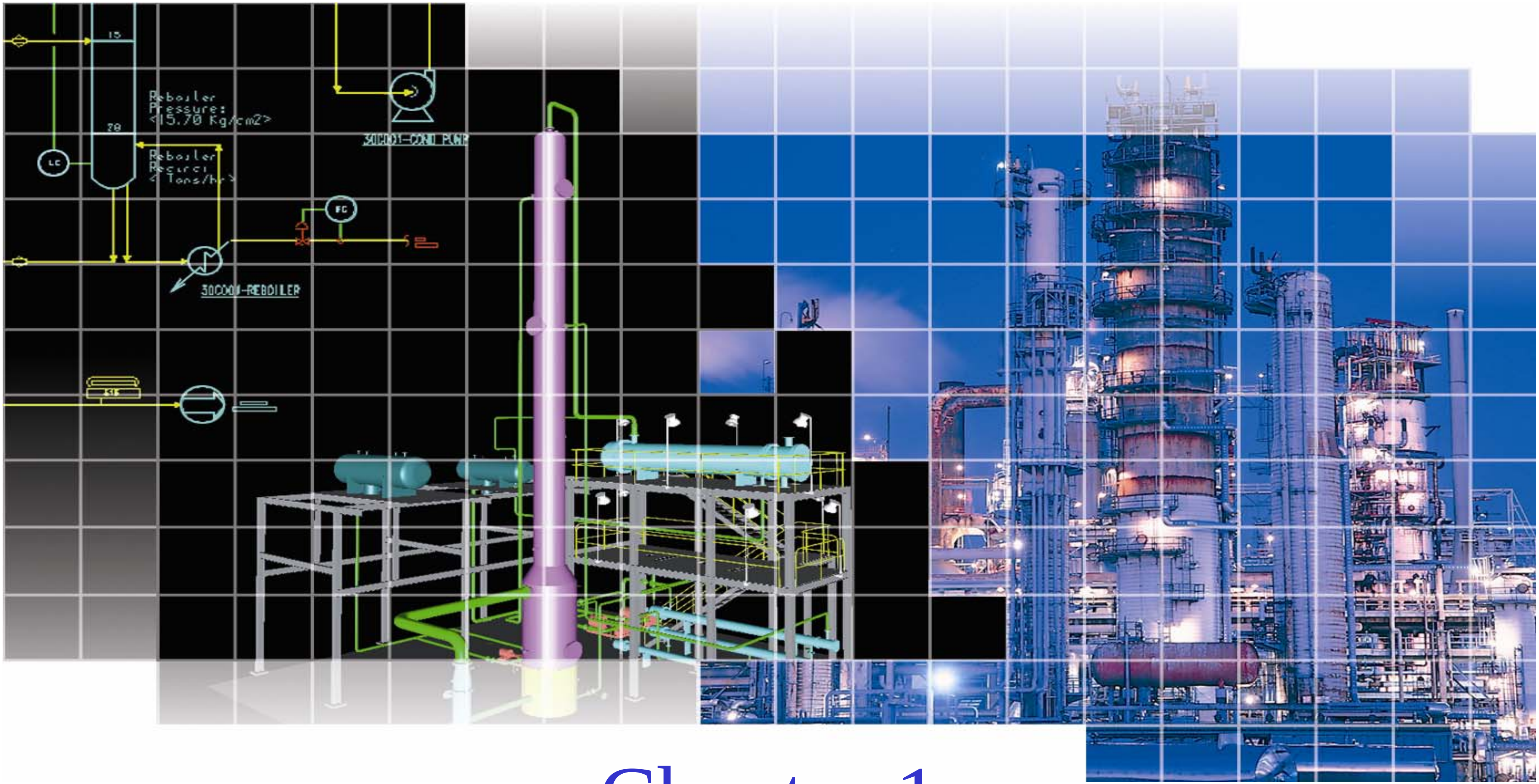
Please Read This Slide!

Process Control & Safety

It is very important that each student attend **every** class for the following reasons:

- This is a short (6-week) course with a total of 12 classes. Each missed class represents 8% of the material covered!

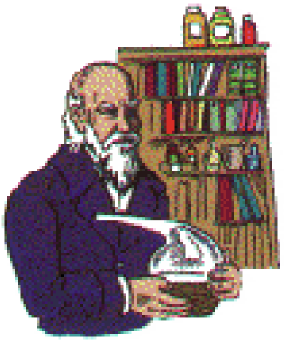
- Each class builds on the material learned from the previous class. A clear understanding of the material covered in each class will ensure that the student is prepared to understand the material that will be covered in the following class.



Chapter 1

Oil and Gas: From Formation to Production

Introduction



Samuel Kier converted petroleum to lamp oil by distillation. Early 1800s

- What is crude oil?
  - A complex mixture of hydrocarbons with minor proportions of other chemicals such as S, N and O.
  - To use the different parts of the mixture, they must be separated – refining.
  - Crude oil vary from light coloured volatile liquids to thick, dark oils-so viscous that difficult to pump.

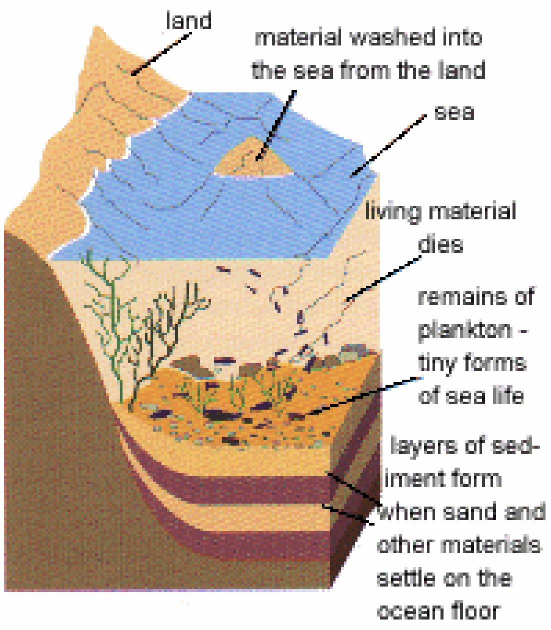
- What is natural gas?
  - A mixtures of hydrocarbons with small molecules.
  - These molecules are made of atoms of C and H i.e. CH_4.

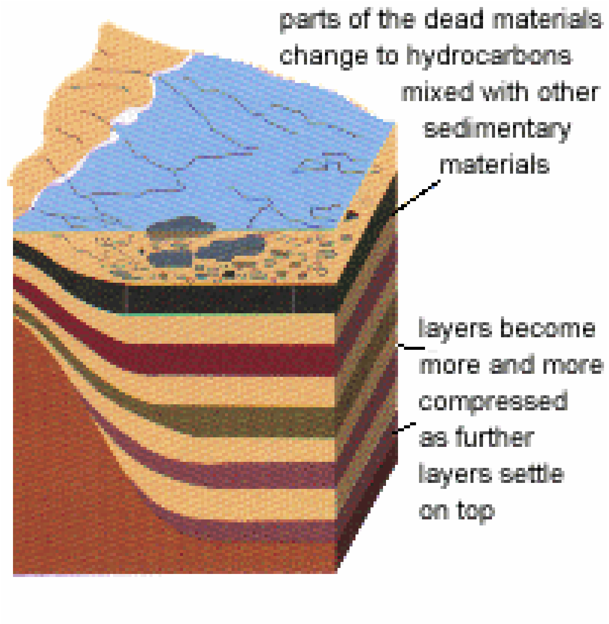
Introduction (cont.)

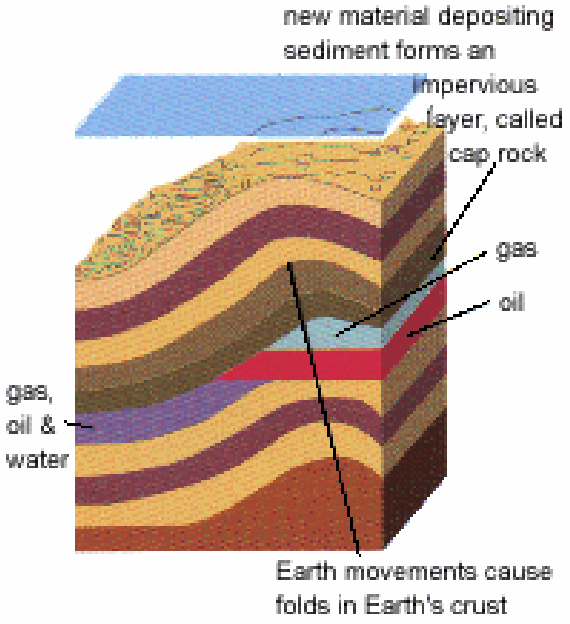
- Why are oil and gas so useful?
  - Oil is a liquid. Meaning that oil may be transported and delivered through pipes.
  - Compare oil to coal-coal is a solid, which comes in lumps. To get it, miners have to work underground.
  - HC with small molecules make good fuels. Methane (smallest molecules, gas) used for cooking, heating and generating electricity. Gasoline, diesel, jet fuel and fuel oil are all liquid fuels.
  - HC molecules can be split up into small ones, built up into bigger ones, altered in shape or modified by adding other atoms.
  - Even the thick black tarry residue left after distillation is useful – bitumen (for road surfacing and roofing).

Formation of Oil and Gas

- Where have crude oil and natural gas come from?

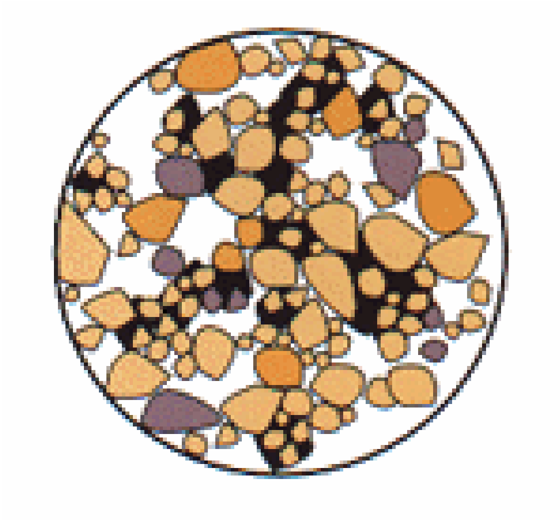


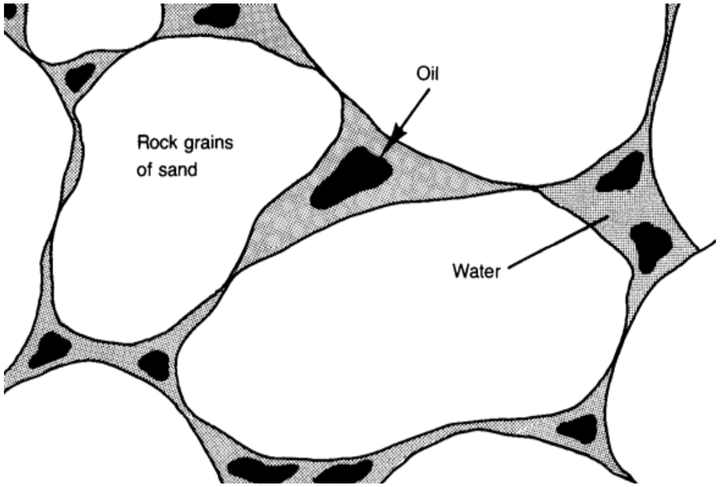




Accumulation of Oil and Gas

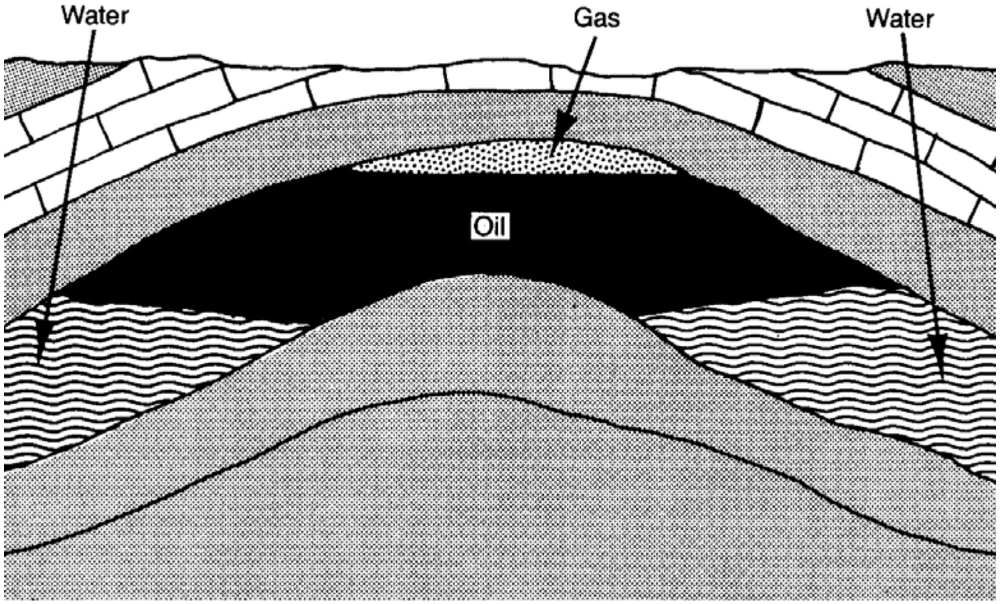
- The oil, gas, and salt water occupied the pore spaces between the grains of the sandstones.
- Whenever these rocks were sealed by a layer of impermeable rock, the *cap rock*, the petroleum accumulating within the pore spaces of the source rock was trapped and formed the petroleum reservoir.





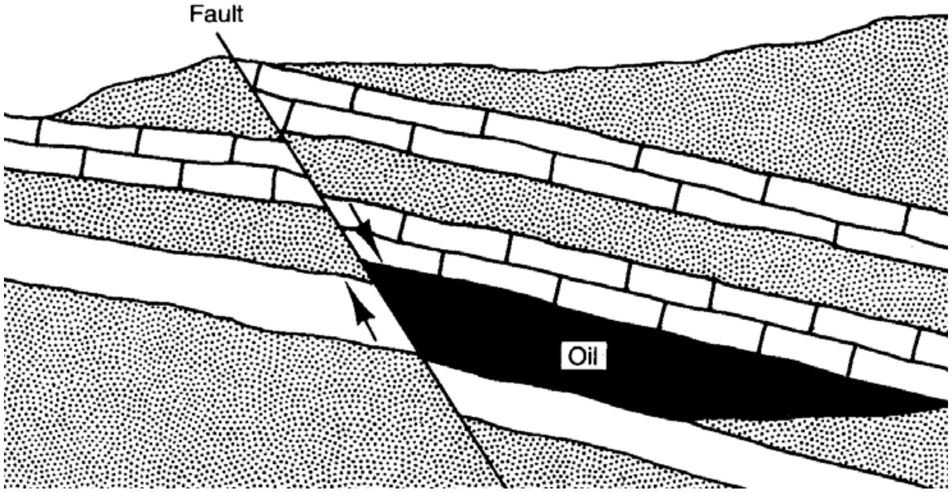
Types of Petroleum Reservoir

- Dome-Shaped and Anticline Reservoirs:
  - These reservoirs are formed by the folding of the rock layer.
  - The dome is circular in outline, and the anticline is long and narrow.
  - Oil and/or gas moved upward through the porous strata where it was trapped by the sealing cap rock and the shape of the structure.

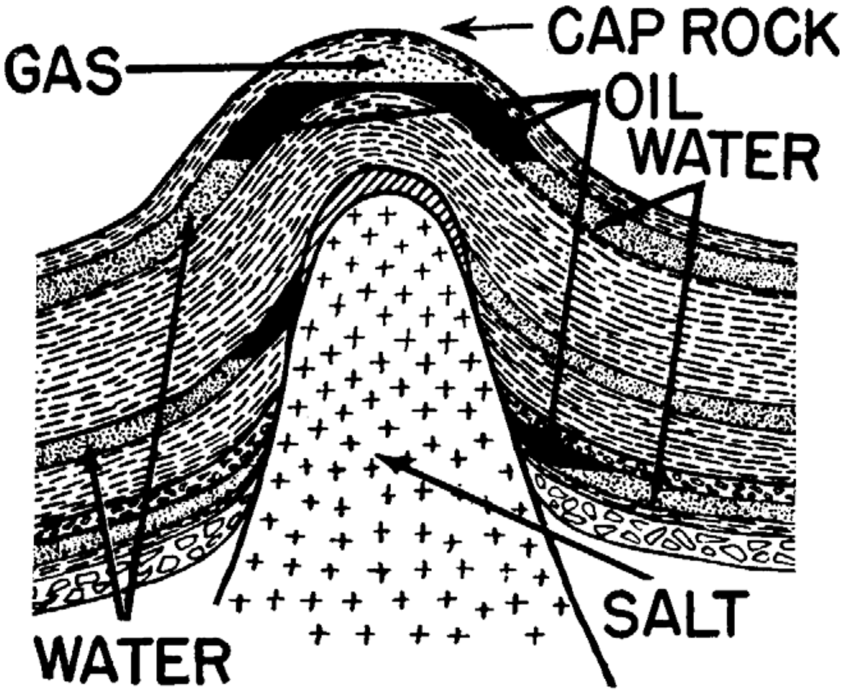


Types of Petroleum Reservoir (cont.)

- Faulted Reservoirs:
  - These reservoirs are formed by shearing and offsetting of the strata (faulting).
  - The movement of the nonporous rock opposite the porous formation containing the oil/gas creates the sealing.
  - The tilt of the petroleum-bearing rock and the faulting trap the oil/gas in the reservoir.



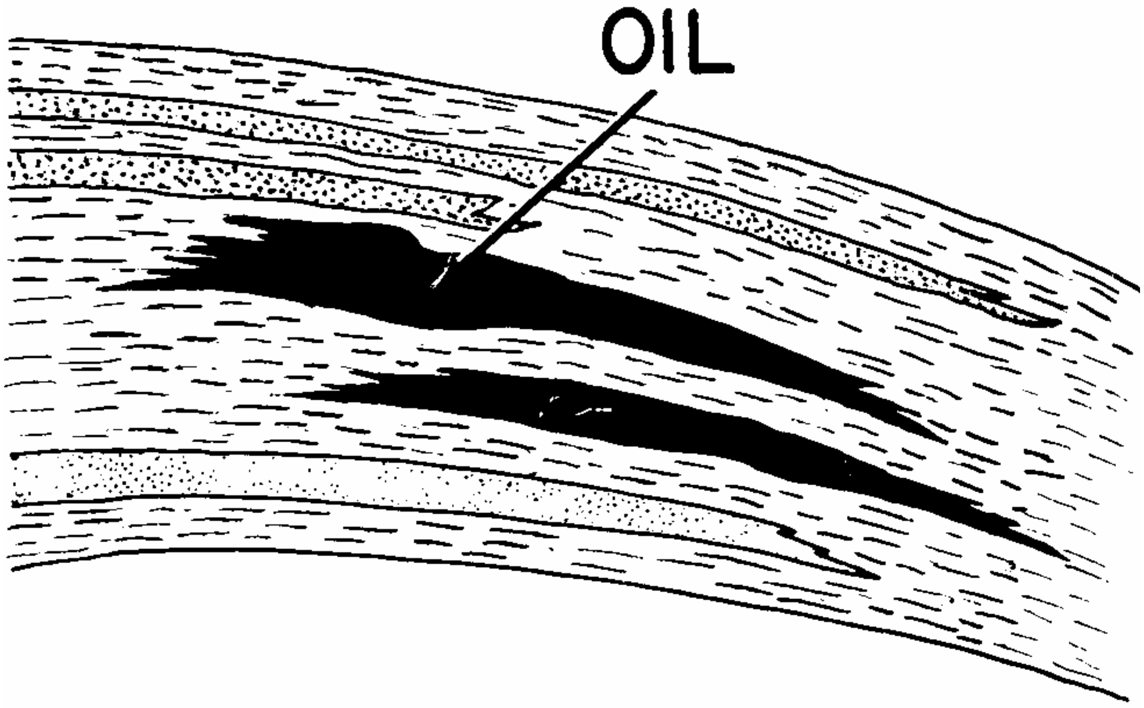
Types of Petroleum Reservoir (cont.)



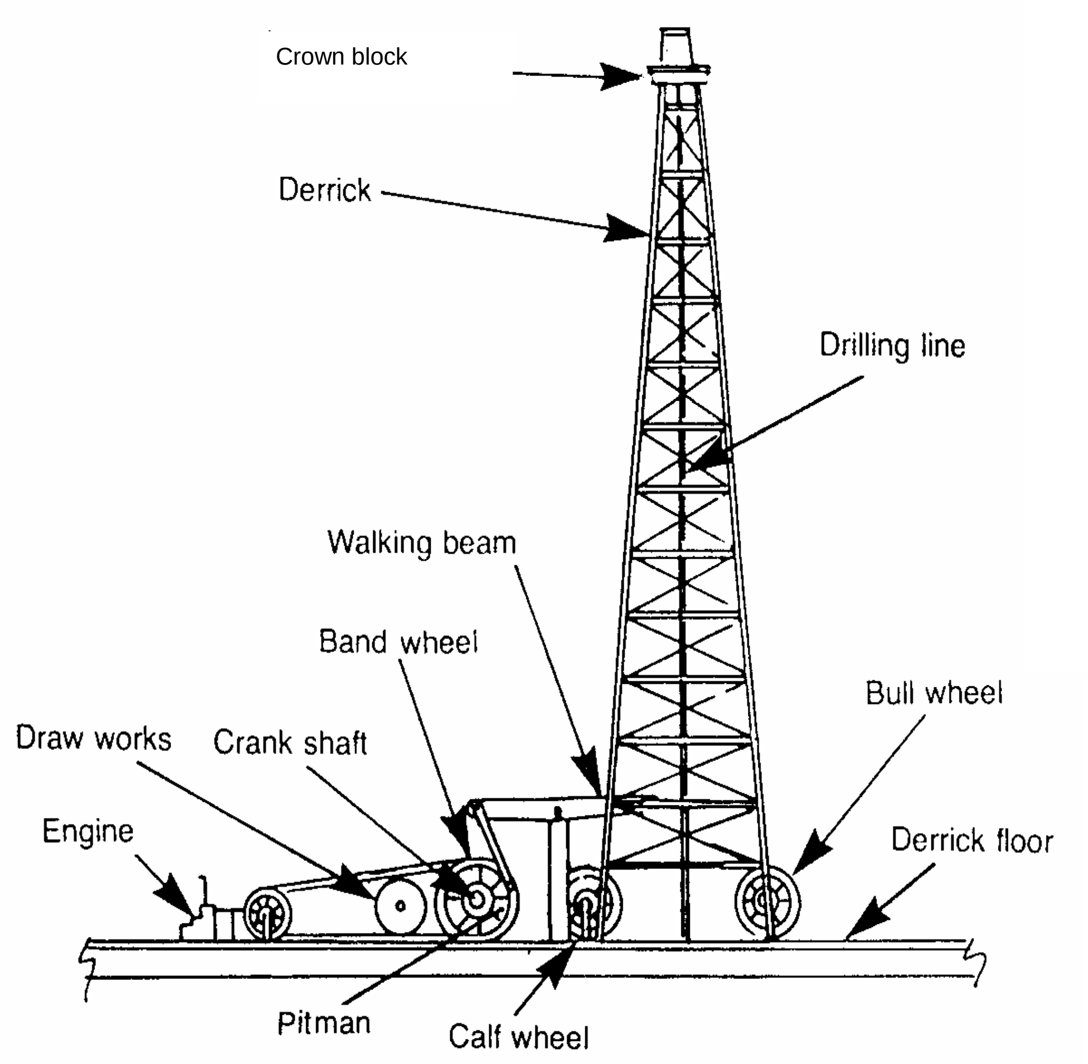
- Salt-Dome Reservoirs:
  - This type of reservoir structure, which takes the shape of a dome, was formed due to the upward movement of large, impermeable salt dome that deformed and lifted the overlying layers of rock.
  - Petroleum is trapped between the cap rock and the underlying impermeable rock layer, or between two impermeable layers of rock and the salt dome.

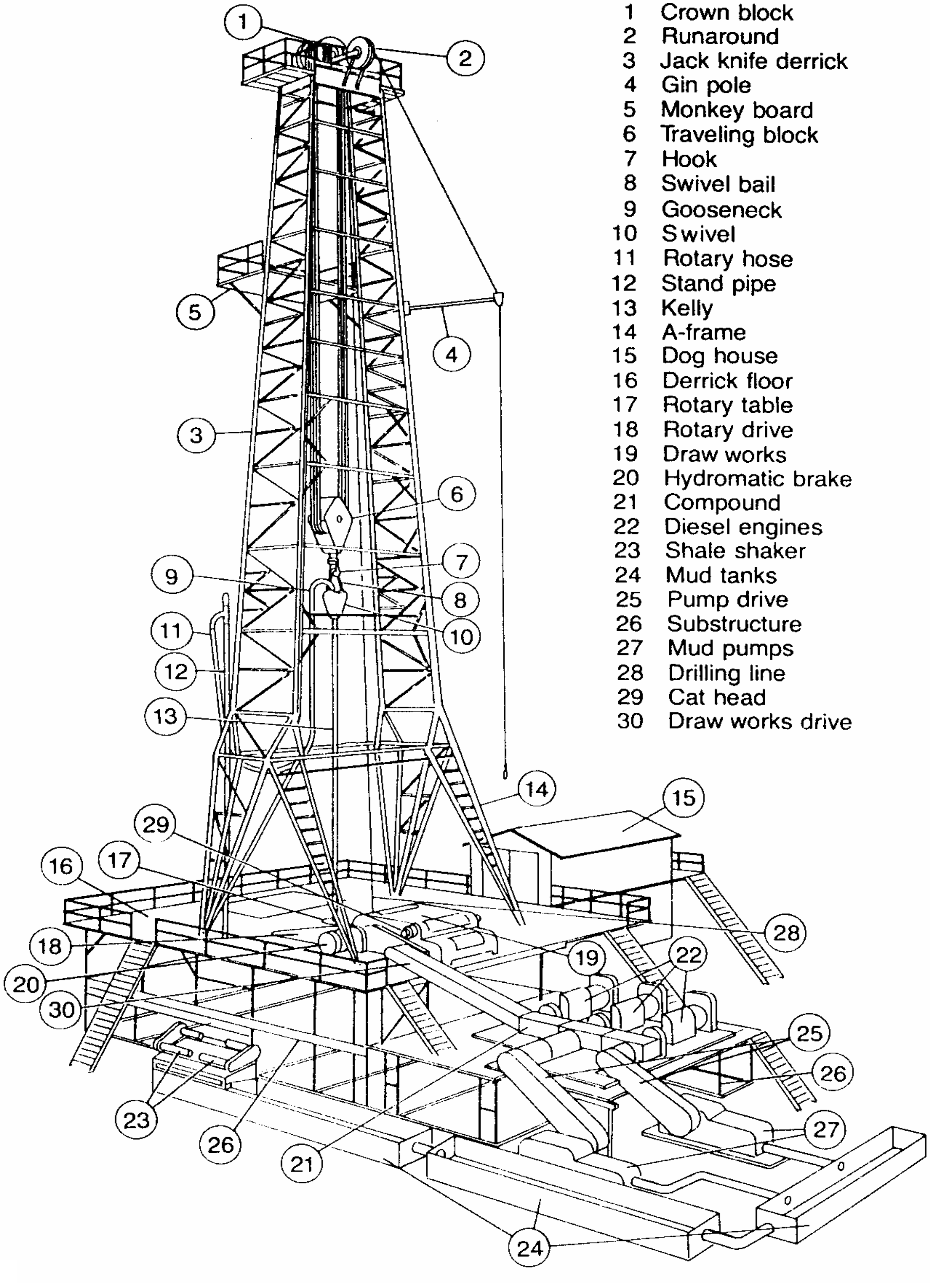
Types of Petroleum Reservoir (cont.)

- Lense-Type Reservoirs:
  - In this type of reservoir, the petroleum-bearing porous formation is sealed by the surrounding, nonporous formation.

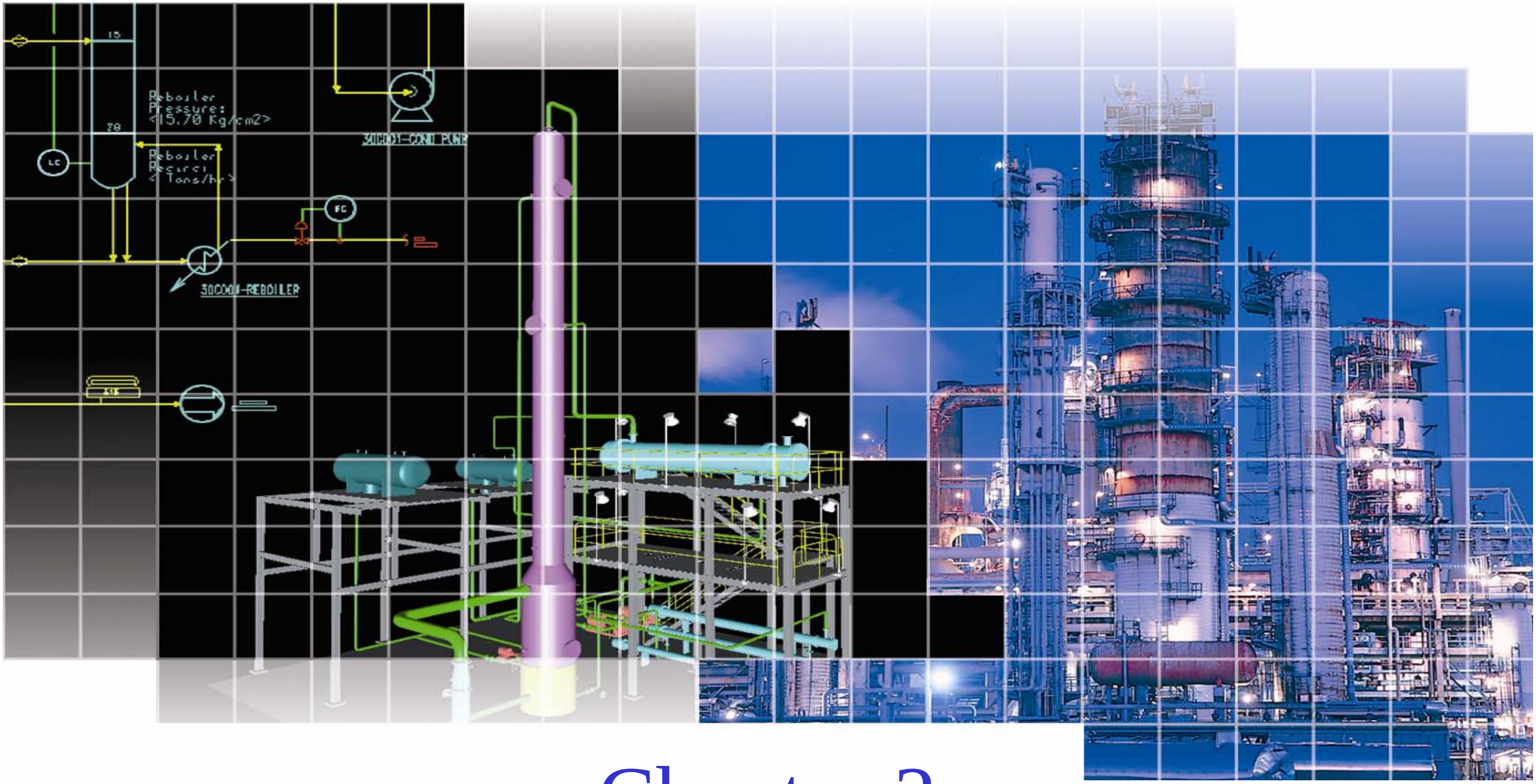


Drilling the Well





1	Crown block
2	Runaround
3	Jack knife derrick
4	Gin pole
5	Monkey board
6	Traveling block
7	Hook
8	Swivel bail
9	Gooseneck
10	Swivel
11	Rotary hose
12	Stand pipe
13	Kelly
14	A-frame
15	Dog house
16	Derrick floor
17	Rotary table
18	Rotary drive
19	Draw works
20	Hydromatic brake
21	Compound
22	Diesel engines
23	Shale shaker
24	Mud tanks
25	Pump drive
26	Substructure
27	Mud pumps
28	Drilling line
29	Cat head
30	Draw works drive



Chapter 2

Crude Oils, Hydrocarbons and Refinery Products

Basics of Crude Oil

- Crude oils are complex mixtures containing many different HC compounds that vary in appearance and composition from one oil field to another.
- Crude oils range in consistency from water to tar-like solids, and in color from clear to black.
- An “average” crude oil contains about 84% C, 14% H, 1%-3% S, and less 1% each of N, O, metals and salts.
- Crude oils are generally classified as paraffinic, naphthenic, or aromatic, based on the predominant proportion of similar HC molecules.
- Crude oils are defined in terms of API (American Petroleum Institute) gravity. The higher the API, the lighter the crude.
- Crude oils that contain appreciable quantities of hydrogen sulfide or other reactive sulfur compounds are called “sour”.
- Those with less sulfur are called “sweet”

TABLE IV: 2-2. TYPICAL APPROXIMATE CHARACTERISTICS AND PROPERTIES AND GASOLINE POTENTIAL OF VARIOUS CRUDES

(Representative average numbers)

Crude source	Paraffins (% vol)	Aromatics (% vol)	Naphthenes (% vol)	Sulfur (% wt)	API gravity (approx.)	Napht. yield (% vol)	Octane no (typical)
Nigerian -Light	37	9	54	0.2	36	28	60
Saudi -Light	63	19	18	2	34	22	40
Saudi -Heavy	60	15	25	2.1	28	23	35
Venezuela -Heavy	35	12	53	2.3	30	2	60
Venezuela -Light	52	14	34	1.5	24	18	50
USA -Midcont. Sweet	-	-	-	0.4	40	-	-
USA -W. Texas Sour	46	22	32	1.9	32	33	55
North Sea -Brent	50	16	34	0.4	37	31	50

Basics of Hydrocarbon Chemistry

- Crude oil is a mixture of HC molecules that may include from one to 60 carbon atoms.
- The property of HCs depend on the number and arrangement of the C and H atoms in the molecules.
- The simplest HC molecule is methane (CH_4).
- HCs containing up to four C atoms are usually gases, 5-19 C atoms are liquids, and with 20 or more are solids.
- The refining process uses chemicals, catalysts, heat, and pressure to separate and combine the basic types of HC molecules naturally found in crude oil into groups of imilar molecules.
- The refining process also rearranges their structures and bonding patterns into different HC molecules and compounds.
- Three principal groups or series of HC compounds that occur naturally in crude oil are paraffins, aromatics and naphthenes.

Paraffins

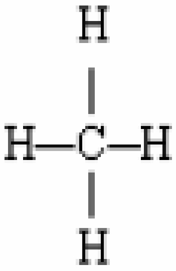
- The paraffinics series of HC compounds found in crude oil have the general formula C_nH_{2n+2} and can be either straight chains (normal) or branched chains (isomers).
- The lighter, straight-chain paraffin molecules are found in gases and paraffin waxes (methane, ethane, propane and butane; pentane and hexane).
- The branched-chain (isomer) paraffins are usually found in heavier fractions of crude oil and have higher octane number than normal paraffins.
- These compounds are saturated HCs, with all C bonds satisfied, that is, the HC chain carries the full complement of H atoms.

FIGURE IV:2-1. TYPICAL PARAFFINS.

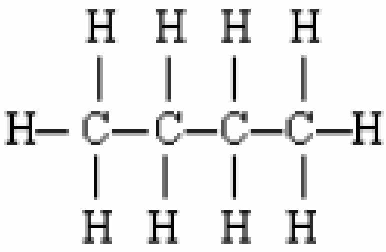
Example of simplest HC molecule (CH_4):

Examples of straight chain paraffin molecule (Butane) and branched paraffin molecule (Isobutane) with same chemical formula (C_4H_{10}):

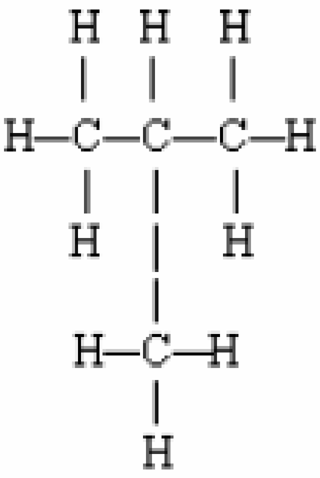
METHANE (CH_4)



BUTANE (C_4H_{10})



ISOBUTANE (C_4H_{10})



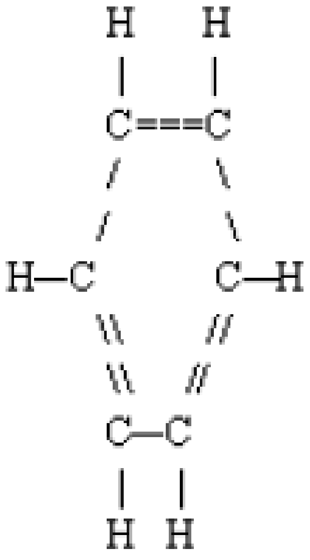
Aromatics

- Aromatics are unsaturated ring-type (cyclic) compounds which react readily because they have C atoms that are deficient in H.
- All aromatics have at least one benzene ring as part of their molecular structure.
- Naphthalenes are fused double-ring aromatic compounds.
- The most complex aromatics, polynuclears (three or more fused aromatic ring), are found in heavier fractions of crude oil.

FIGURE IV:2-2. TYPICAL AROMATICS.

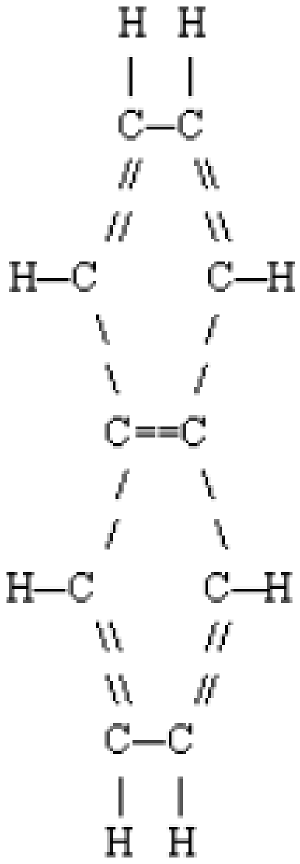
Example of simple aromatic compound:

BENZENE (C_6H_6)



Examples of simple double-ring aromatic compound:

NAPTHALENE ($C_{10}H_8$)



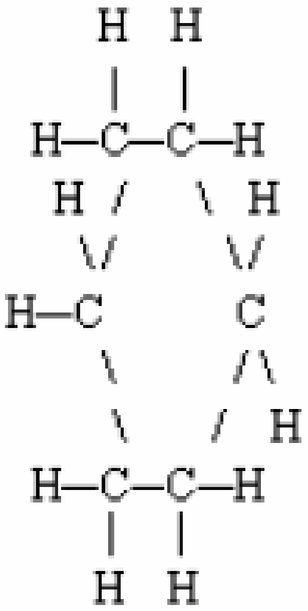
Naphthenes

- Naphthenes are saturated hydrocarbon groupings with the general formula C_nH_{2n}, arranged in the form of closed rings (cyclic).
- Naphthenes are usually found in all fractions of crude oil except the very lightest.
- Single-ring naphthenes (monocycloparaffins) with five and six C atoms predominate, with two-ring naphthenes (dicycloparaffins) found in the heavier ends of naphtha.

FIGURE IV:2-3. TYPICAL NAPHTHENES.

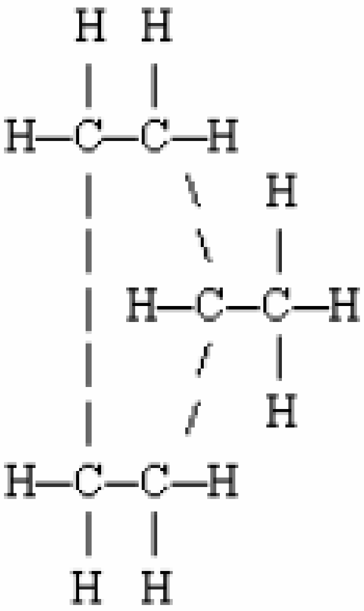
Example of typical single-ring naphthene:

CYCLOHEXANE (C_6H_{12})



Examples of naphthene with same chemical formula (C_6H_{12}) but different molecular structure:

METHYL CYCLOPENTANE (C_6H_{12})



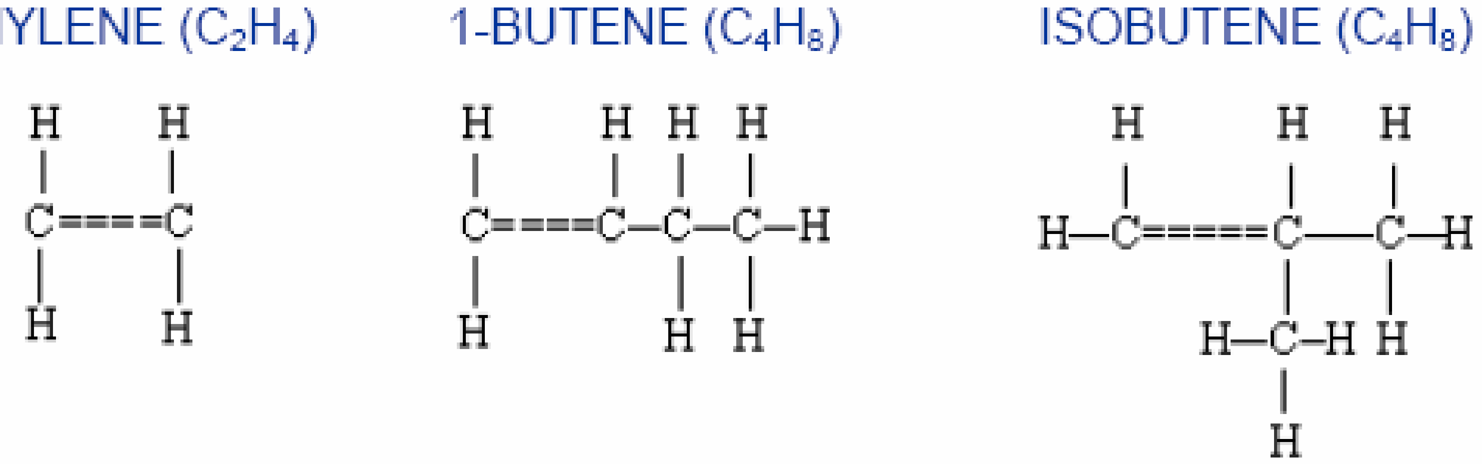
Other Hydrocarbons: Alkenes

- Alkenes are mono-olefins with the general formula C_nH_{2n} and contain only one C=C double bond in the chain.
- The simplest alkene is ethylene, with two C atoms joined by a double bond and four H atoms.
- Olefins are usually formed by thermal and catalytic cracking and rarely occur naturally in unprocessed crude oil.

FIGURE IV:2-4. TYPICAL ALKENES.

Simplest Alkene (C_2H_4):

Typical Alkenes with the same chemical formula (C_4H_8) but different molecular structures:



ETHYLENE (C_2H_4)

1-BUTENE (C_4H_8)

ISOBUTENE (C_4H_8)

Other Hydrocarbons: Dienes and Alkynes

- Dienes, also known as diolefins, have two C=C double bonds.
- The alkynes, another class of unsaturated HCs, have a C-C triple bond within the molecule.
- Both these series of HCs have the general formula C_nH_{2n-2}.
- Diolefins such as 1,2-butadiene and 1,3-butadiene, and alkynes such as acetylene, occur in C_5 and lighter fractions from cracking.
- The olefins, diolefins and alkynes are said to be unsaturated because they contain less than the amount of H necessary to saturate all the valences of the C atoms.
- These compounds are more reactive than paraffins or naphthenes and readily combine with other elements such as H, Cl and Br.

FIGURE IV:2-5. TYPICAL DIOLEFINS AND ALKYNES.

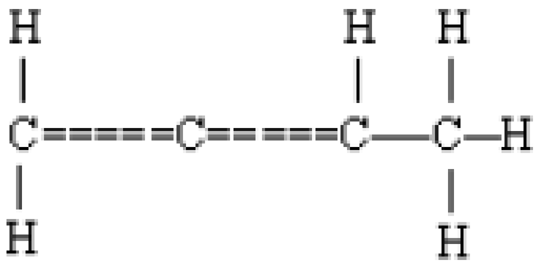
Simplest Alkyne:
(C_2H_2):

Typical Diolefins with the same chemical formula
(C_4H_6) but different molecular structures:

ACETYLENE (C_2H_2)

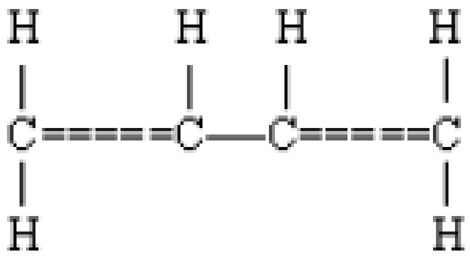
$H-C\equiv C-H$

1,2-BUTADIENE (C_4H_6)



$H_2C=C=CH-CH_3$

1,3-BUTADIENE (C_4H_6)



$H_2C=CH-CH=CH_2$

Nonhydrocarbons

- Sulfur Compounds:
  - Sulfur may be present in crude oil as hydrogen sulfide (H_2S), as compounds (e.g. mercaptans, sulfides, disulfides, thiophenes, etc.) or as element sulfur.
  - H_2S is a primary contributor to corrosion in refinery processing units.
- Oxygen Compounds:
  - Oxygen compounds such as phenols, ketones, and carboxylic acids occur in crude oil in varying amounts.
- Nitrogen Compounds:
  - Nitrogen is found in lighter fractions of crude oil as basic compounds.
- Trace Metals:
  - Metals, including nickel, iron and vanadium are often found in crude oils in small quantities and are removed during the refining process.
- Salts:
  - Crude oils often contain inorganic salts such as sodium chloride, magnesium chloride and calcium chloride in suspension or dissolved in entrained water.
- Carbon Dioxide:
  - Carbon dioxide may result from the decomposition of bicarbonates present in or added to crude, or from steam used in the distillation process.

Major Refinery Products

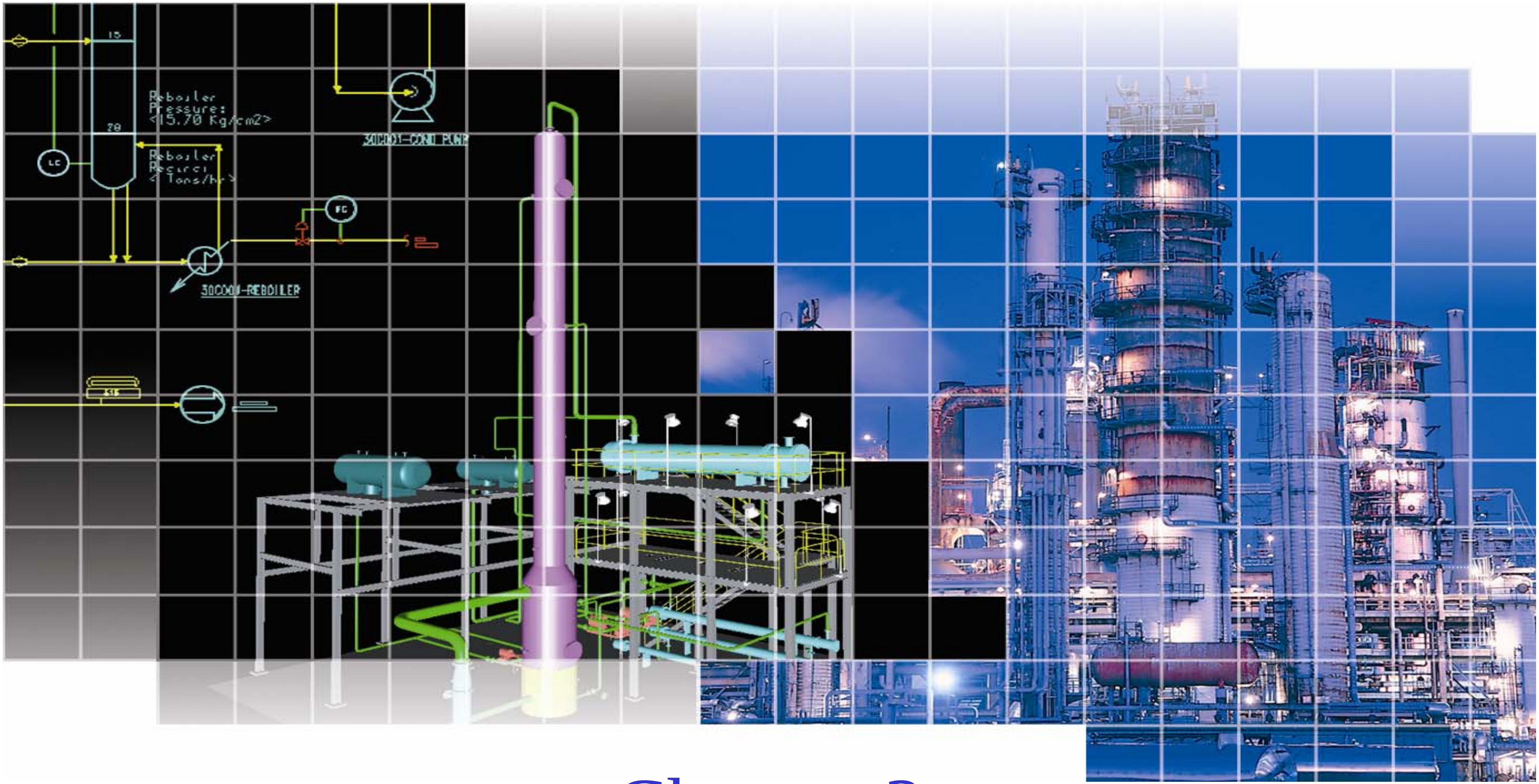
- **Gasoline**. The most important refinery product. The important qualities for gasoline are octane number (antiknock), volatility (starting and vapor lock), and vapor pressure (environmental control).
- **Kerosene**. Kerosene is a refined middle-distillate petroleum product that finds considerable use as a jet fuel and around the world in cooking and space heating. Kerosene, with less-critical specifications, is used for lighting, heating, solvents, and blending into diesel fuel.
- **Liquified Petroleum Gas (LPG)**. LPG, which consists principally of propane and butane, is produced for use as fuel and is an intermediate material in the manufacture of petrochemicals.
- **Distillate Fuels**. Diesel fuels and domestic heating oils have boiling ranges of about 400°-700° F.

Major Refinery Products

- **Residual Fuels**. Many marine vessels, power plants, commercial buildings and industrial facilities use residual fuels or combinations of residual and distillate fuels for heating and processing.
- **Coke and Asphalt**. Coke is almost pure carbon with a variety of uses from electrodes to charcoal briquets. Asphalt, used for roads and roofing materials.
- **Solvents**. These include benzene, toluene, and xylene.
- **Petrochemicals**. Ethylene, propylene, butylene, and isobutylene, are primarily intended for use as petrochemical feedstock in the production of plastics, synthetic fibers, synthetic rubbers, and other products.
- **Lubricants**. Special refining processes produce lubricating oil base stocks. Additives such as demulsifiers, antioxidants, and viscosity improvers are blended into the base stocks to provide the characteristics required for motor oils, industrial greases, lubricants, and cutting oils.

Common Refinery Chemicals

- **Leaded Gasoline Additives**. Tetraethyl lead (TEL) and tetramethyl lead (TML) are additives formerly used to improve gasoline octane ratings but are no longer in common use except in aviation gasoline.
- **Oxygenates**. Ethyl tertiary butyl ether (ETBE), methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), and other oxygenates improve gasoline octane ratings and reduce carbon monoxide emissions.
- **Caustics**. Caustics are added to desalting water to neutralize acids and reduce corrosion. They are also added to desalted crude in order to reduce the amount of corrosive chlorides in the tower overheads. They are used in some refinery treating processes to remove contaminants from hydrocarbon streams.
- **Sulfuric Acid and Hydrofluoric Acid**. Sulfuric acid and hydrofluoric acid are used primarily as catalysts in alkylation processes. Sulfuric acid is also used in some treatment processes.



Chapter 3

Basic Refinery Process: Description and History

Introduction

- Petroleum refining has evolved continuously in response to changing consumer demand for better and different products.
- The original requirement was to produce kerosene as a cheaper and better source of light than whale oil.
- The development of the internal combustion engine led to the production of gasoline and diesel fuels.
- The evolution of the airplane created a need first for high-octane aviation gasoline and then for jet fuel, a sophisticated form of the original product, kerosene.
- Present-day refineries produce a variety of products including many required as feedstock for the petrochemical industry.

Distillation Processes

- The first refinery, opened in 1861, produced kerosene by simple atmospheric distillation.
- Its by-products included tar and naphtha.
- It was soon discovered that high quality lubricating oils could be produced by distilling petroleum under vacuum.
- However, for the next 30 years kerosene was the product consumers wanted.
- Two significant events changed this situation: (1) invention of the electric light decreased the demand for kerosene, and (2) invention of the internal combustion engine created a demand for diesel fuel and gasoline (naphtha).

Thermal Cracking Processes

- With the advent of mass production and World War I, the number of gasoline-powered vehicles increased dramatically and the demand for gasoline grew accordingly.
- However, distillation processes produced only a certain amount of gasoline from crude oil.
- In 1913, the thermal cracking process was developed, which subjected heavy fuels to both pressure and intense heat, physically breaking the large molecules into smaller ones to produce additional gasoline and distillate fuels.
- Visbreaking, another form of thermal cracking, was developed in the late 1930's to produce more desirable and valuable products.

Catalytic Processes

- Higher-compression gasoline engines required higher-octane gasoline with better antiknock characteristics.
- The introduction of catalytic cracking and polymerization processes in the mid- to late 1930's met the demand by providing improved gasoline yields and higher octane numbers.
- Alkylation, another catalytic process developed in the early 1940's, produced more high-octane aviation gasoline and petrochemical feedstock for explosives and synthetic rubber.

Catalytic Processes cont.

- Subsequently, catalytic isomerization was developed to convert hydrocarbons to produce increased quantities of alkylation feedstock.
- Improved catalysts and process methods such as hydrocracking and reforming were developed throughout the 1960's to increase gasoline yields and improve antiknock characteristics.
- These catalytic processes also produced hydrocarbon molecules with a double bond (alkenes) and formed the basis of the modern petrochemical industry.

Treatment Processes

- Throughout the history of refining, various treatment methods have been used to remove nonhydrocarbons, impurities, and other constituents that adversely affect the properties of finished products or reduce the efficiency of the conversion processes.
- Treating can involve chemical reaction and/or physical separation.
- Typical examples of treating are chemical sweetening, acid treating, clay contacting, caustic washing, hydrotreating, drying, solvent extraction, and solvent dewaxing.

Treatment Processes cont.

- Sweetening compounds and acids desulfurize crude oil before processing and treat products during and after processing.
- Following the Second World War, various reforming processes improved gasoline quality and yield and produced higher-quality products.
- Some of these involved the use of catalysts and/or hydrogen to change molecules and remove sulfur.

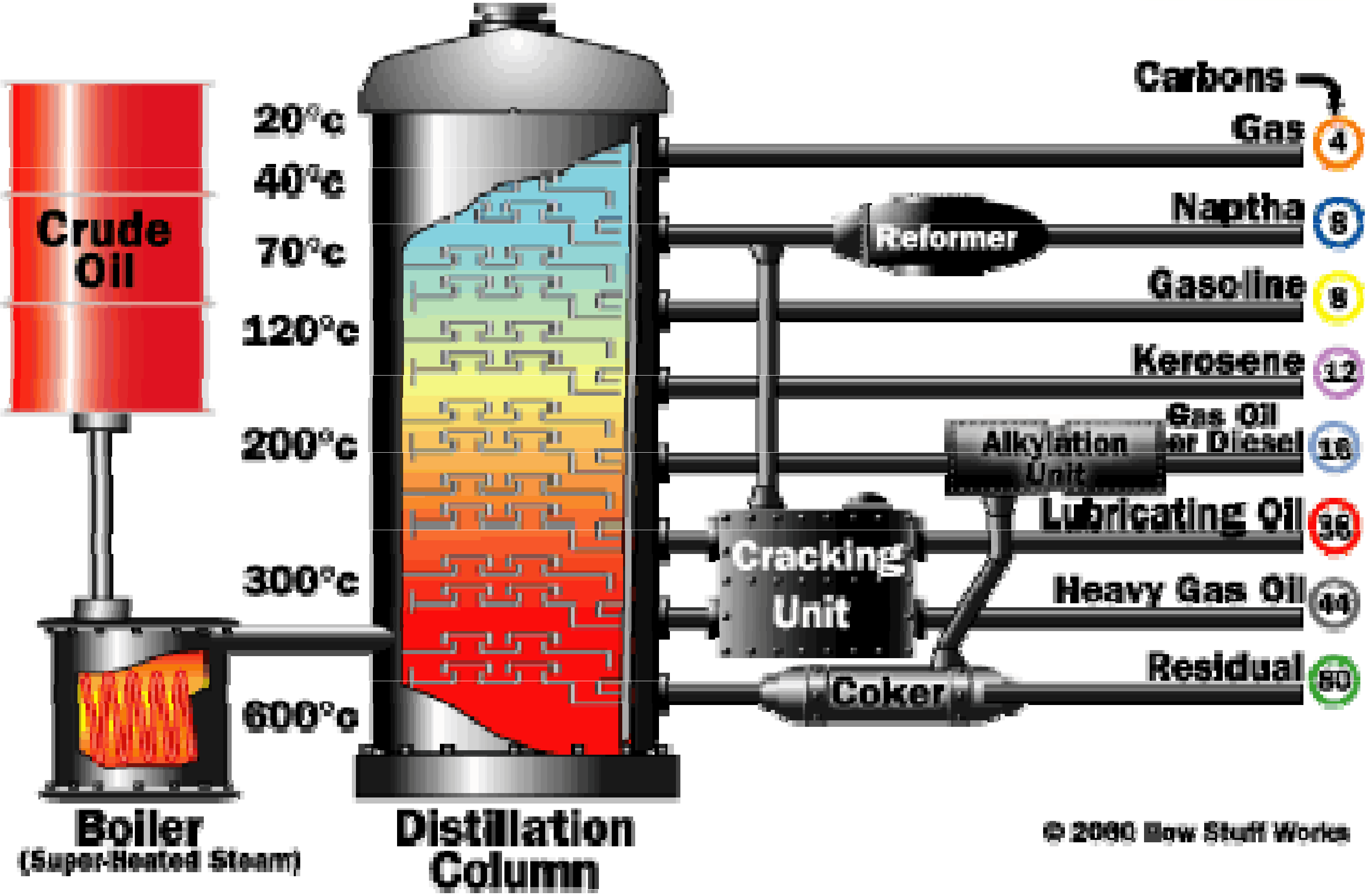


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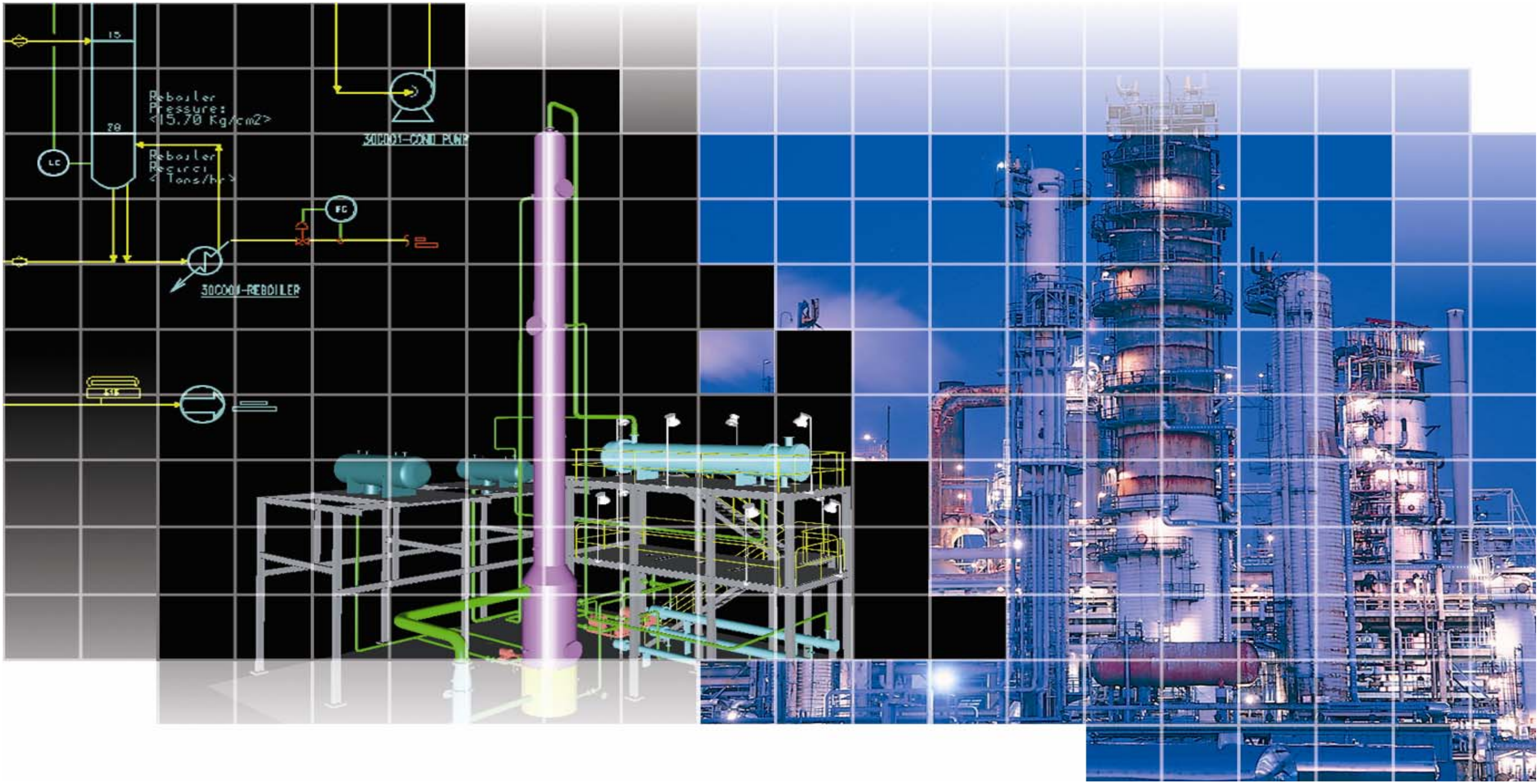
TABLE IV: 2-1. HISTORY OF REFINING

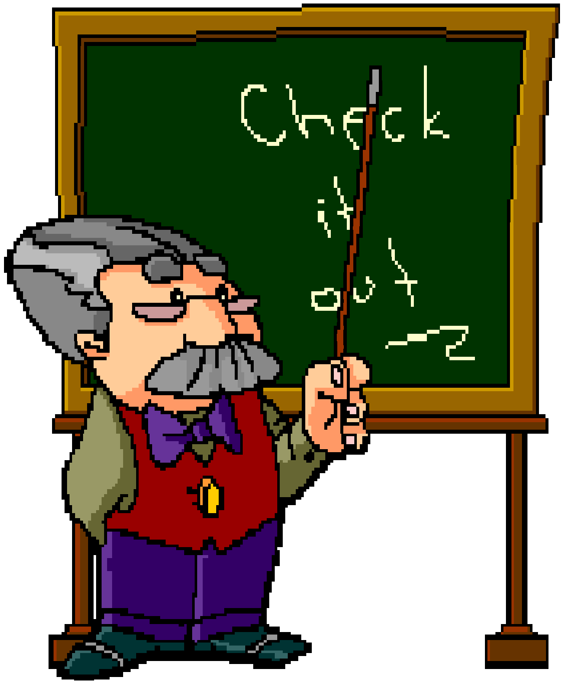
Year	Process name	Purpose	By-products, etc.
1862	Atmospheric distillation	Produce kerosene	Naphtha, tar, etc.
1870	Vacuum distillation	Lubricants (original) Cracking feedstocks (1930's)	Asphalt, residual coker feedstocks
1913	Thermal cracking	Increase gasoline	Residual, bunker fuel
1916	Sweetening	reduce sulfur & odor	Sulfur
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulfur	Sulfur
1932	Coking	Produce gasoline basestocks	Coke
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Solvent dewaxing	Improve pour point	Waxes
1935	Cat. polymerization	Improve gasoline yield & octane number	Petrochemical feedstocks
1937	Catalytic cracking	Higher octane gasoline	Petrochemical feedstocks
1939	Visbreaking	reduce viscosity	Increased distillate,tar
1940	Alkylation	Increase gasoline octane & yield	High-octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield & octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
1954	Hydrodesulfurization	Remove sulfur	Sulfur
1956	Inhibitor sweetening	Remove mercaptan	Disulfides
1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality and reduce sulfur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking	Increase gasoline yield from residual	Heavy residuals



Chapter 4

Two-Phase Gas-Oil Separation

Outline



- Introduction
- Gas-Oil Separation
- Theory of Gas-Oil Separation
- Stage Separation
- Gas-Oil Separator Equipment
- Test Separators
- Low-Temperature Separators
- Modern GOSPs

Introduction

- At the high pressure existing at the bottom of the producing well, crude oil contains great quantities of dissolved gases.
- When crude oil is brought to the surface, it is at a much lower pressure.
- Consequently, the gases that were dissolved in it at the high pressure tend to come out from the liquid.
- Some means must be provided to separate the gas from oil without losing too much oil.
- In general, well effluents flowing from producing wells come out in two phases: vapor and liquid under a relatively high pressure.
- The fluid emerges as a mixture of crude oil and gas that is partly free and partly in solution.
- Fluid pressure should be lowered and its velocity should be reduced in order to separate the oil and obtain it in a stable form.

Introduction (cont.)

- This is usually done by admitting the well fluid into a Gas-Oil Separator Plant (GOSP) through which the pressure of the gas-oil mixture is successively reduced to atmospheric pressure in a few stages.
- Upon decreasing the pressure in the GOSP, some of the lighter and more valuable hydrocarbon components that belong to oil will be unavoidably lost along with the gas into the vapor phase.
- This puts the gas-oil separation step as the initial one in the series of field treatment operations of crude oil.
- Here, the primary objective is to allow most of the gas to free itself from these valuable hydrocarbons, hence increasing the recovery of crude oil.

Gas-Oil Separation

- High-pressure crude oils containing large amount of free and dissolved gas.
- In the GOSP, crude oil separates out, settles, and collects in the lower part of the vessel.
- The gas, lighter than oil, fills the upper part of the vessel.
- Crude oils with a high gas-oil ratio (GOR) must go through two or more stages of separation.
- Gas goes out the top of the separators to a gas collection system, a vapor recovery unit (VRU), or a gas flow line.
- Crude oil, on the other hand, goes out the bottom and is routed to other stages of separation, if necessary, and then to the stock tank (Fig. 1).

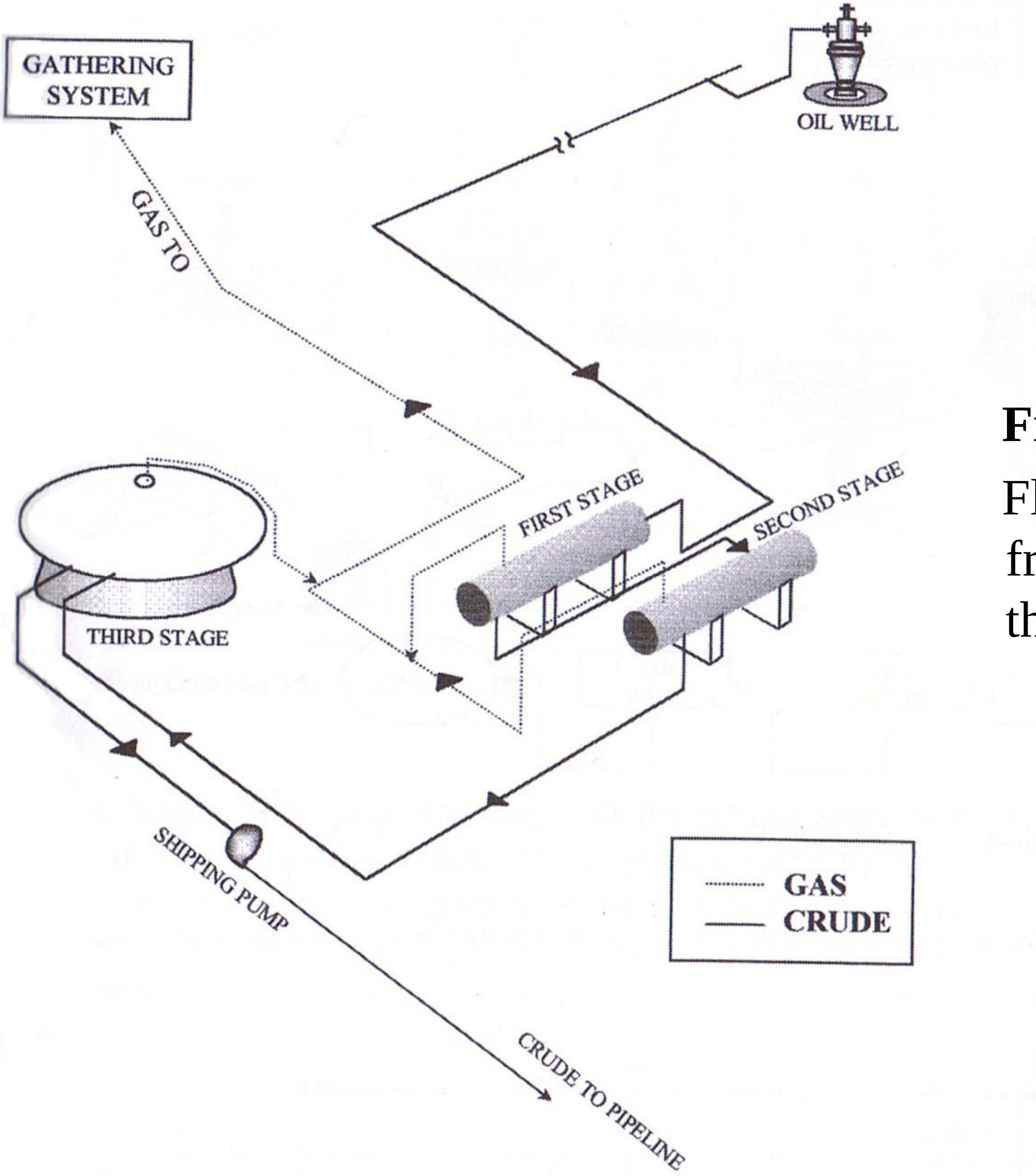


Figure 1

Flow of crude oil from oil well through GOSP.

Gas-Oil Separation (cont.)

- Movement of the crude oil within the GOSP takes place under the influence of its own pressure.
- Pumps, however, are used to transfer the oil in its final trip to the tank farm, or pipeline (Fig. 2).
- Pressure reduction in moving the oil from stage to stage is illustrated in Fig. 3.
- In Fig. 4, which summarizes the results of a three-stage gas-oil separation pilot plant.

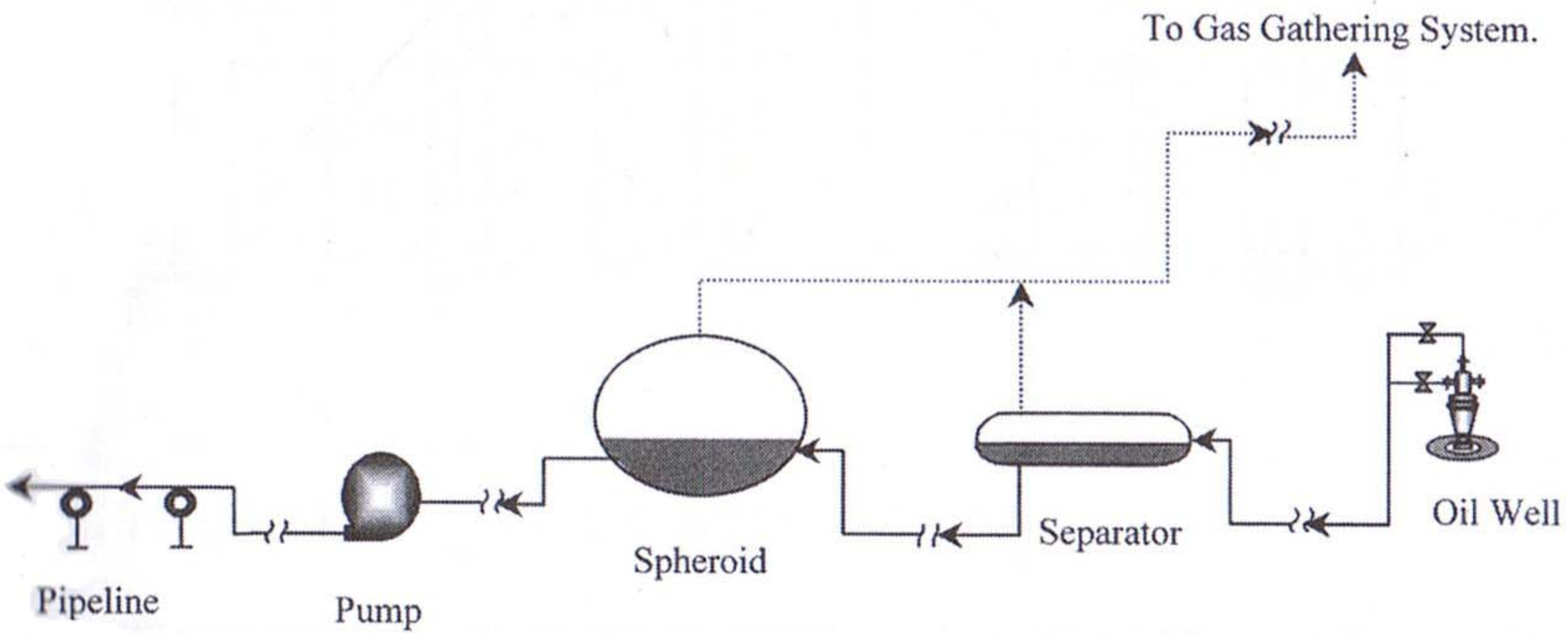


Figure 2 Separation of gas from oil.

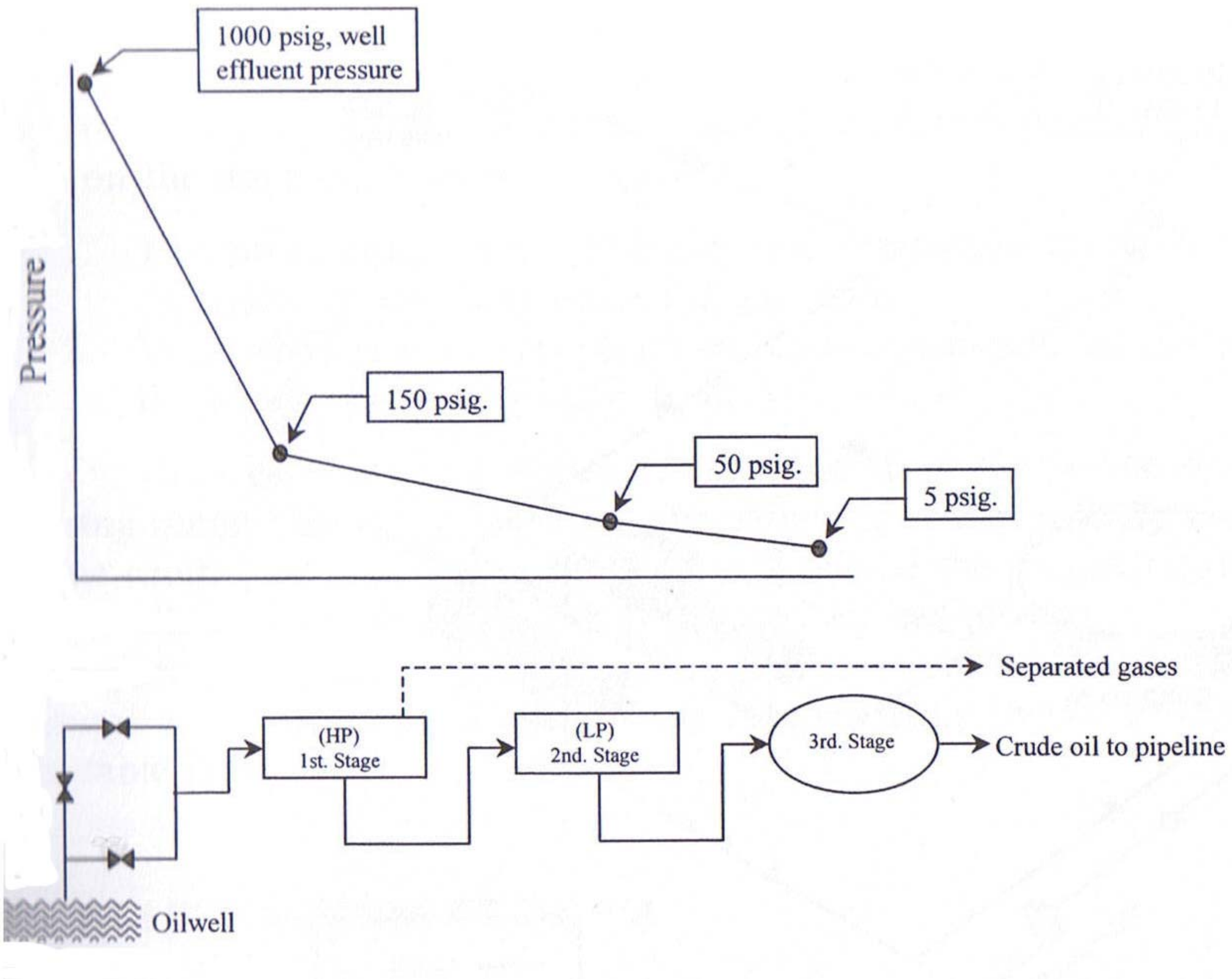
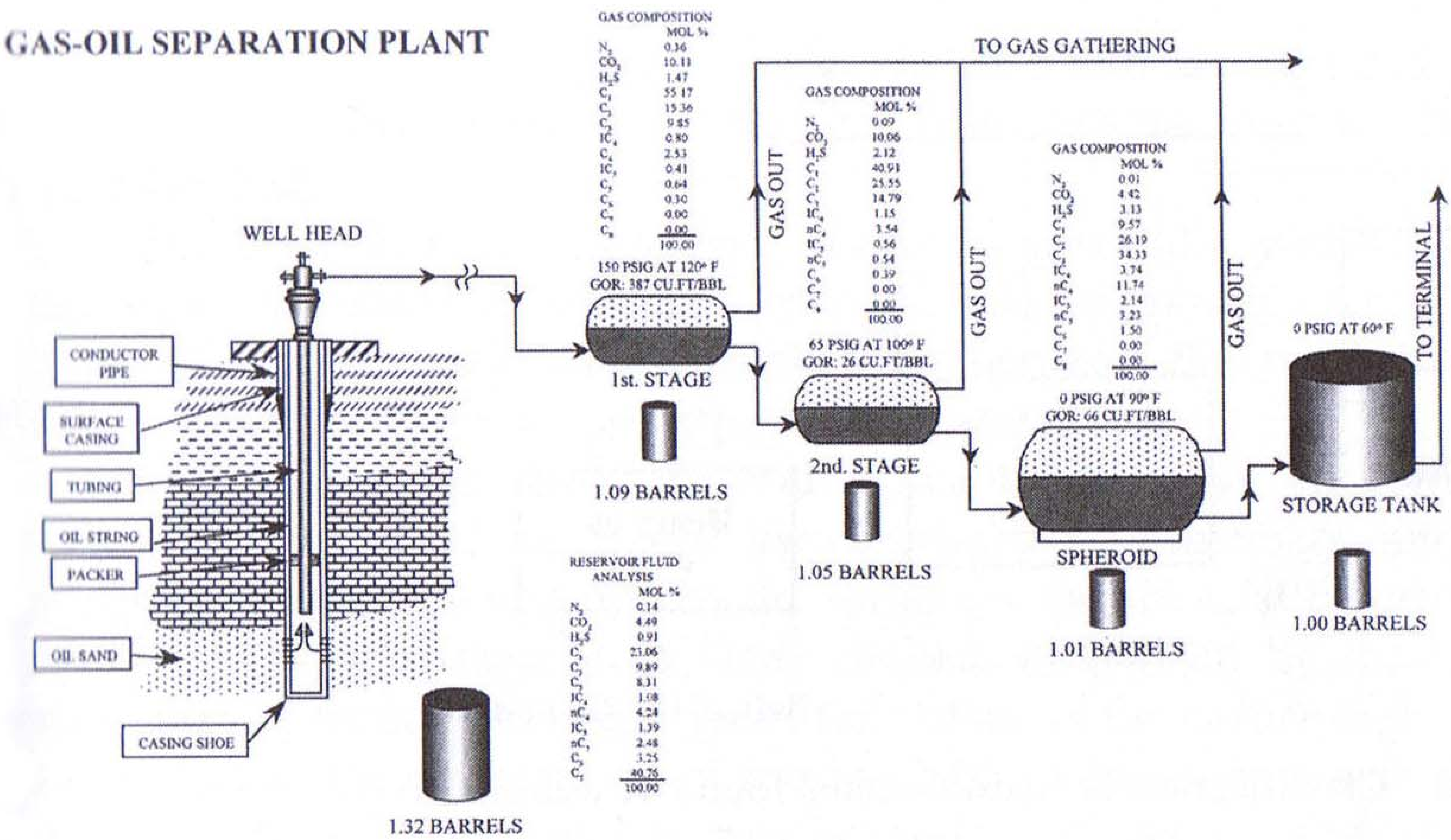


Figure 3

Pressure-drop profile for a typical GOSP.



GAS COMPOSITION

	MOL %
N_2	0.36
CO_2	10.11
H_2S	1.47
C_1	55.17
C_2	15.36
C_3	9.85
IC_4	0.80
C_4	2.53
IC_5	0.41
C_5	0.64
C_6	0.30
C_7	0.00
C_8	0.00
	100.00

GAS COMPOSITION

	MOL %
N_2	0.09
CO_2	10.06
H_2S	2.12
C_1	40.91
C_2	25.55
C_3	14.79
IC_4	1.15
nC_4	3.54
IC_5	0.56
nC_5	0.54
C_6	0.39
C_7	0.00
C_8	0.00
	100.00

GAS COMPOSITION

	MOL %
N_2	0.01
CO_2	4.42
H_2S	3.13
C_1	9.57
C_2	26.19
C_3	34.33
IC_4	3.74
nC_4	11.74
IC_5	2.14
nC_5	3.23
C_6	1.50
C_7	0.00
C_8	0.00
	100.00

RESERVOIR FLUID ANALYSIS

	MOL %
N_2	0.14
CO_2	4.49
H_2S	0.91
C_1	23.06
C_2	9.89
C_3	8.31
IC_4	1.98
nC_4	4.24
IC_5	1.39
nC_5	2.48
C_6	3.25
C_7	40.76
	100.00

Figure 4 Gas-Oil separation plant.

Theory of Gas-Oil Separation

- In order to understand the theory underlying the separation of well-effluent hydrocarbon mixtures into a gas stream and oil product, it is assumed that such mixtures contain essentially three main groups of hydrocarbon:
    1. Light group; CH_4 and C_2H_6.
    2. Intermediate group; C_3H_8/C_4H_{10} group and C_5H_{12}/C_6H_{14} group.
    3. Heavy group; $C_7H_{16}+$ group.
- In carrying out the gas-oil separation process, the main target is to try to achieve the following objectives:
    1. Separate the C_1 and C_2 light gases from oil.
    2. Maximize the recovery of heavy components of the intermediate group in crude oil.
    3. Save the heavy group components in liquid product.

Theory of Gas-Oil Separation (cont.)

- To accomplish these objectives, some HCs of the intermediate group are unavoidably lost in the gas stream.
- In order to minimize this loss and maximize liquid recovery, two methods for the mechanics of separation are compared:
  1. Differential or enhanced separation
  2. Flash or equilibrium separation
- In differential separation, light gases (light group) are gradually and most completely separated from oil in a series of stages, as the total pressure on the well-effluent mixture is reduced.
- Differential separation is characterized by the fact that light gases are separated as soon as they are liberated (due to reduction in pressure).
- In other words, light components do not come into contact with heavier HCs; instead, they find their way out.

Stage Separation

- Stage separation is a process in which gaseous and liquid hydrocar-bons are separated into vapour and liquid phases by two or more equilibrium flashes at consecutively lower pressures.
- The tank is always counted as the final stage of vapour-liquid separation because the final equilibrium flash occurs in the tank.
- The purpose of stage separation is to reduce the pressure on the reservoir liquids a little at a time, in steps or stages, so that a more stable stock-tank liquid will result.
- The ideal method of separation, to attain maximum liquid recovery, would be that of differential liberation of gas by means of a steady decrease in pressure from that existing in the reservoir to the stock-tank pressure.

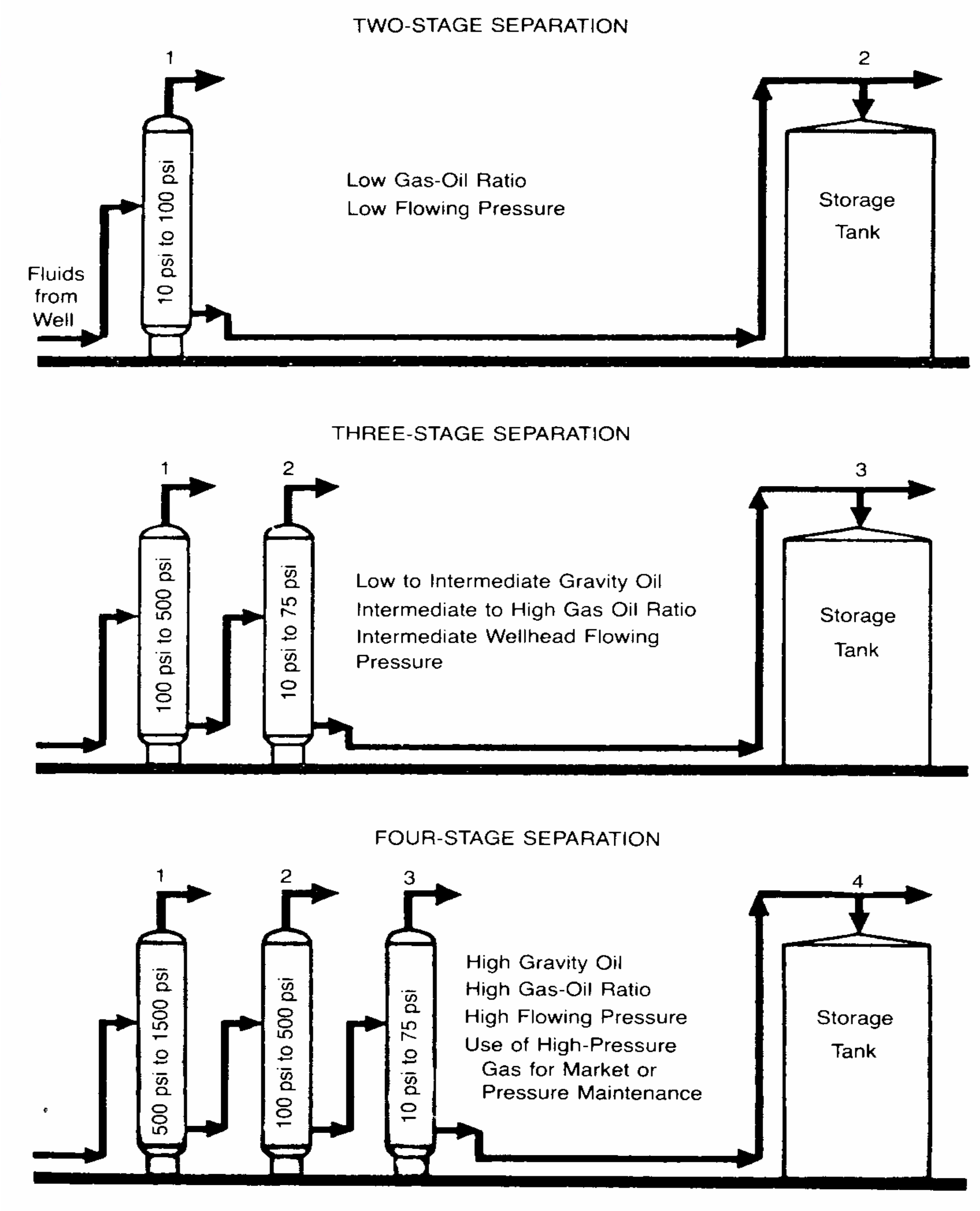
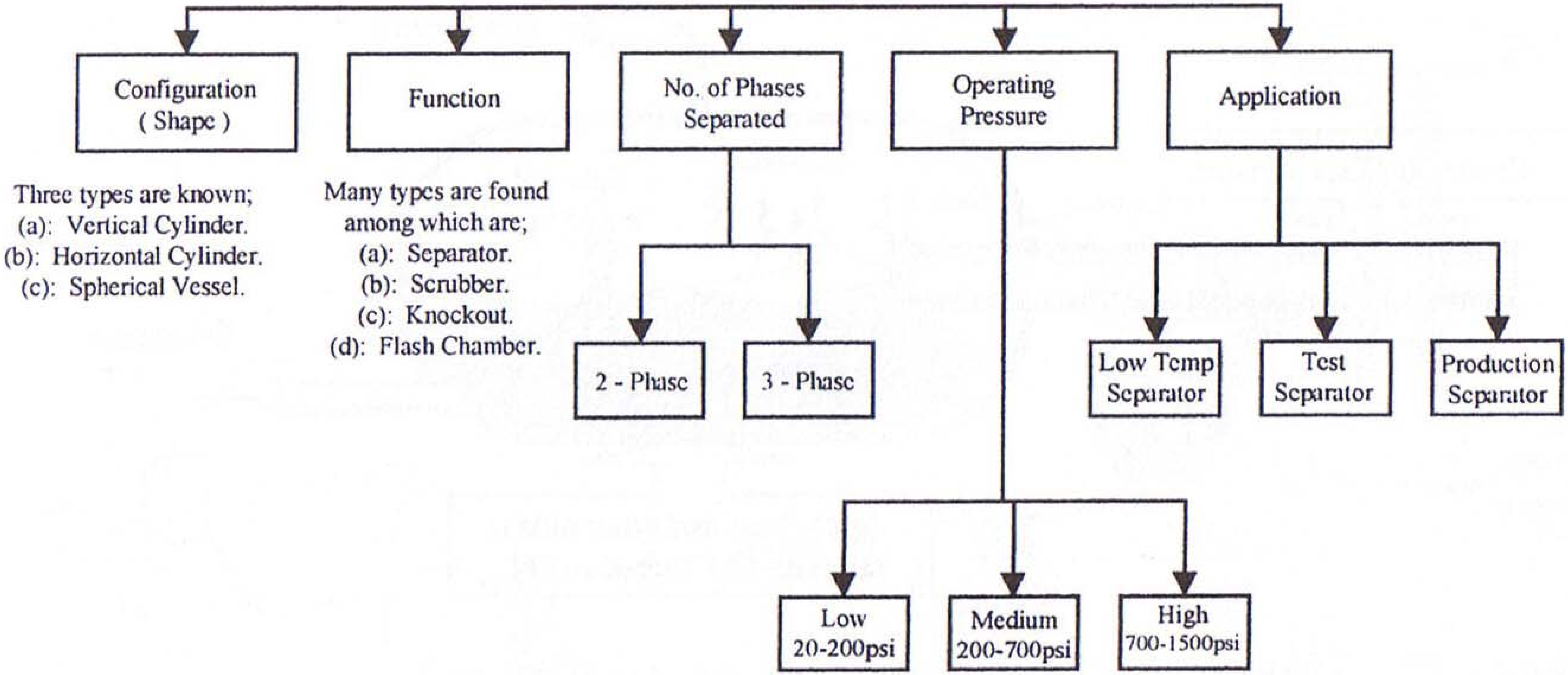


Figure 5

Stage separation flow diagrams.

Gas-Oil Separator Equipment

- The conventional separator is the very first vessel through which the well-effluent mixture flows.
- In some special cases, other equipment (heaters, water knockout drums) may be installed upstream of the separator.
- The choice of a separator for the processing of gas-oil mixtures containing water or without water under given operating conditions and for a specific application normally takes place guided by the general classification illustrated in Fig. 6.



- Configuration (Shape)
  - Three types are known;
  - (a): Vertical Cylinder.
  - (b): Horizontal Cylinder.
  - (c): Spherical Vessel.
- Function
  - Many types are found among which are;
  - (a): Separator.
  - (b): Scrubber.
  - (c): Knockout.
  - (d): Flash Chamber.
- No. of Phases Separated
  - 2 - Phase
  - 3 - Phase
- Operating Pressure
  - Low 20-200psi
  - Medium 200-700psi
  - High 700-1500psi
- Application
  - Low Temp Separator
  - Test Separator
  - Production Separator

Figure 6 Classification of separators.

Functional Components of GOS

Regardless of their configuration, gas-oil separators usually consist of four functional sections, as shown in Fig. 7:

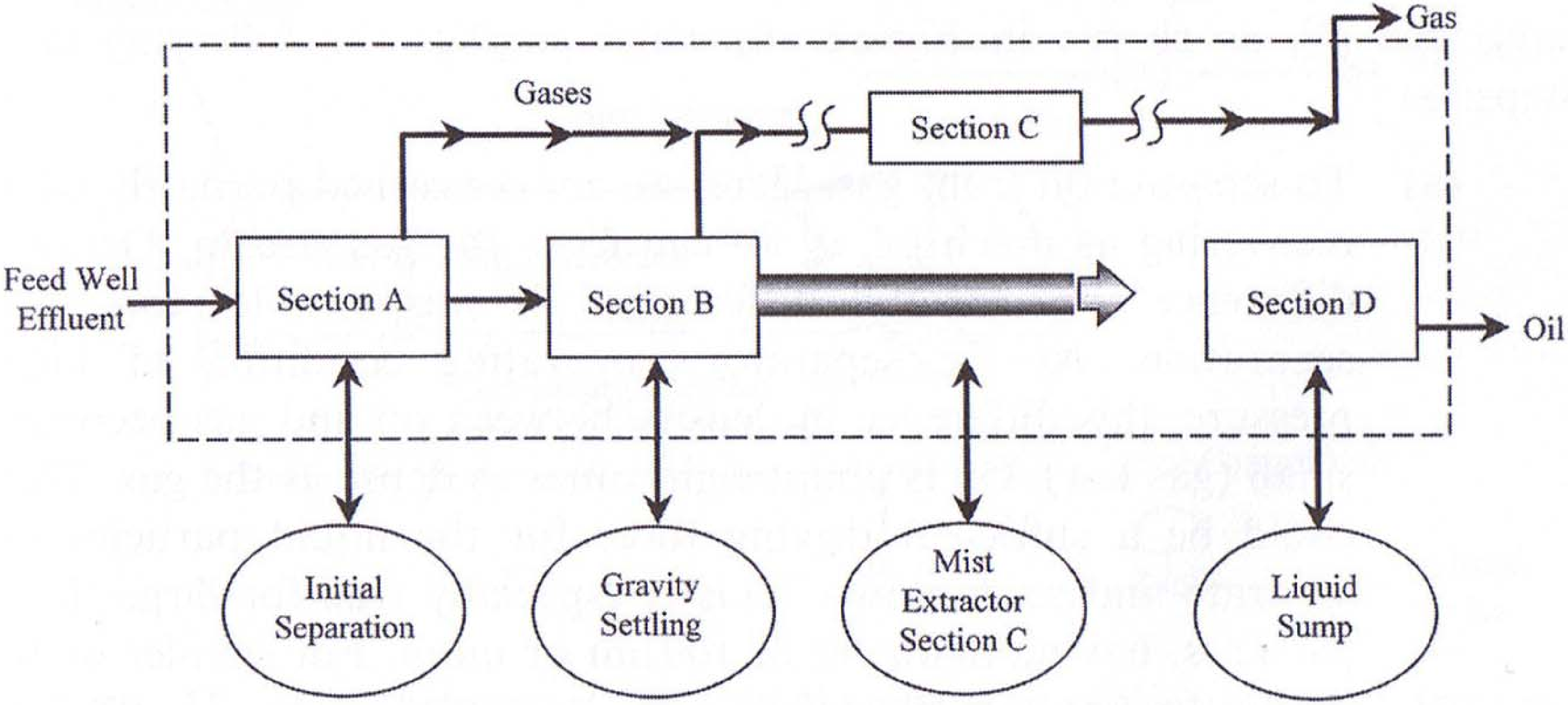


Figure 7 Schematic outline of the main components in a gas-oil separator.

Functional Components of GOS (cont.)

1. *Section A:* Initial bulk separation of oil and gas takes place in this section. The entering fluid mixture hits the inlet diverter will cause a sudden change in momentum and, due to the gravity difference, results in bulk separation of the gas from the oil. The gas then flows through the top part of the separator and the oil through the lower part.
2. *Section B:* Gravity settling and separation is accomplished in this section of the separator. Because of the substantial reduction in gas velocity and the density difference, oil droplets settle and separate from the gas.
3. *Section C:* Known as the mist extraction section, it is capable of removing the very fine oil droplets which did not settle in the gravity settling section from the gas stream.
4. *Section D:* Known as the liquid sump or liquid collection section. Its main function is collecting the oil and retaining it for a sufficient time to reach equilibrium with the gas before it is discharged from the separator.

Commercial Types of Gas-Oil Separator

- Base on the configuration, the most common types of separator are vertical (Fig. 8), horizontal single tube (Fig. 9), horizontal double tube (Fig. 10) and spherical (Fig. 11).
- A concise comparison among these three types is presented in Table 1.

TWO-PHASE VERTICAL SEPARATOR

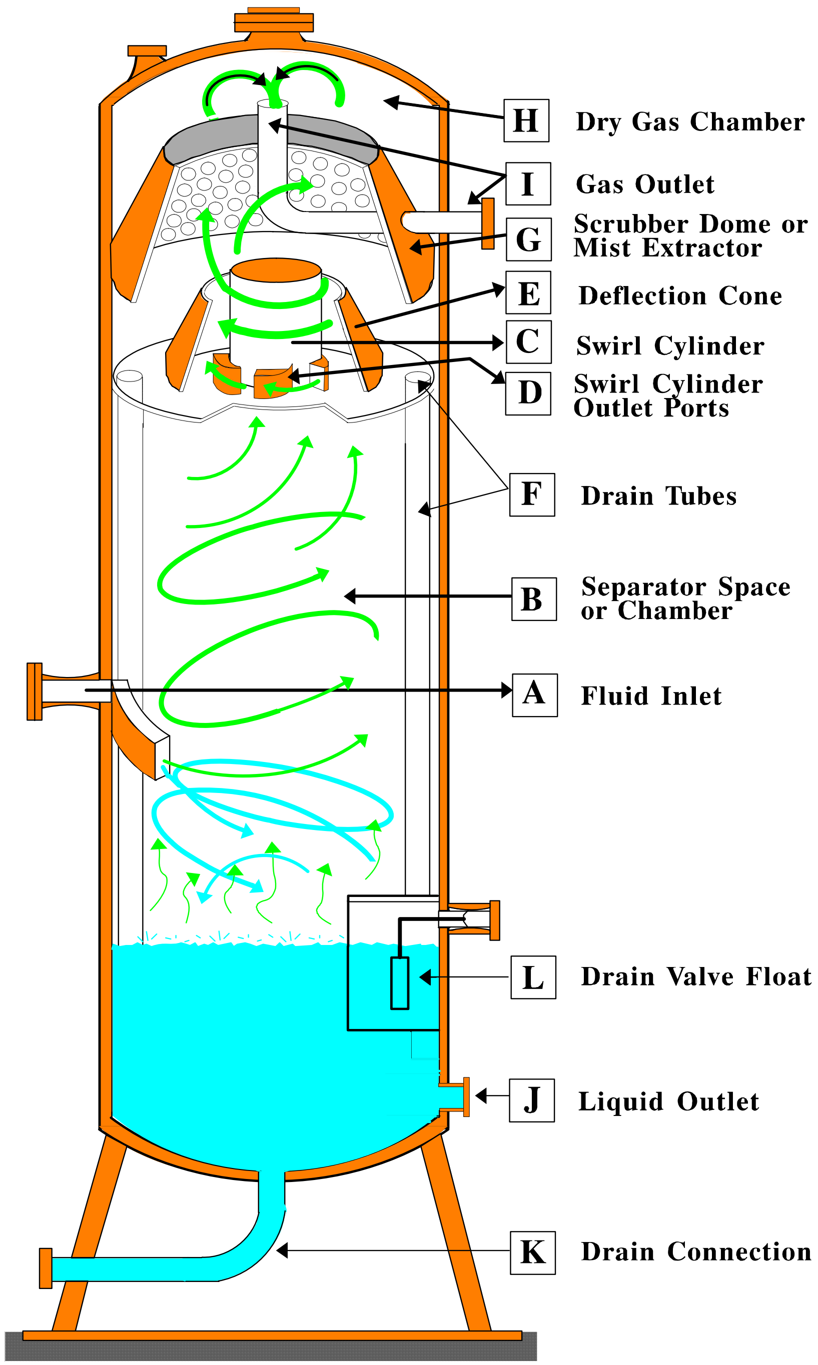


Figure 8
Conventional vertical separator

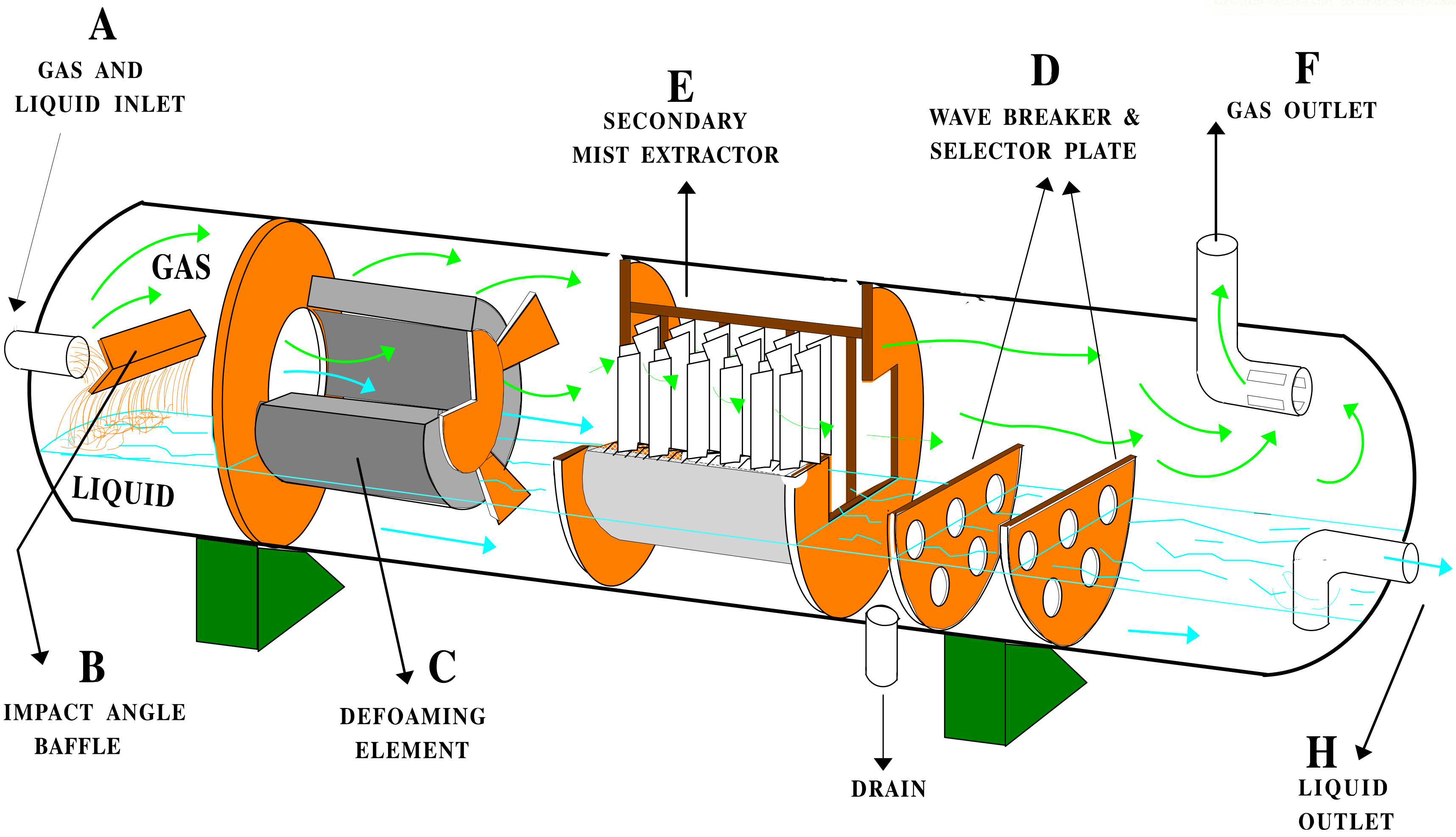


Figure 9 Conventional horizontal separator

Process Control & Safety

A: Inlet B: Upper Tube Liquid Outlet C: Mist Extractor (Large Droplets)

D: Mist Extractor (Small Droplets) E: Gas Outlet F: Liquid Outlet

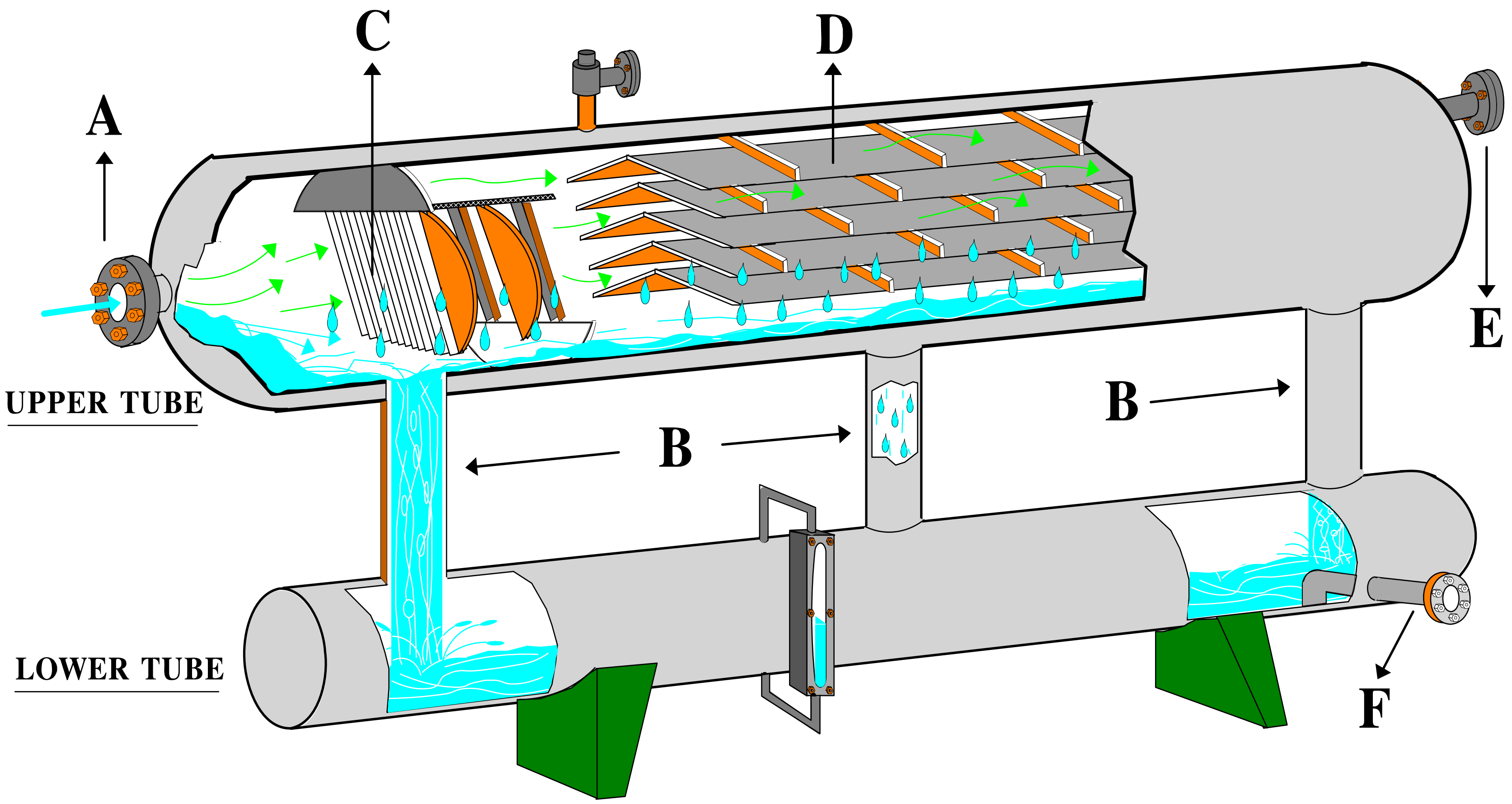


Figure 10 Conventional horizontal double-barrel separator

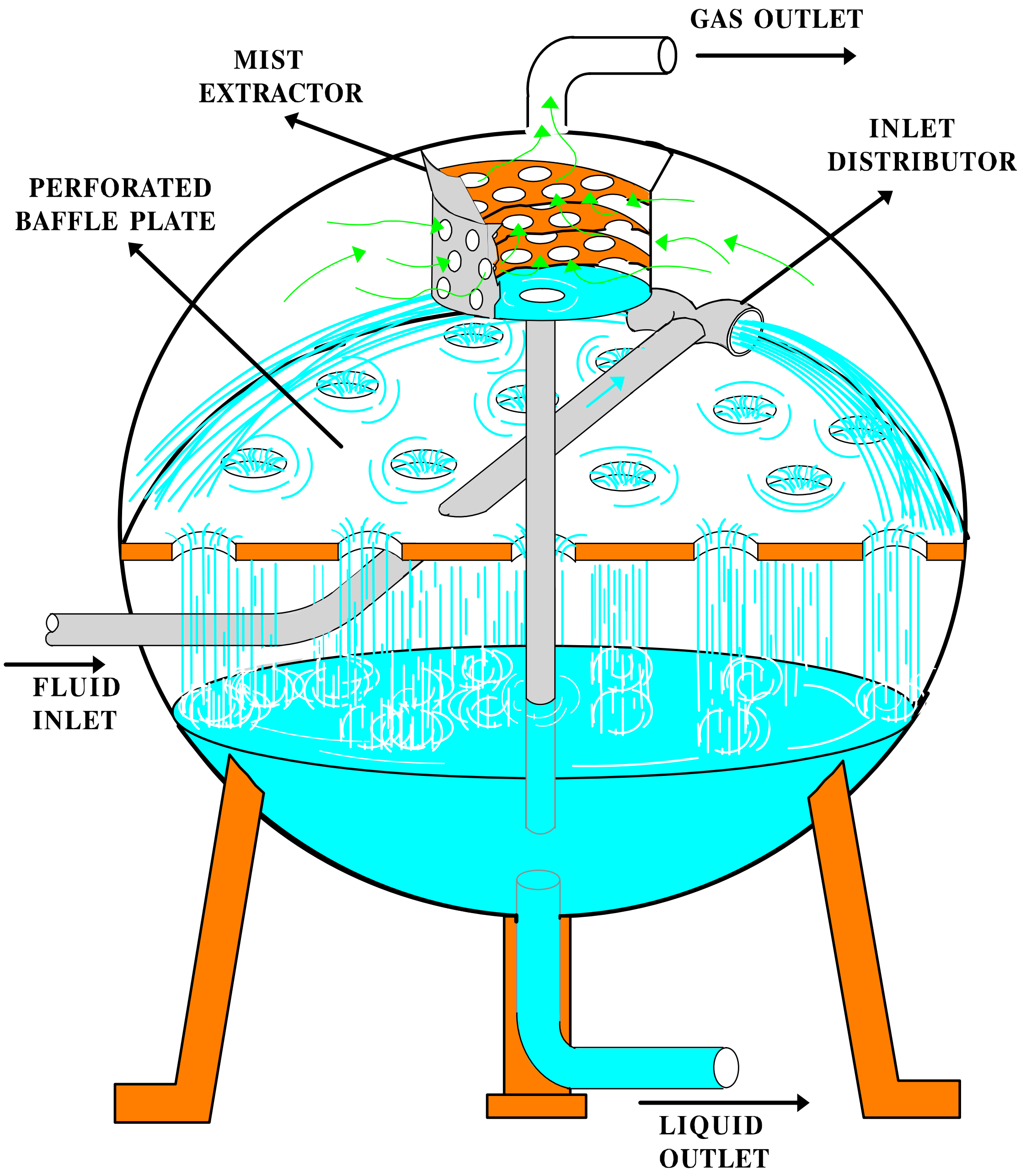
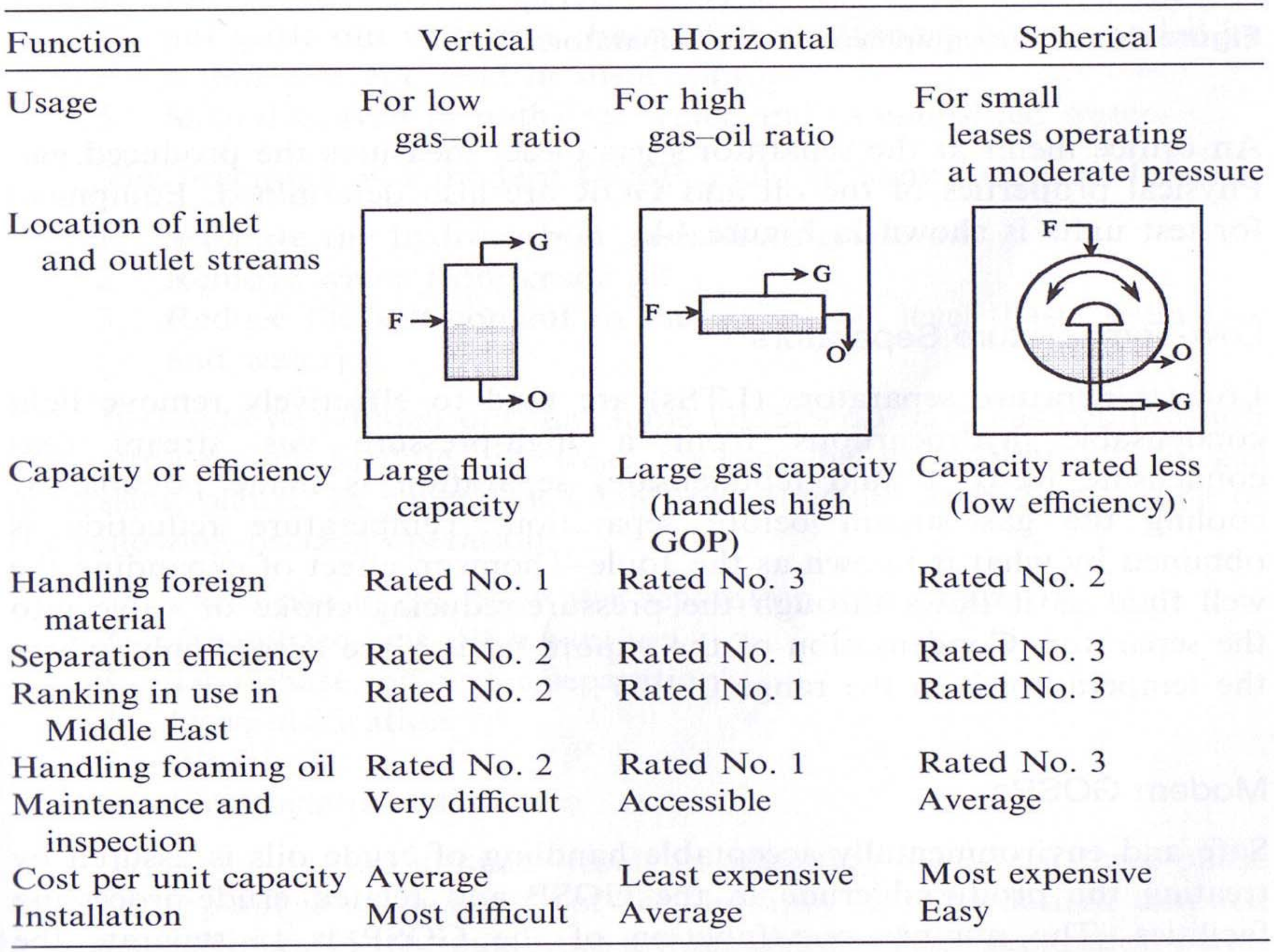


Figure 11 Conventional spherical separator

Table 1 Comparison among different configurations of Gas-Oil Separators



Function	Vertical	Horizontal	Spherical
Usage	For low gas–oil ratio	For high gas–oil ratio	For small leases operating at moderate pressure
Location of inlet and outlet streams			
Capacity or efficiency	Large fluid capacity	Large gas capacity (handles high GOP)	Capacity rated less (low efficiency)
Handling foreign material	Rated No. 1	Rated No. 3	Rated No. 2
Separation efficiency	Rated No. 2	Rated No. 1	Rated No. 3
Ranking in use in Middle East	Rated No. 2	Rated No. 1	Rated No. 3
Handling foaming oil	Rated No. 2	Rated No. 1	Rated No. 3
Maintenance and inspection	Very difficult	Accessible	Average
Cost per unit capacity	Average	Least expensive	Most expensive
Installation	Most difficult	Average	Easy

Test Separators

- These units are used to separate and measure at the same time the well fluids.
- Potential test is one of the recognized tests for the measuring the quantity of both oil and gas produced by the well in 24 hours period under steady state of operating conditions.
- The oil produced is measured by a flow meter at the separator’s liquid outlet and the cumulative oil production is measured in the receiving tanks.
- An orifice meter at the separator’s gas outlet measures the produced gas.
- Physical properties of the oil and GOR are also determined.
- Equipment for test units is shown in Fig. 12.

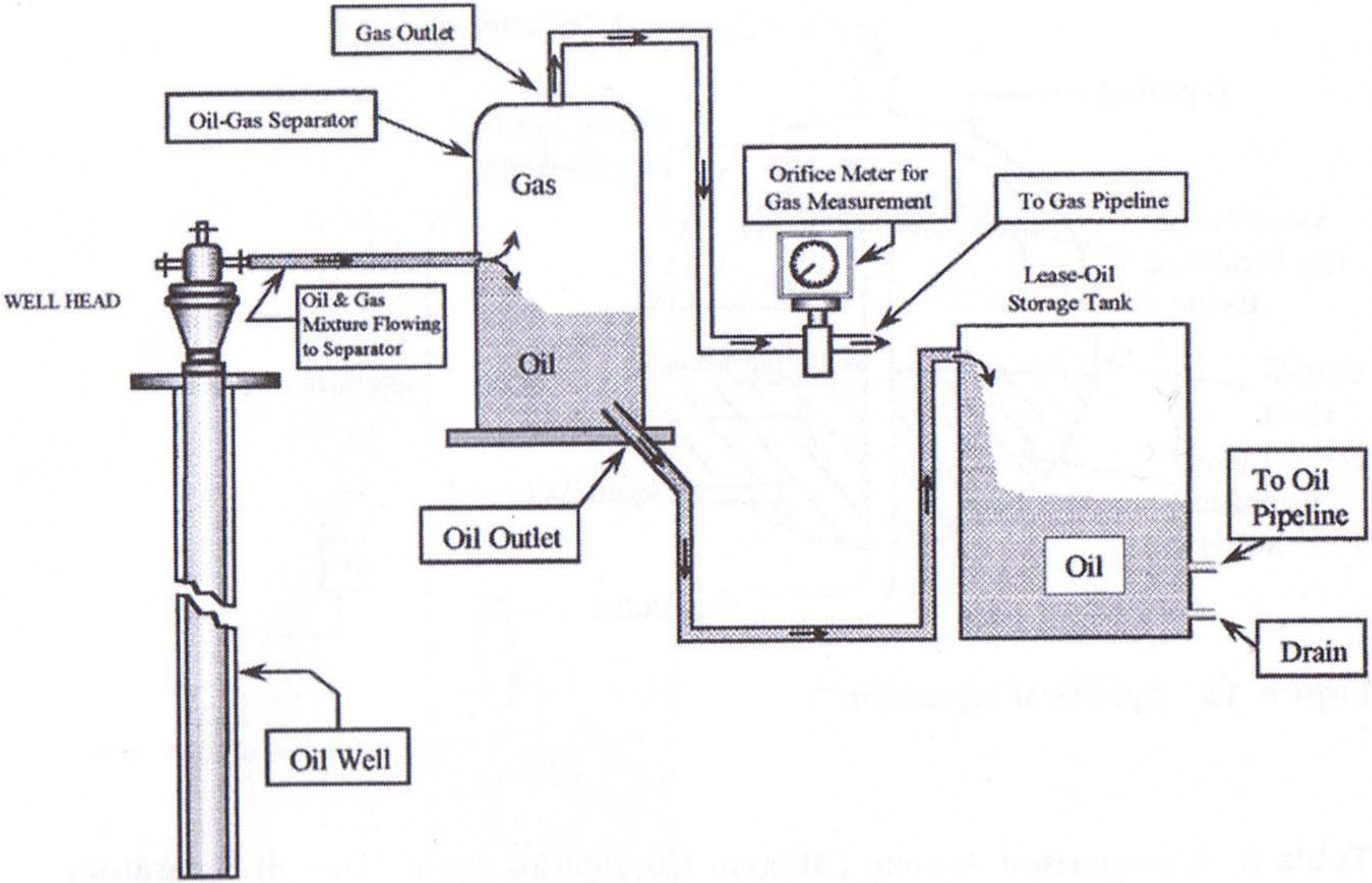


Figure 12 Main equipment for test separator.

Low-Temperature Separators

- A LTS unit is another type of equipment employed for gas-liquid separation, which consists primarily of a high-pressure separator, pressure-reducing chokes and various pieces of heat exchanger equipment.
- As described previously, lowering the operating temperature of a separator increases the liquid recovery.
- When the pressure is reduced on a high-pressure gas condensate stream by use of a pressure-reducing choke, the fluid temperature also decreases.
- LTS is probably the most efficient means yet devised for handling high-pressure gas and condensate at the wellhead.
- The process separates water and HC liquids from the inlet well stream, recovers more liquids from the gas than can be recovered with normal-temperature separators, and dehydrates gas, usually to pipeline specifications.

Modern GOSPs

The input of wet crude oil into a modern GOSP consists of the following:

1. Crude oil
2. Hydrocarbon gases
3. Free water dispersed in oil as relatively large droplets, which will separate and settle out rapidly when wet crude is retained in the vessel
4. Emulsified water, dispersed in oil as very small droplets that do not settle out with time. Each of these droplets is surrounded by a thin film and held in suspension
5. Salts dissolved in both free water and in emulsified water

Modern GOSPs (cont.)

The function of a modern GOSP could be summarized as follows:

1. Separate the hydrocarbon gases from crude oil
2. Remove water from crude oil
3. Reduce the salt content to the acceptable level

To conclude, the ultimate result in operating a modern GOSP is to change “wet” crude input into the desired output, as given in Fig. 13.

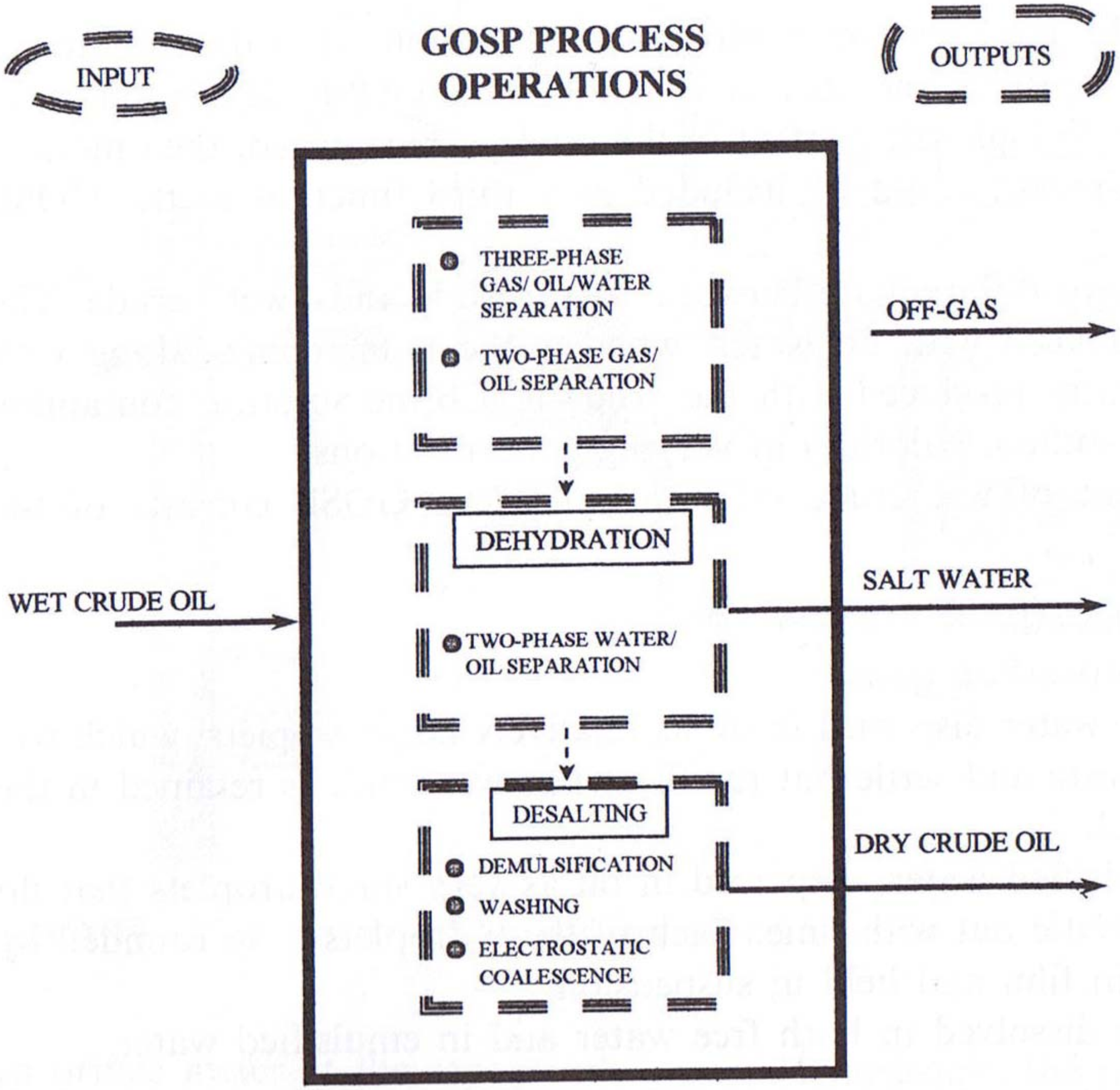
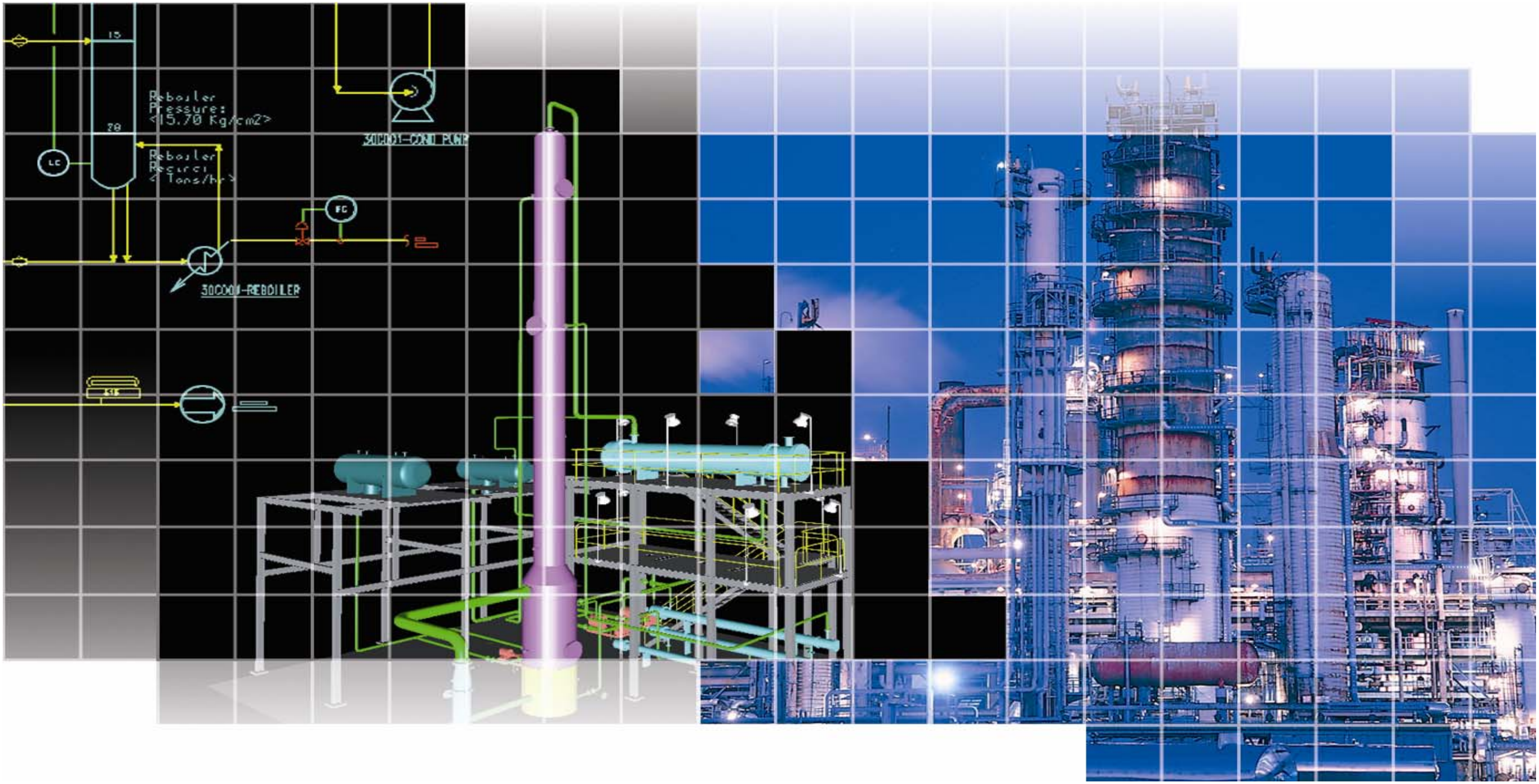


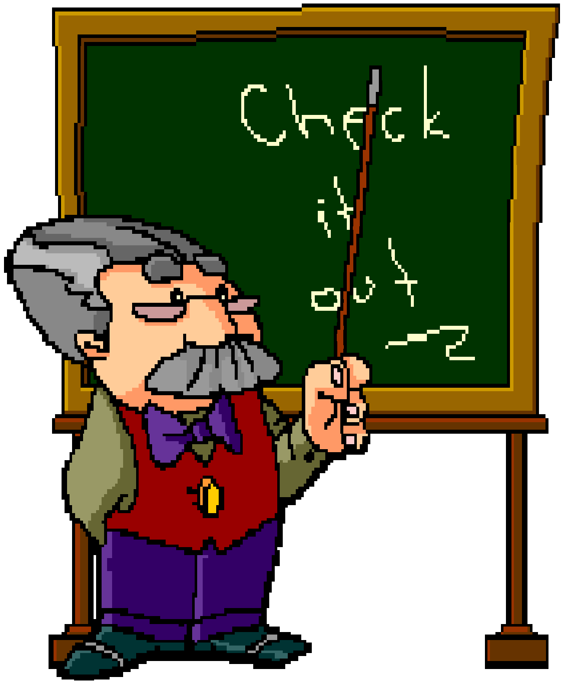
Figure 13 Functions of modern GOSPs.



Chapter 5

Three-Phase Oil-Water-Gas Separation

Outline



- Introduction
- Horizontal Three-Phase Separators
- Vertical Three-Phase Separators

Introduction

- In almost all production operations, the produced fluid stream consists of three phases; oil, water and gas.
- Generally, water produced with the oil exists partly as free water and partly as water-in-oil emulsion.
- In some cases, however, when the water-oil ratio is very high, oil-in-water rather than water-in-oil emulsion will form.
- Free water produced with the oil is defined as the water that will settle and separate from the oil by gravity.
- To separate the emulsified water, however, heat treatment, chemical treatment, electrostatic treatment, or a combination of these treatments would be necessary in addition to gravity settling (Chap 6).
- Therefore, it is advantageous to first separate the free water from the oil to minimize the treatment costs of the emulsion.

Introduction (cont.)

- Along with the water and oil, gas will always be present and, therefore, must be separated from the liquid.
- The volume of gas depends largely on the producing and separation conditions.
- When the volume of gas is relatively small compared to the volume of liquid, the method used to separate free water, oil and gas is called a *free-water knockout*.
- In a such case, the separation of the water from oil will govern the design of the vessel.
- When there is a large volume of gas to be separated from the liquid (oil and water), the vessel is called a *three-phase separator* and either the gas capacity requirements or the water-oil separation constraints may govern the vessel design.

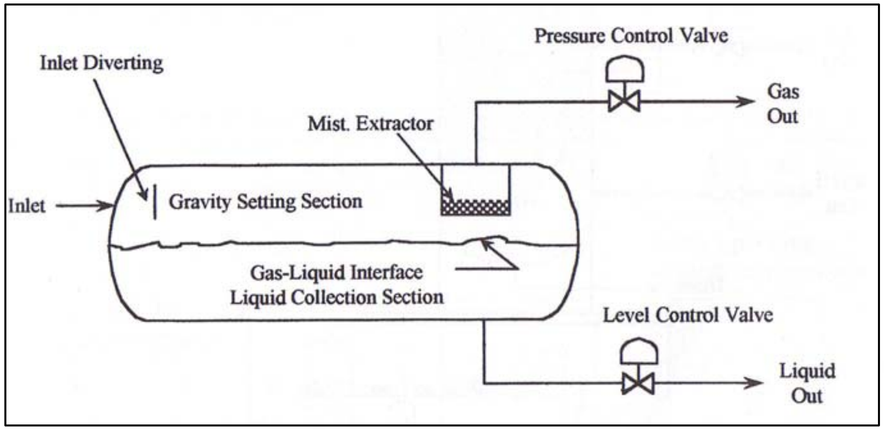
Introduction (cont.)

- Free-water knockout and three-phase separators are basically similar in shape and components.
- Further, the same design concepts and procedures are used for both types of vessel.
- Three-phase separators may be either horizontal or vertical pressure vessels similar to the two-phase separators described in Chapter 4.
- However, three-phase separators will have additional control devices and may have additional internal components.

Horizontal Three-Phase Separators

Process Control & Safety

- Three-phase separators differ from two-phase separators in that the liquid collection section of the three-phase handles two immiscible liquids (oil and water) rather than one.
- This section should, therefore, be designed to separate the two liquids, provide means for controlling the level of each liquids, and provide separate outlets for each liquid.
- Figures 1 and 2 show schematics of two common types of horizontal three-phase separators.
- The difference between the two types is mainly in the method of controlling the levels of the oil and water phases.



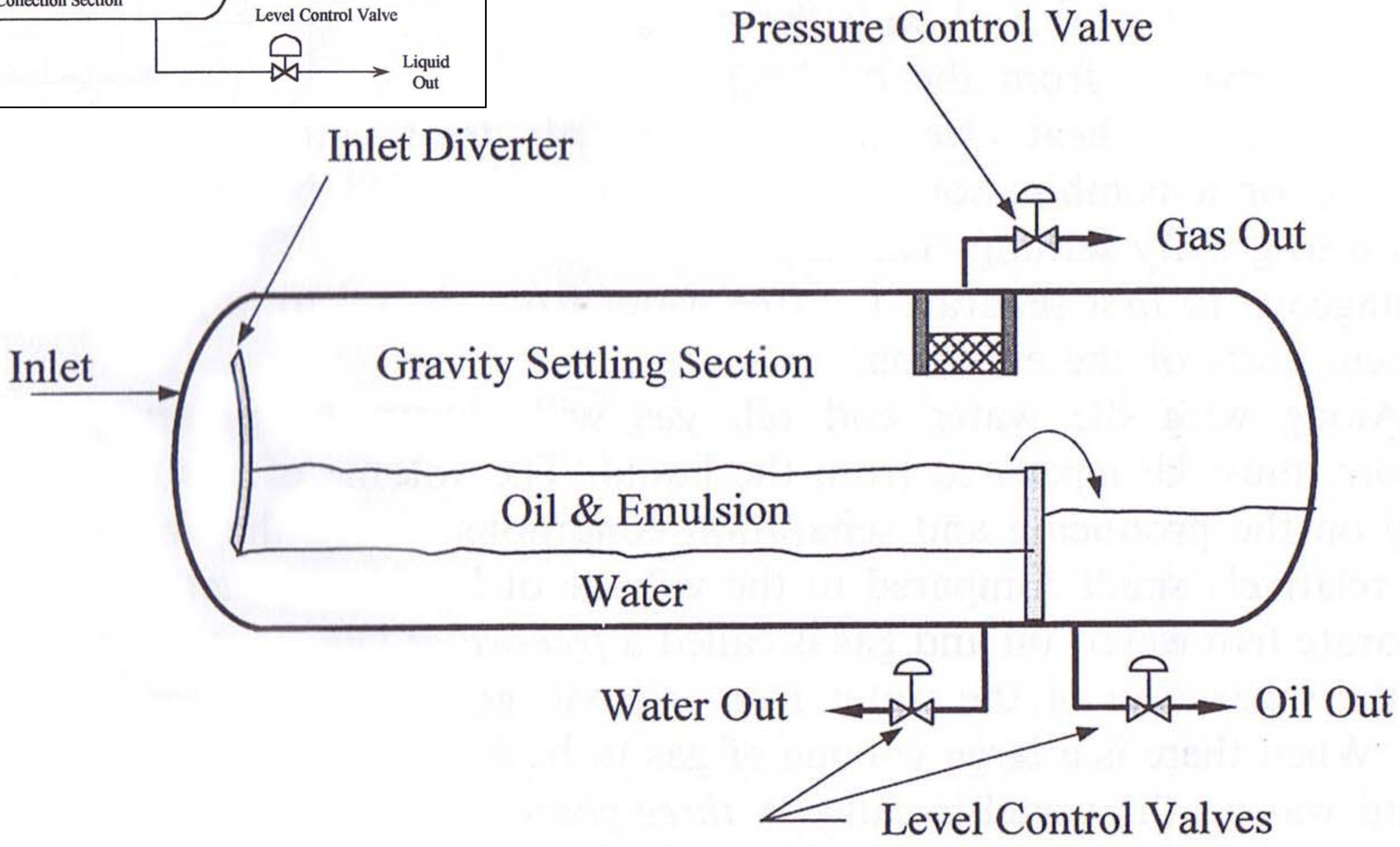


Figure 1 Horizontal three-phase separator schematic of one type.

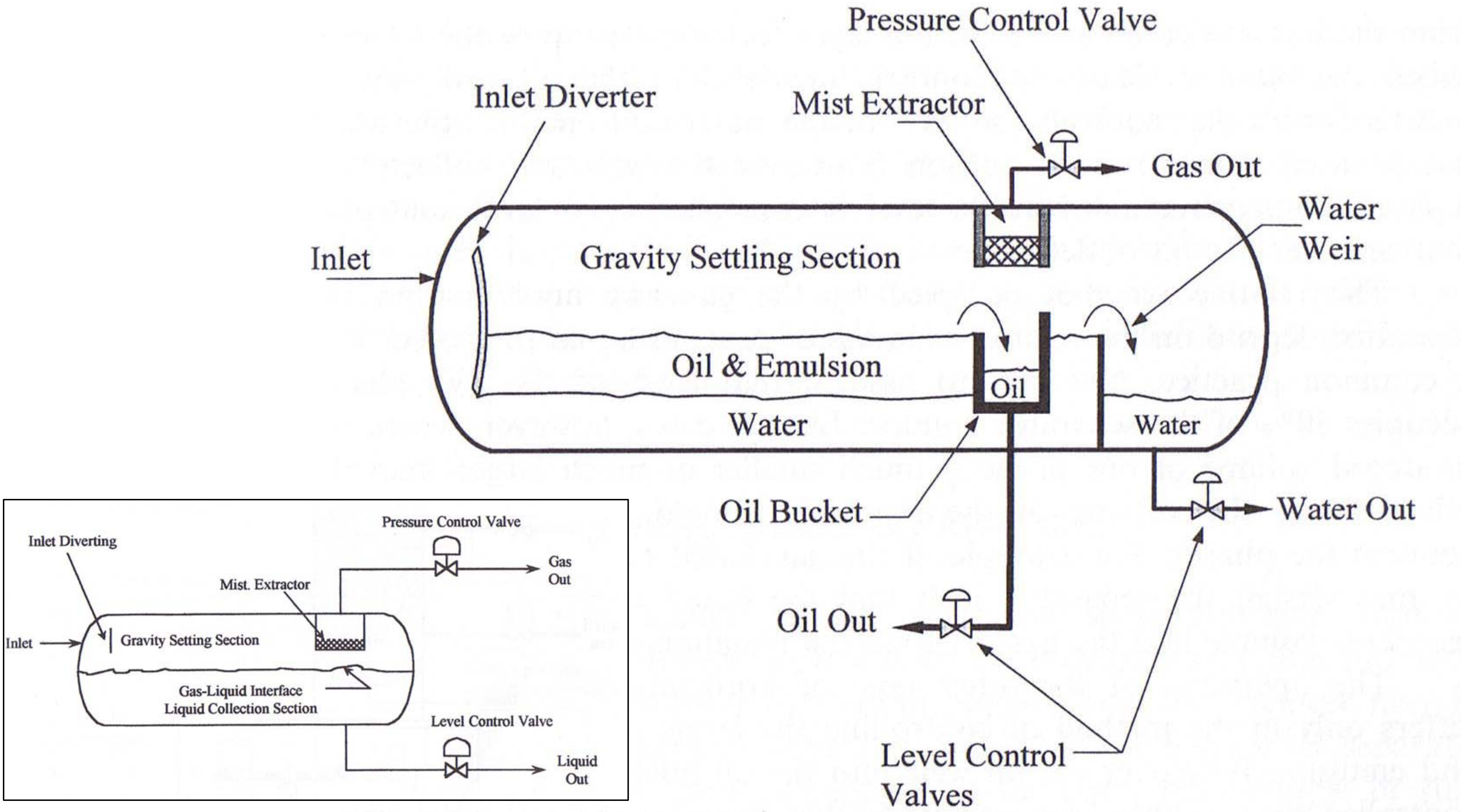
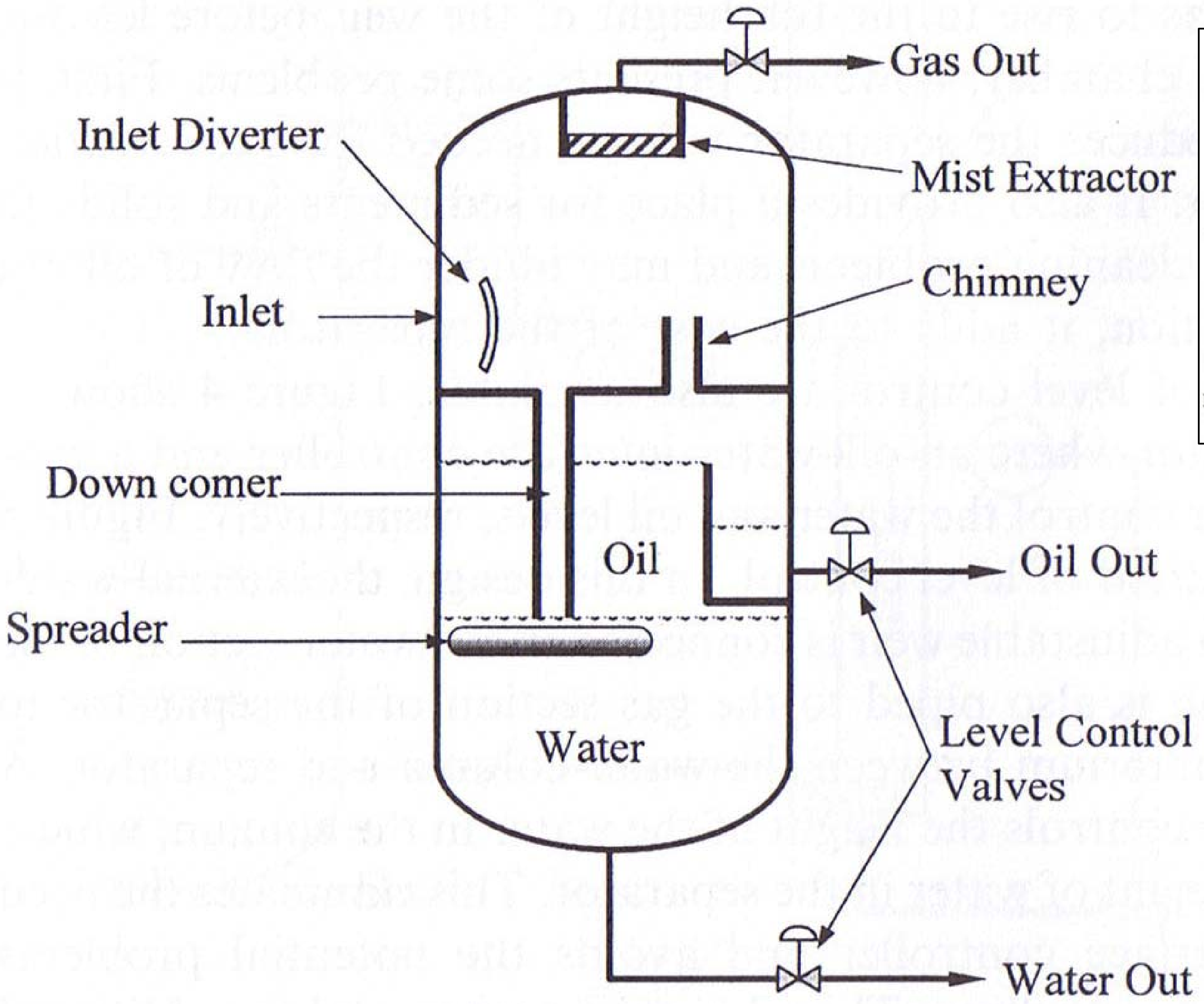


Figure 2 Horizontal three-phase separator; bucket and weir design.

Vertical Three-Phase Separators

- As discussed in Chapter 4, the horizontal separators are normally preferred over vertical separators due to the flow geometry that promotes phase separation.
- However, in certain applications, the engineer may be forced to select a vertical separator instead of a horizontal separator.
- An example of such applications is found in offshore operations, where the space limitations on the production platform may necessitate the use of a vertical separator.
- Figure 3 shows a schematic of a typical three-phase vertical separator.
- Figure 4 shows a schematic of a separator where an oil-water-interface controller and a gas-oil-interface controller control the water and oil levels.
- Figure 5 shows another method of level control.



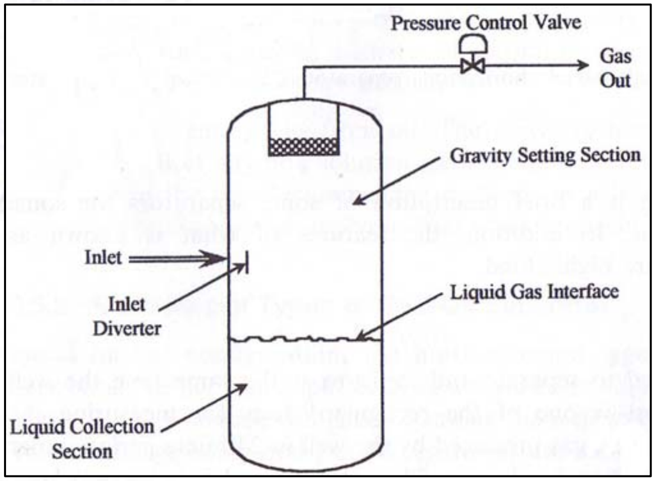


Figure 3

Schematic of a three-phase vertical separator.

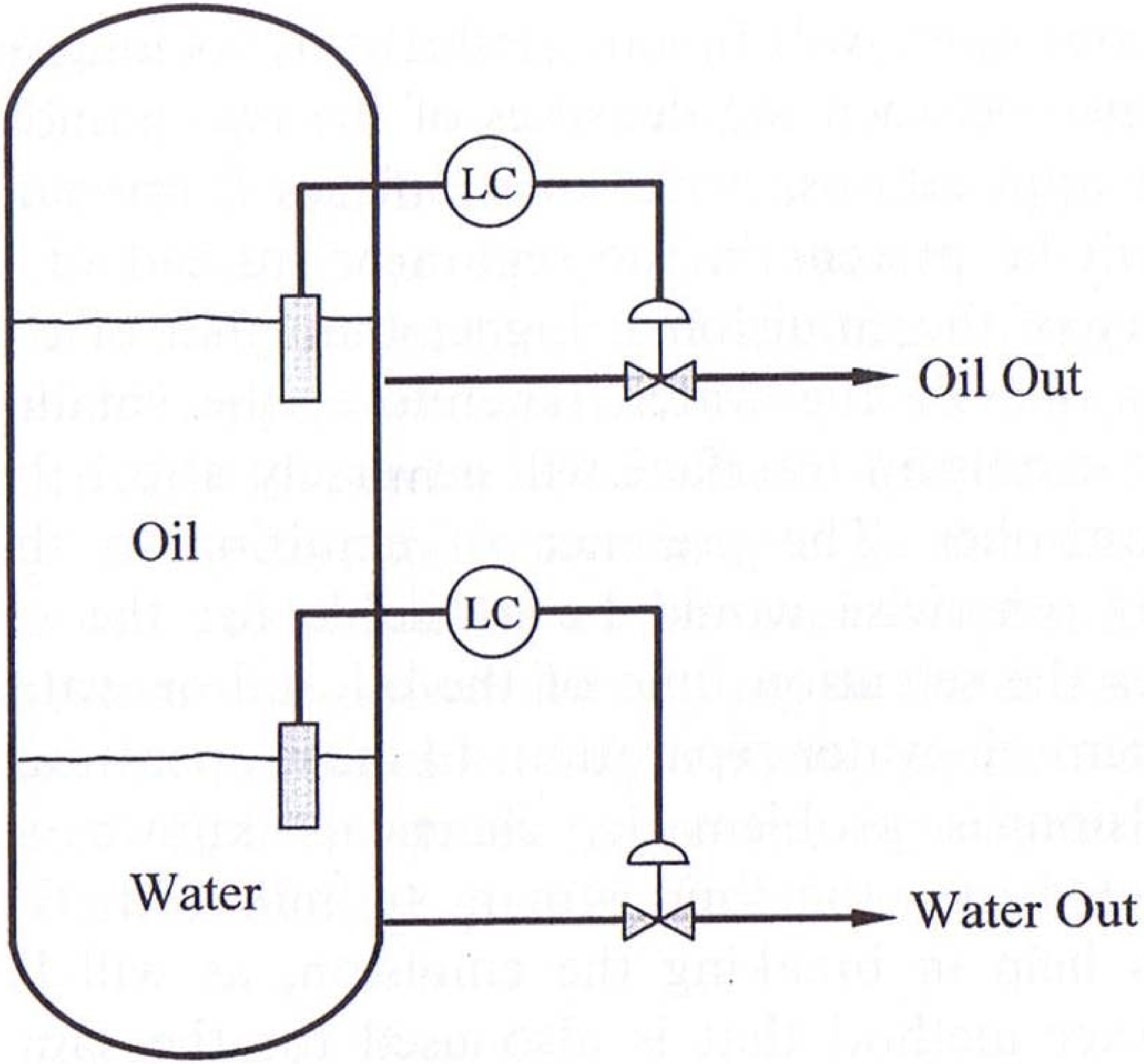


Figure 4

Interface level control.

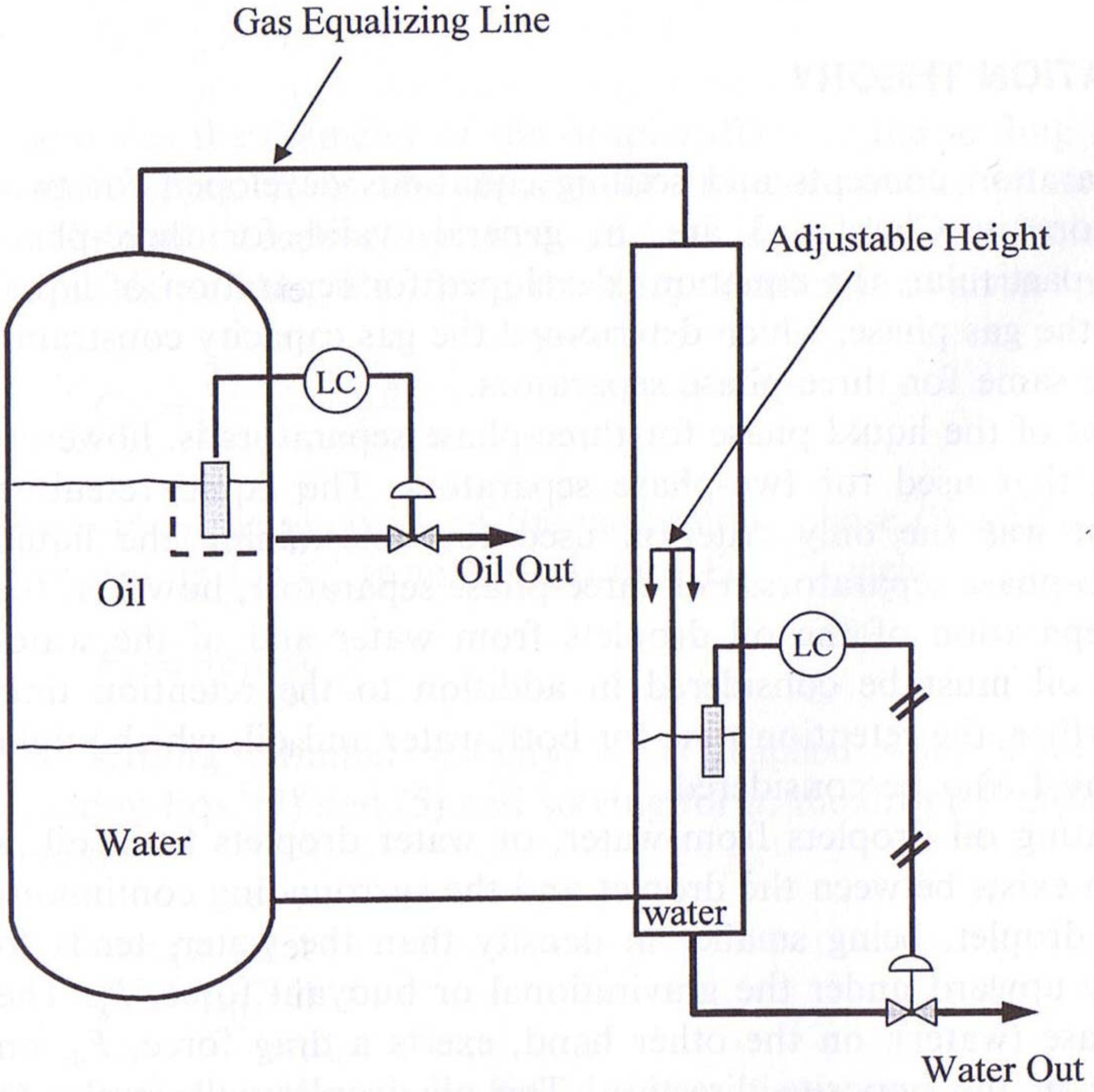
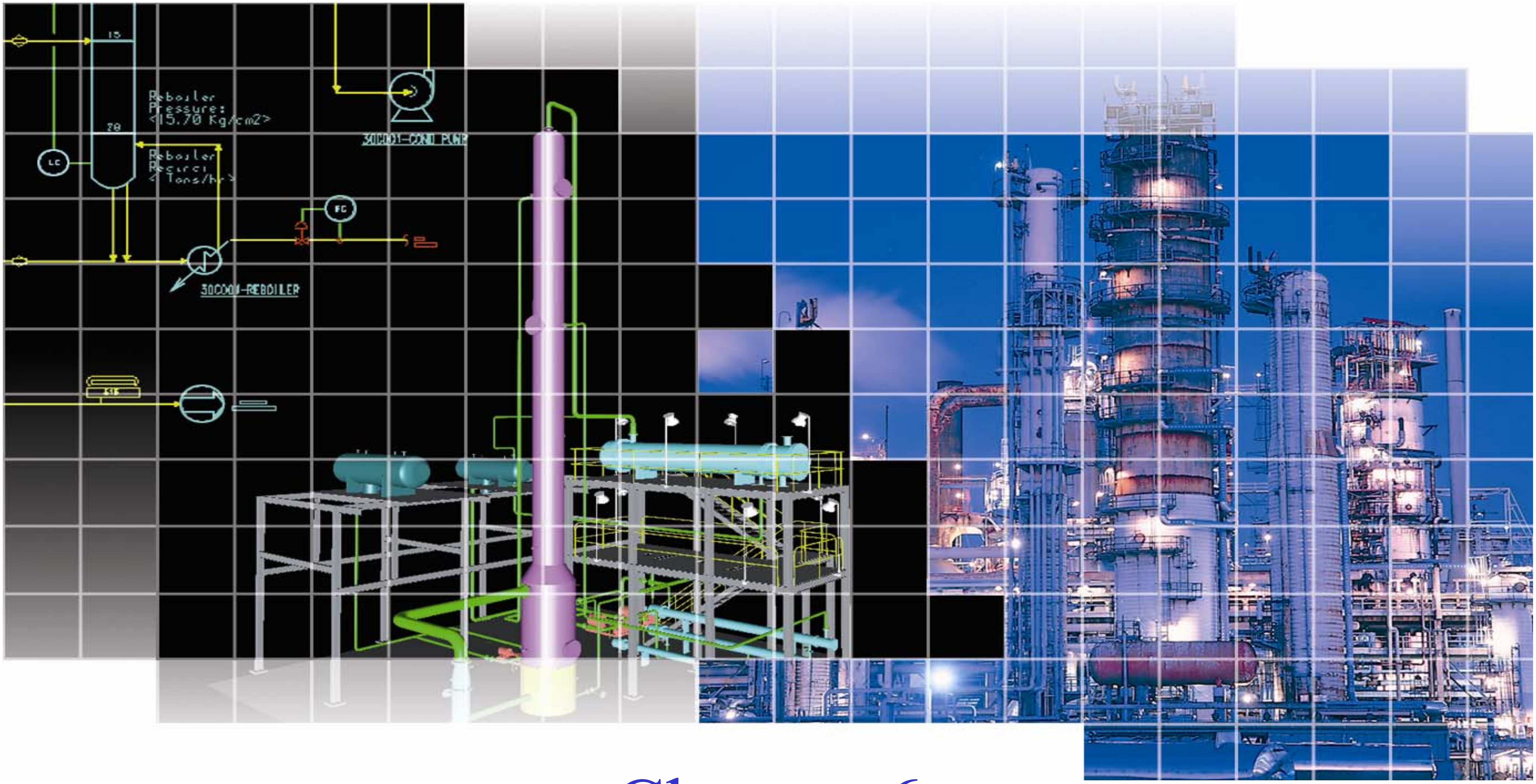


Figure 5

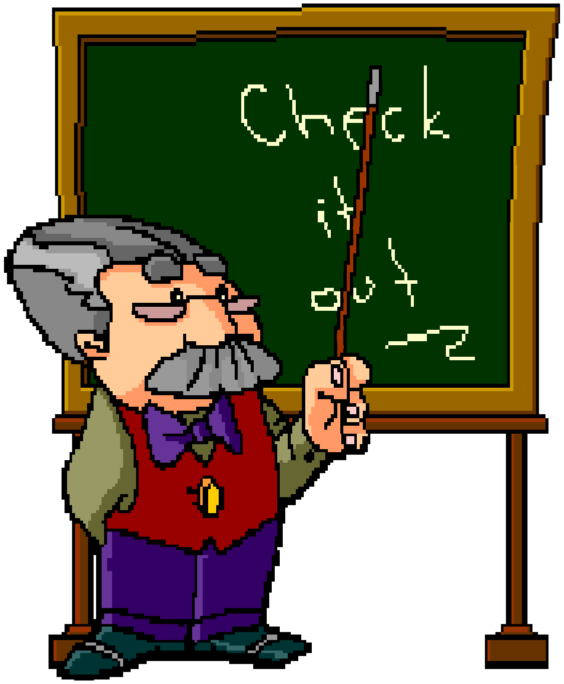
Water leg with or without oil chamber.



Chapter 6

Emulsion Treatment and Dehydration of Crude Oil

Outline



- Introduction
- Oil Emulsions
- Dehydration/Treating Processes
  - Removal of Free Water
  - Resolution of Emulsified Oil
  - Treating the Emulsion
- Heating
  - Methods of Heating Oil Emulsions
- Chemical Treatment

Introduction

- The fluid produced at the wellhead consists usually of gas, oil, free water and emulsified water.
- Before oil treatment, we must first remove the gas and free water from the well stream.
- This is essential in order to reduce the size of the oil-treating equipment.
- As presented in Chapters 4 and 5, the gas and most of the free water in the well stream are removed using separators.
- Gas, which leaves the separator, is known as "primary gas".
- Additional gas will be liberated during the oil treatment processes because of the reduction in pressure and application of heat.
- This gas known as "secondary gas" has to be removed.

Introduction

- The free water removed in separators is limited normally to water droplets of 500 μm and larger.
- The oil stream leaving the separator would normally contain free water droplets that are 500 μm and smaller in addition to water emulsified in the oil.
- This oil has yet to go through various treatment processes (dehydration, desalting, and stabilization) before it can be sent to refineries or shipping facilities.
- The objectives of dehydration process is first to remove free water and then break the oil emulsions to reduce the remaining emulsified water in the oil.

Introduction

- Depending on the original water content of the oil as well as its salinity and the process of dehydration used, oil-field treatment can produce oil with a remnant water content of 1%.
- The remnant water is normally called the *bottom sediments and water* (B.S.&W.)
- The basic principles for the treating process are as follows:
  - Breaking the emulsion, which could be achieved by either any, or a combination of the addition of heat, the addition of chemical, or the application of electrostatic field.
  - Coalescence of smaller water droplets into larger droplets.
  - Settling, by gravity, and removal of free water.

Oil Emulsions

- Rarely does oil production takes place without water accompanying the oil.
- Salt water is thus produced with oil in different forms as illustrated in Figure 1.
- Apart from free water, emulsified water (water-in-oil emulsion) is the one form that poses all of the concerns in the dehydration of crude oil.

Oil Emulsions

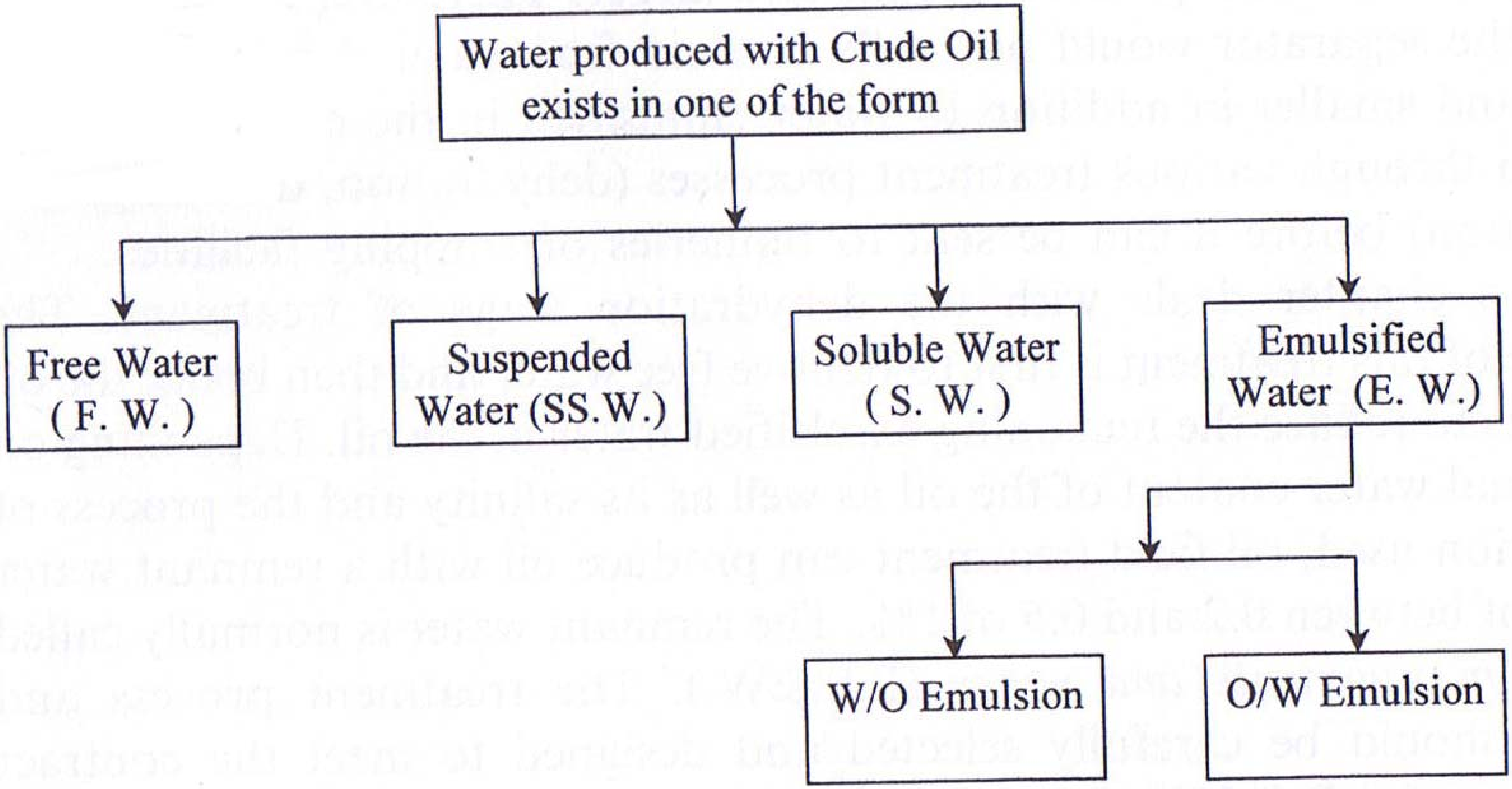
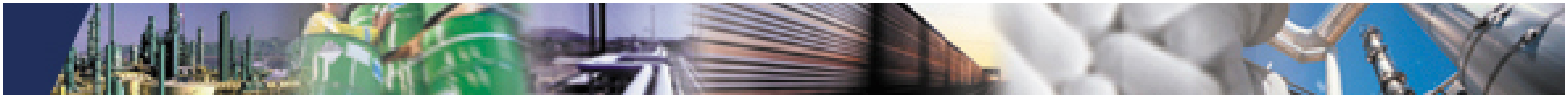


Figure 1 Forms of saline water produced with crude oil.



Oil Emulsions

- Oil emulsions are mixtures of oil and water.
- In general, an emulsion can be defined as a mixture of two immiscible liquids, one of which is dispersed as droplets in the other, and is stabilized by an emulsifying agent.
- In the oil field, crude oil and water are encountered as the two immiscible phases together.
- They normally form water-in-oil emulsion (W/O emulsion), in which water is dispersed as fine droplets in the bulk of oil, as shown in Figure 2.

Oil Emulsions

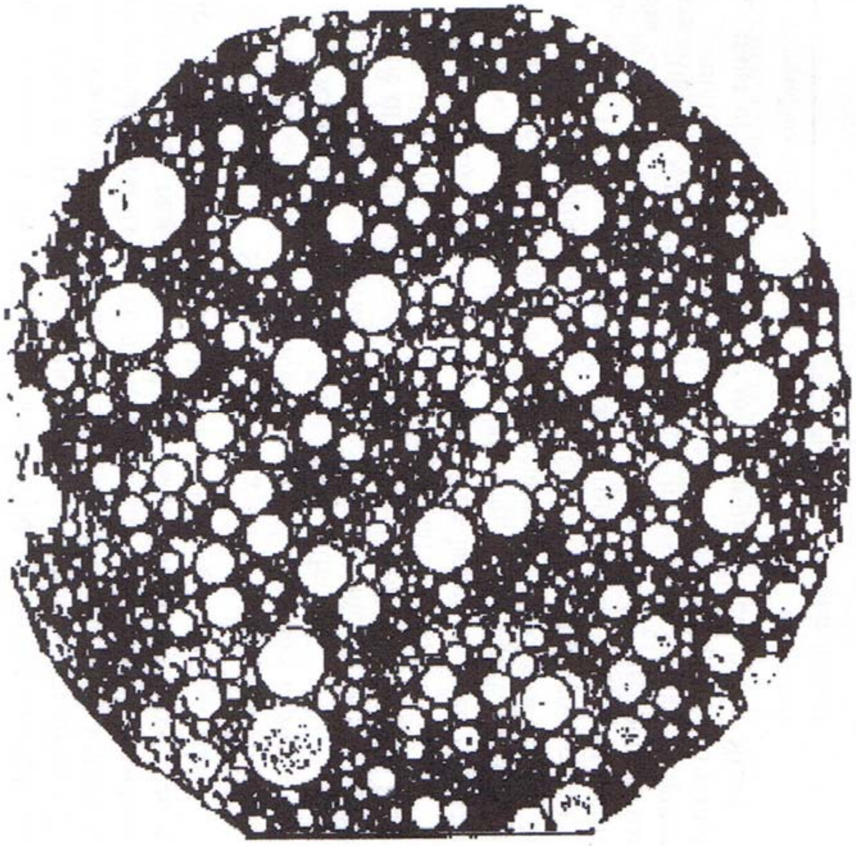


Figure 2 Photomicrograph of loose emulsion containing about 30% emulsified water in the form of droplets ranging in diameter from about 60 µm downward.

Dehydration/Treating Processes

- The method of treating "wet" crude oil for the separation of water associated with it varies according to the form in which water is found with the crude.
- Free-water removal comes first in the treating process, followed by the separation of "combined" or emulsion water along with any foreign matter such as sand and other sediments.
- The basic approaches of handling "wet" crude oils are illustrated in Figure 3.

Dehydration/Treating Processes

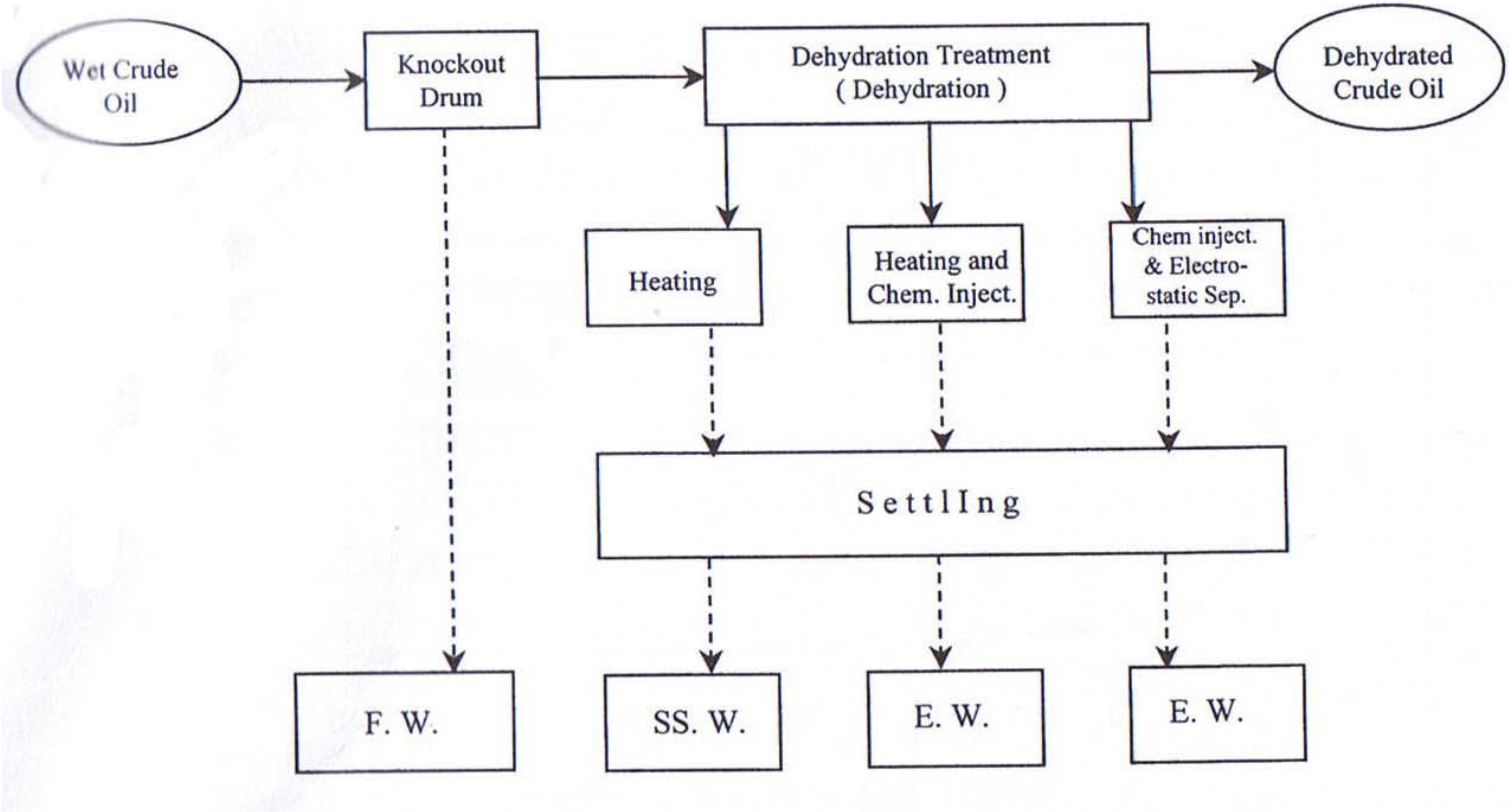
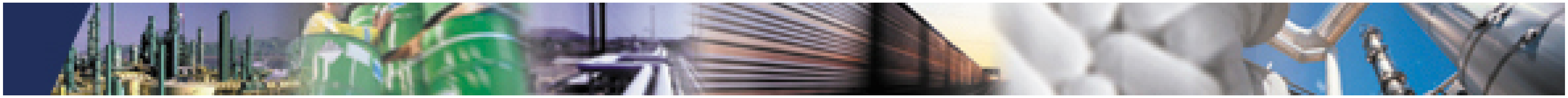


Figure 3 Basic approach of handling wet crude oil.



Removal of Free Water

- Free water is simply defined as that water produced with crude oil and will settle out of the oil phase if given little time.
- There are several good reasons for separating the free water first:
  - Reduction of the size of flow pipes and treating equipment.
  - Reduction of heat input when heating the emulsion (water takes about twice as much heat as oil).
  - Minimization of corrosion because free water comes into direct contact with the metal surfaces, whereas emulsified water does not.
- Free water removal takes place using a knockout vessel, which could be an individual piece of equipment or incorporated in a flow treater.
- Figures 4 and 5 show some of the common types of two-phase and three-phase free-water knockout drums, respectively.

Removal of Free Water

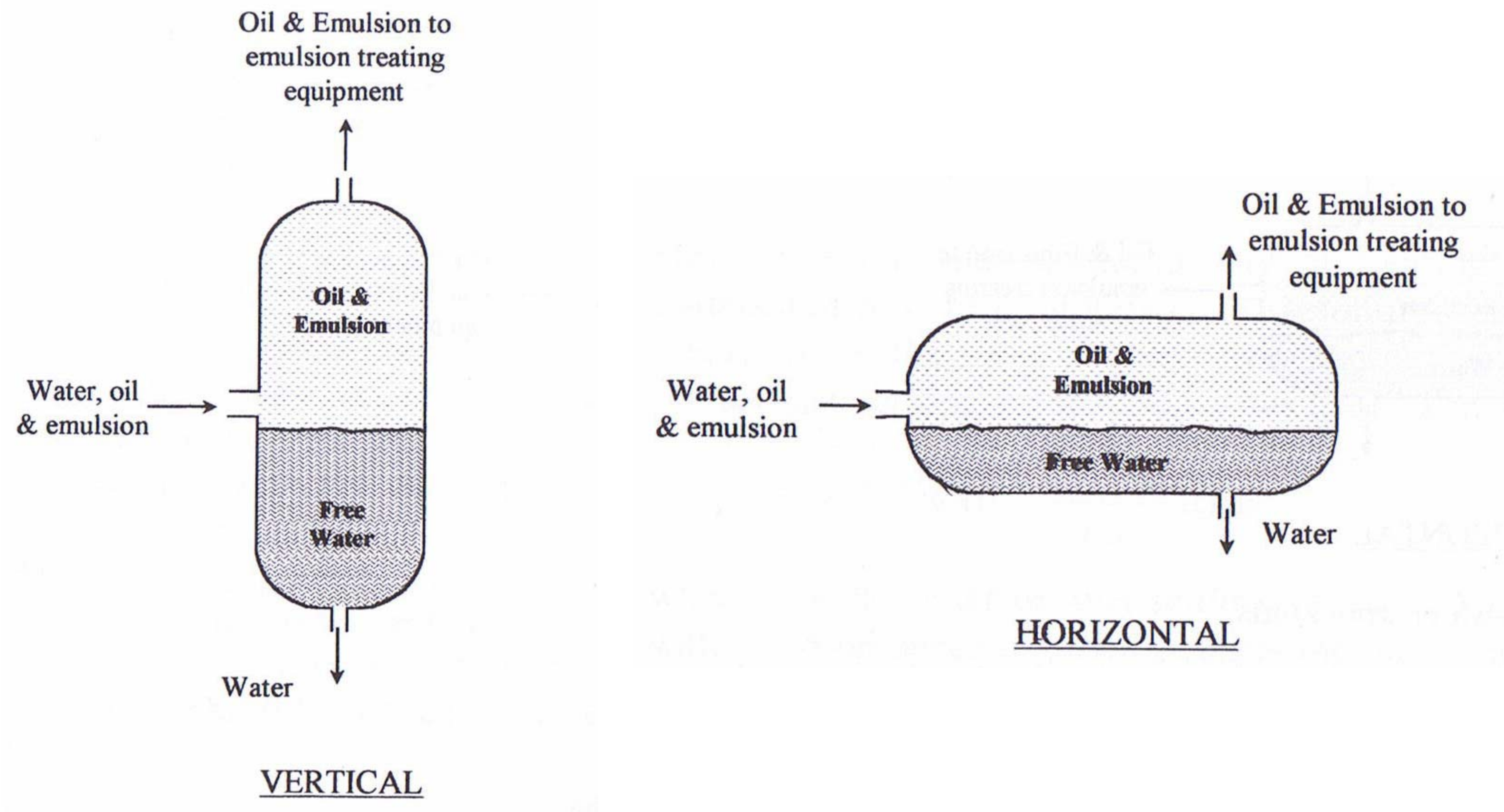


Figure 4 Two-phase free-water knockouts.

Removal of Free Water

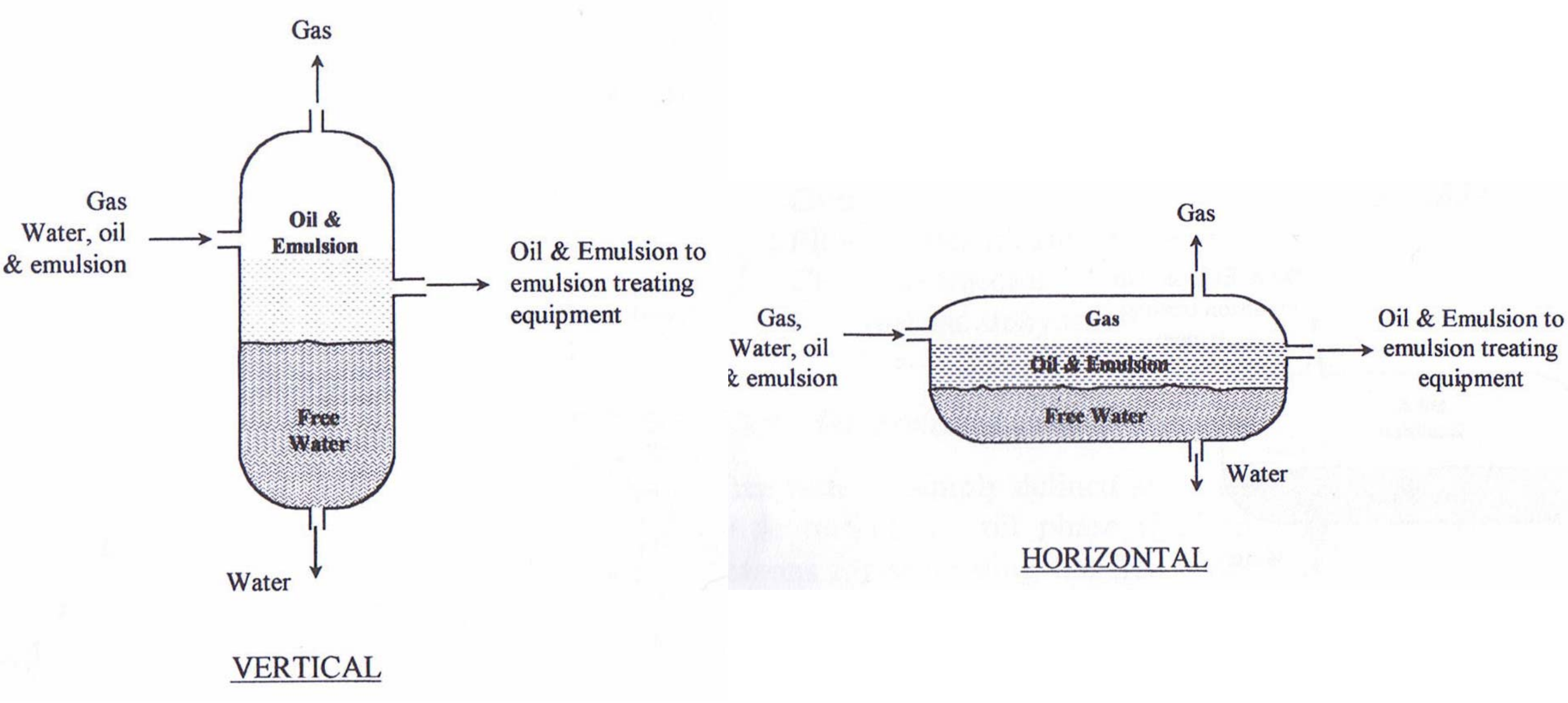
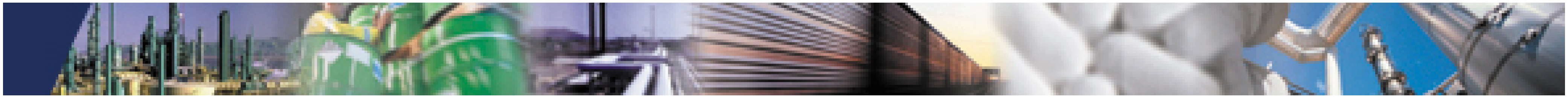


Figure 5 Three-phase free-water knockouts.



Resolution of Emulsified Oil

- This is the heart of the dehydration process, which consists of three consecutive steps:
  1. *Breaking the emulsion:* This requires weakening and rupturing the stabilizing film surrounding the dispersed water droplets. This is destabilization process and is affected by using what is called an “aid”, such as chemicals and heat.
  2. *Coalescence:* This involves the combination of water particles that became free water after breaking the emulsion, forming larger drops.
  3. *Gravitational settling and separation of water drops:* The larger water droplets resulting from the coalescence step will settle out of the oil by gravity and be collected and removed.

Treating the Emulsion

- As explained earlier, using chemicals followed by settling can break some emulsions.
- Other emulsions require heating and allowing the water to settle out of the bulk of oil.
- More difficult (tight) emulsions require, however, both chemicals and heat, followed by coalescence and gravitational settling.
- Basically, a dehydration process that utilizes any or a combination of two or more of the treatment aids mentioned earlier (heating, adding chemicals) is used to resolve water-oil emulsions.

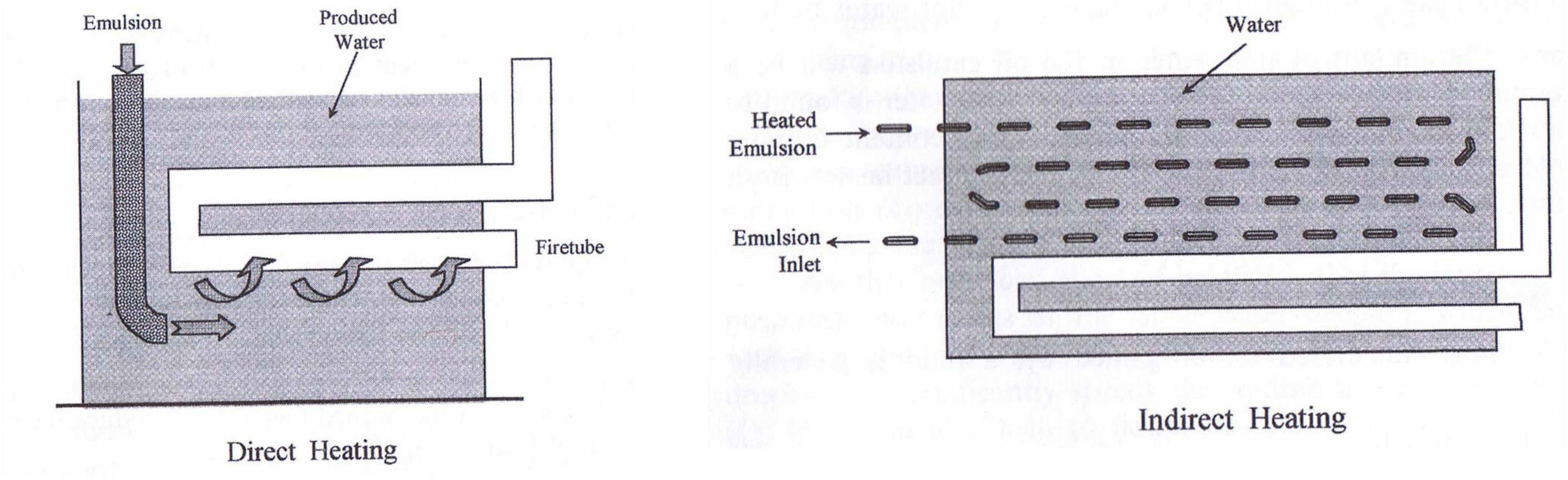
Heating

- Heating is the most common way of treating water-oil emulsions.
- The most significant effect is the reduction of oil viscosity with temperature.
- The viscosity of all types of crude oil drops rapidly with temperature, resulting in increasing the water droplet settling velocity and, thus, speeds and promotes the separation of water from the oil.

Methods of Heating Oil Emulsions

- The fuel used to supply heat in oil-treating operations is practically natural gas. Under some special conditions, crude oil may be used.
- Heaters are generally of two basic types:
  1. *Direct heaters*, in which oil is passed through a coil exposed to the hot flue gases of the burned fuel or to introduce the emulsion into a vessel heated using a fire tube heater.
  2. *Indirect heaters*, in which heat is transferred from the hot flue gases to the emulsion via water as a transfer medium. The emulsion passes through tubes immersed in a hot water bath.
- In general, the amount of free water in the oil emulsion will be a factor in determining which method is to be used.
- If free water is found to be 1-2%, then use an indirect heater.
- If the free water content is more enough to hold a level around the fire tube, then use a direct heater.

Methods of Heating Oil Emulsions



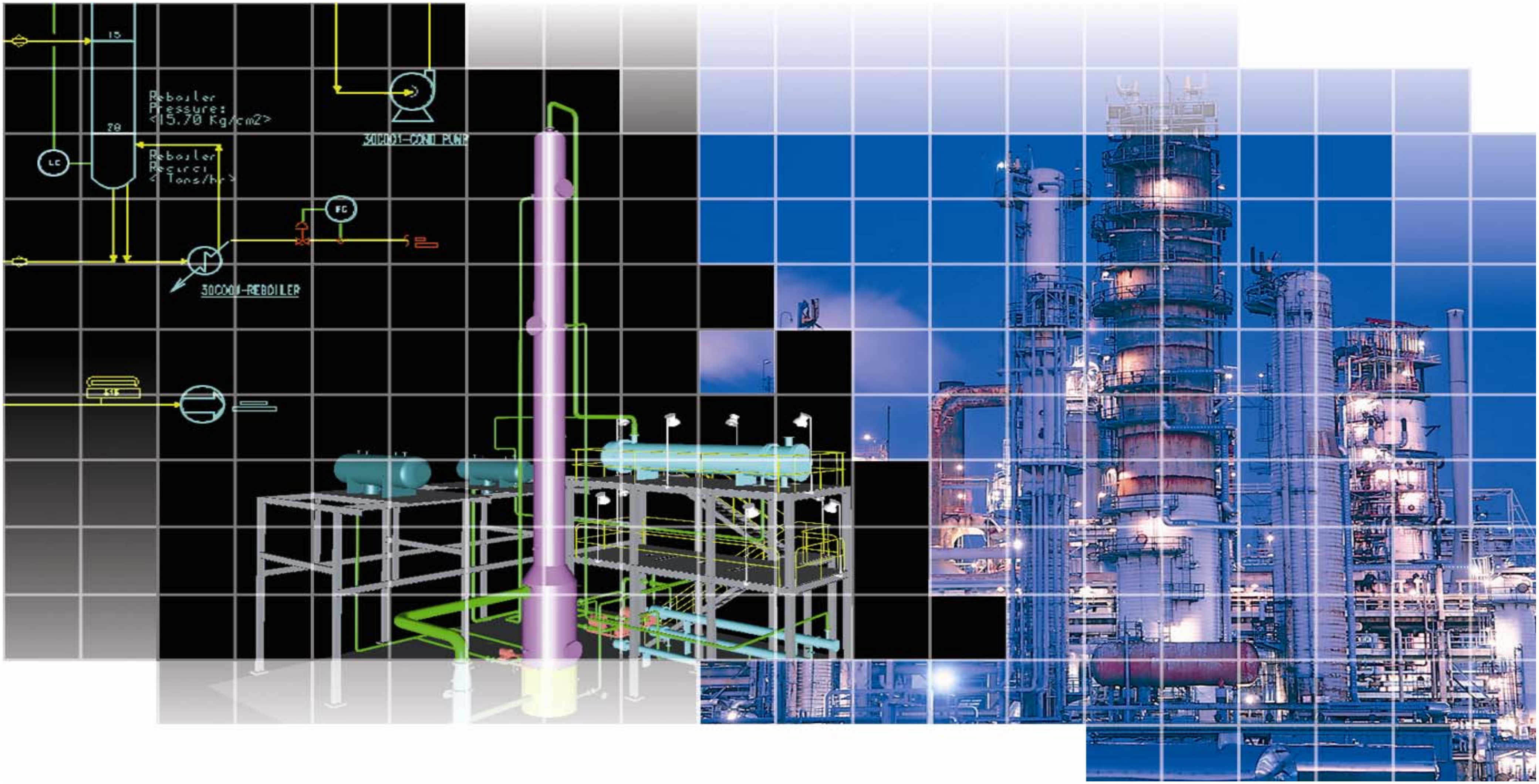
Direct Heating

Indirect Heating

Figure 5 Methods of heating the emulsion.

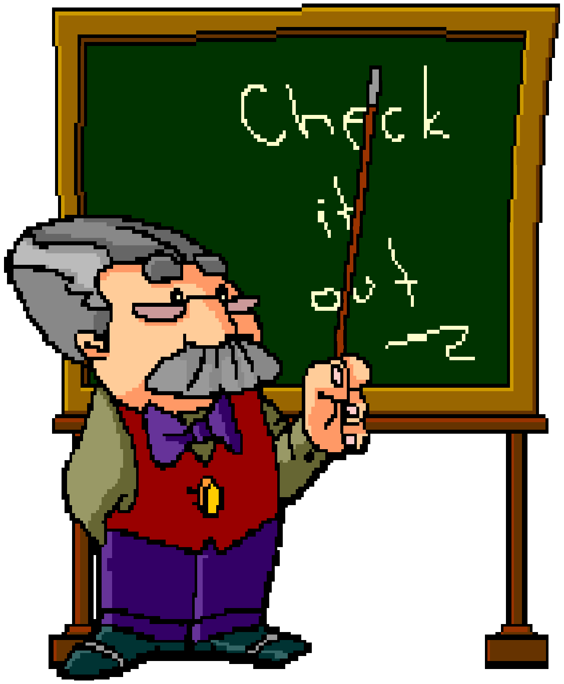
Chemical Treatment

- As mentioned earlier, some oil emulsions will readily break upon heating with no chemicals added.
- Others will respond to chemical treatment without heat.
- A combination of both "aids" will certainly expedite the emulsion-breaking process.
- Chemical additives, recognized as the second "aid" are special surface-active agents comprising relatively high-molecular-weight polymers.
- A deemulsifier, as it reaches to oil-water interface, function in the following pattern: flocculation, then film rupture, followed by coalescence.
- The faster the deemulsifier reaches the oil-water interface, the better job it achieves.

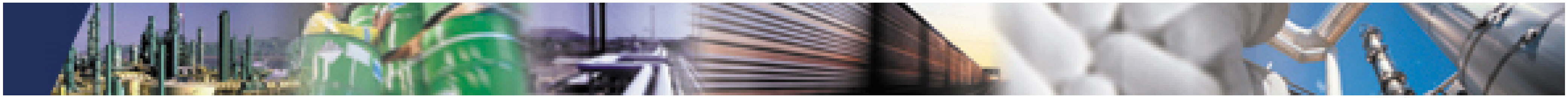


Chapter 7
Desalting of Crude Oil

Outline



- Introduction
- Description of the Desalting Process
- Effect of Operating Parameters

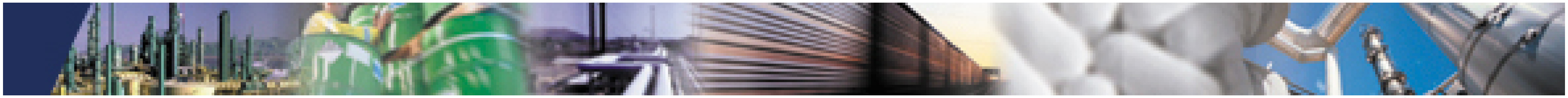


Introduction

- The removal of salt from crude oil for refinery feed stocks has been and still is a mandatory step.
- This is particularly true if the salt content exceeds 20 PTB (pounds of salt per thousand barrels of oil).
- Salt in crude oil is, in most cases, found dissolved in the remnant brine within the oil.
- The remnant brine is that part of the salty water that cannot be further reduced by any of the dehydration methods.
- It is understood that this remnant water exists in the crude oil as a dispersion of very fine droplets highly emulsified in the bulk of oil.
- The amount of salt in the crude oil is a function of the amount of the brine that remains in the oil W_R and of its salinity S_R.

Introduction

- The method of reducing the PTB by lowering the quantity of remnant water W_R is usually referred to as the treating process of oil dehydration.
- The other alternative of reducing the PTB is to substantially decrease the dissolved salt content of the remnant water (S_R).
- Reducing content of dissolved salt in the remnant water is called desalting process.
- Desalting of crude oil will eliminate or minimize problems resulting from the presence of mineral salts in crude oil.
- These salts often deposit chlorides on the heat transfer equipment of the distillation units and cause fouling effects.
- In addition, some chlorides will decompose under high temperature, forming corrosive hydrochloric acid.



Description of the Desalting Process

- From experience, we cannot economically achieve a satisfactory salt content in oil by using dehydration only (single stage).
- This is particularly true if the salinity of the water produced with oil is much greater than 20,000 ppm (formation water has a concentration of 50,000-250,00 mg/L).
- Accordingly, a two-stage system (a dehydration stage and a desalting stage) as shown in Figure 1a.
- Under certain conditions, however, a three-stage system may be used which consists of a dehydration stage and two consecutive desalting units as shown in Figure 1b.

Description of the Desalting Process

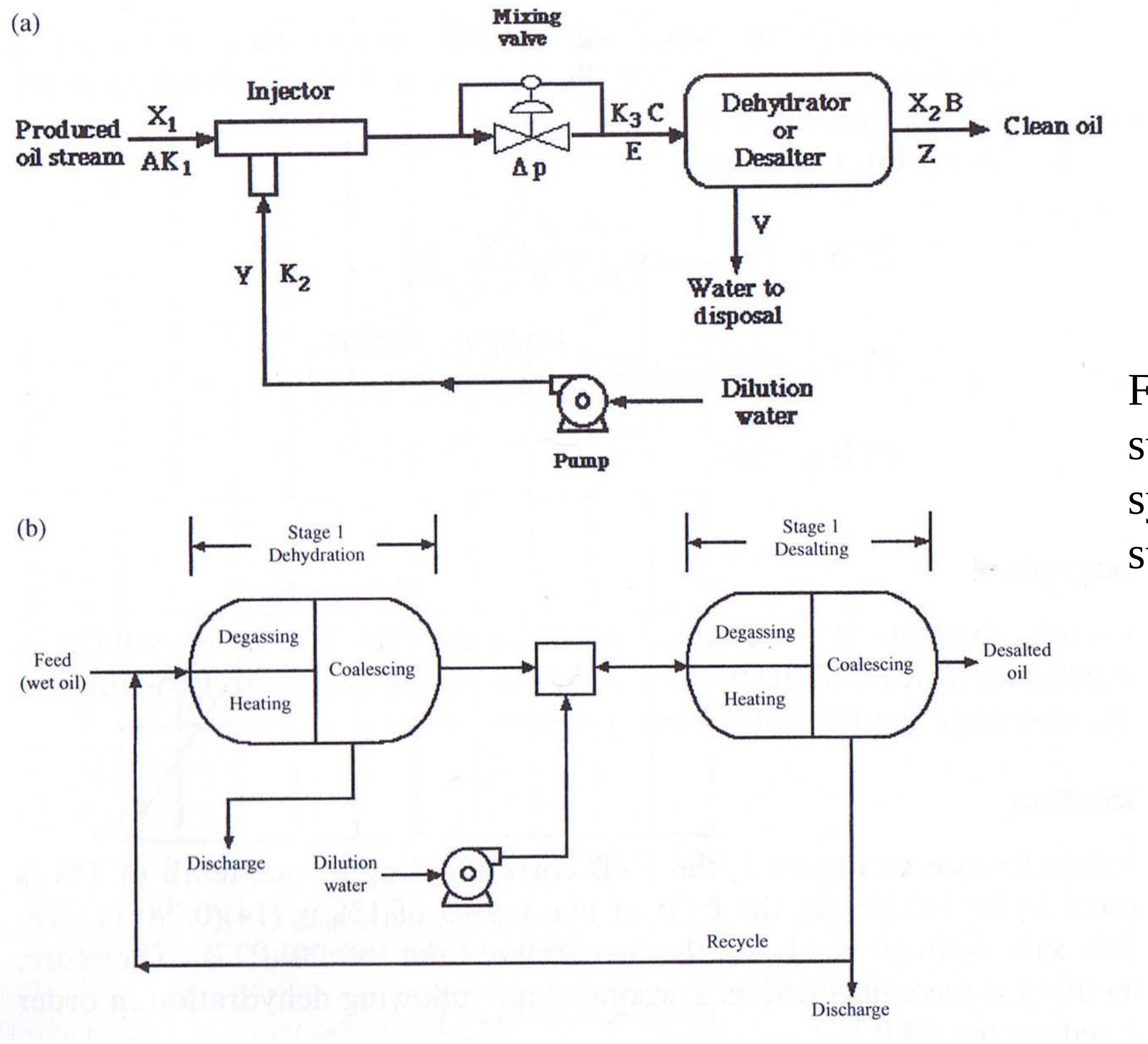
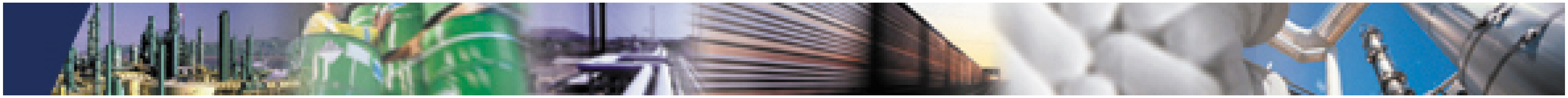


Figure 1 (a) Single-stage desalting system. (b) A two-stage desalting.

Description of the Desalting Process

- As shown in Figure 1, *wash water*, also called *dilution water*, is mixed with the crude oil coming from the dehydration stage.
- The wash water, which could be either fresh water, or water with lower salinity than the remnant water, mixes with the remnant water, thus diluting its salt concentration.
- The mixing results in the formation of water-oil emulsion.
- The oil (and emulsion) is then dehydrated in a manner similar to that described in Chapter 6.
- The separated water is disposed of through the field-produced water treatment and disposal system.
- In the two-stage desalting system, dilution water is added in the second stage and all, or part, of the disposed water in the second stage is recycled and used as the dilution water for the first desalting stage.



Description of the Desalting Process

- Two-stage desalting systems are normally used to minimize the wash water requirements.
- The mixing step in the desalting of crude oil is normally accomplished by pumping the crude oil (which is the continuous phase) and wash water (which is the dispersed phase) separately through a mixing device.
- The usual mixing device is simply a throttling valve.
- The degree of mixing can be enhanced if the interfacial area generated upon mixing is increased.
- A useful device for such a purpose is the application of multiple-orifice-plate mixers (MOMs) shown in Figure 2.

Description of the Desalting Process

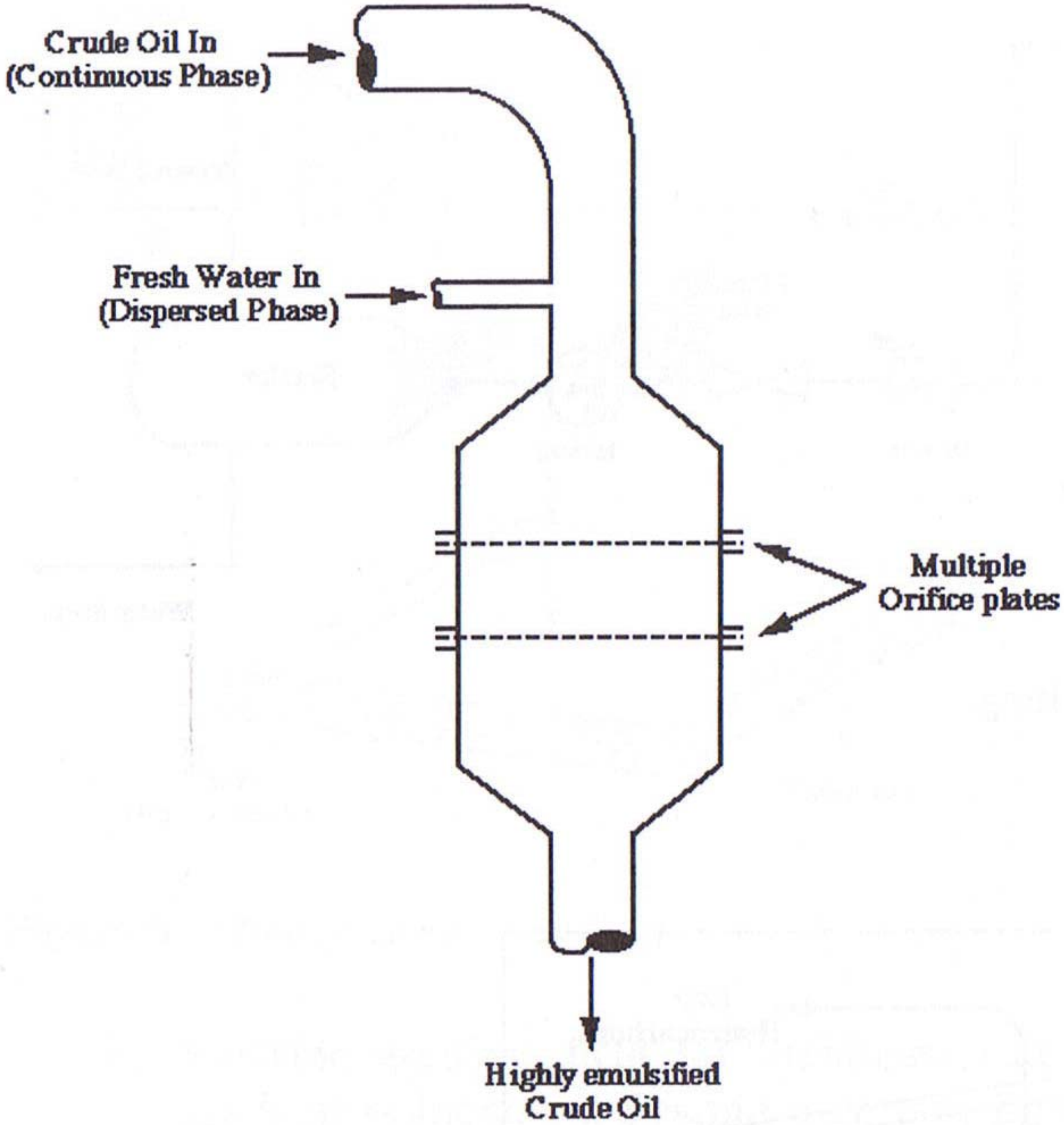


Figure 2 Details of multiple-orifice-plate mixers (MOMs).

Description of the Desalting Process

- It is of importance to point out that although the theory of dilution of remnant water with fresh water is sound in principle, it can become impossible to implement in actual application.
- It all depends on the intimate mixing of remnant water with dilution water.
- In the emulsion-treating step, a heating, chemical, or electrical demulsifying aid (or a combination of them) is commonly used.
- The chemical desalting process involves adding chemical agents and wash water to the preheated oil, followed by settling, as shown in Figure 3.
- The settling time varies from a few minute to 2 h.
- Some of the commonly used chemical agents are sulfonates, long-chain alcohols, and fatty acids.

Description of the Desalting Process

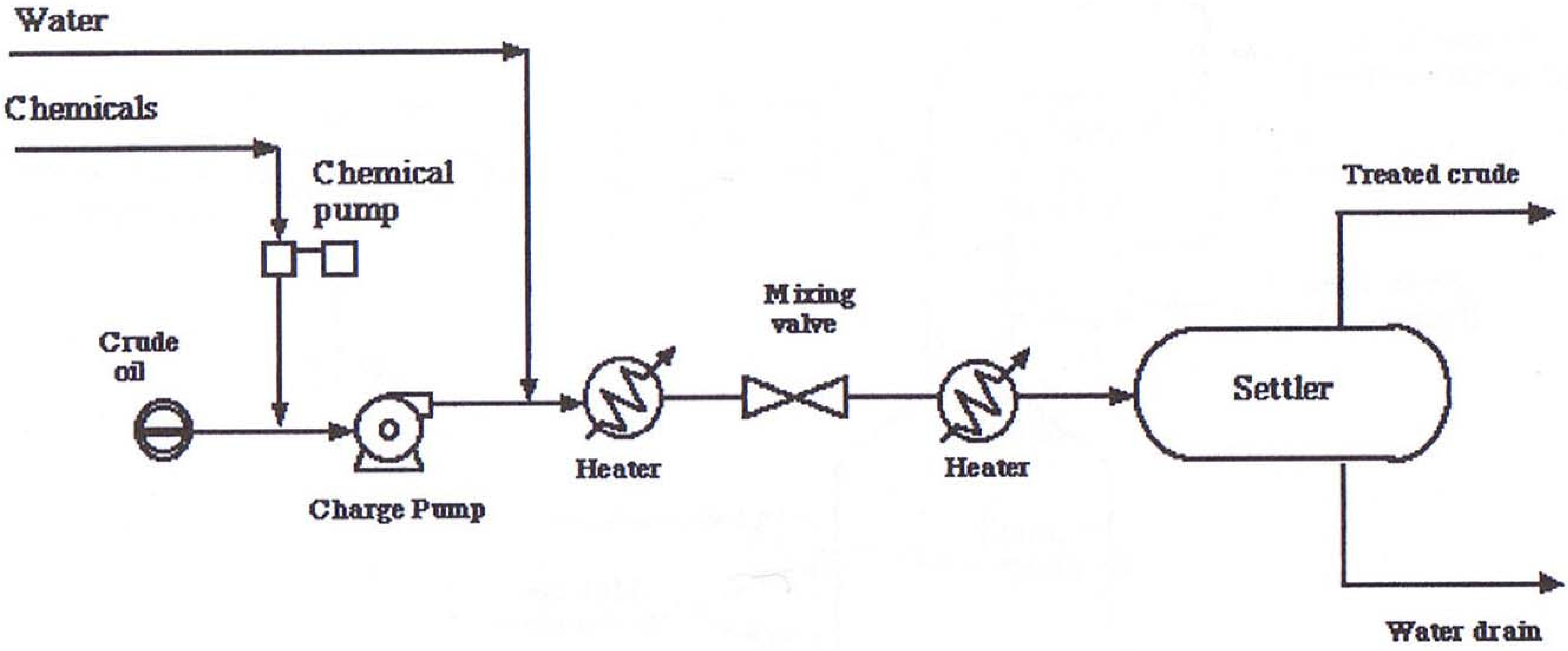
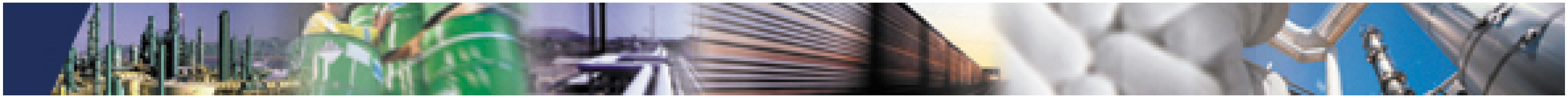
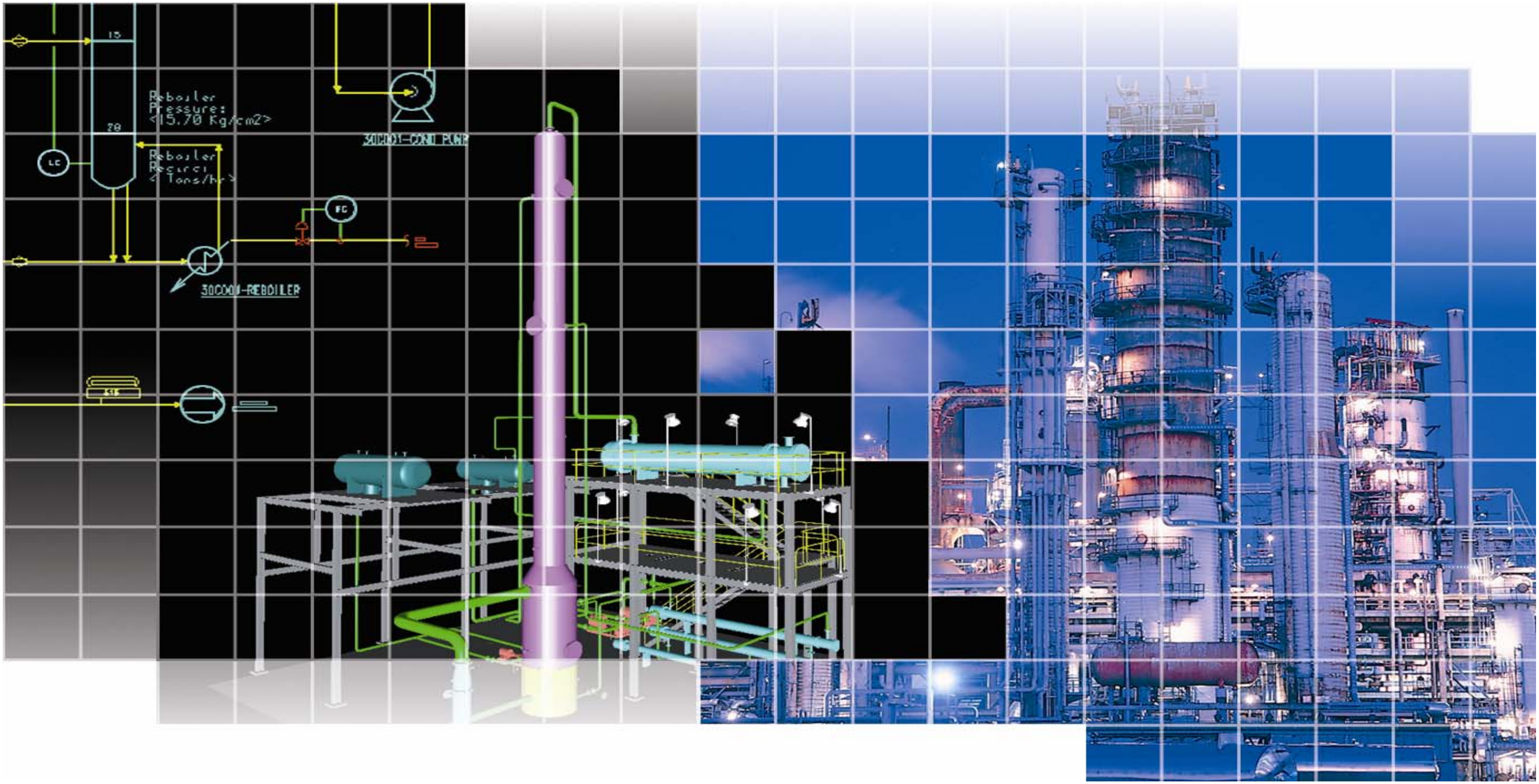


Figure 3 Chemical desalting.



Effect of Operating Parameters

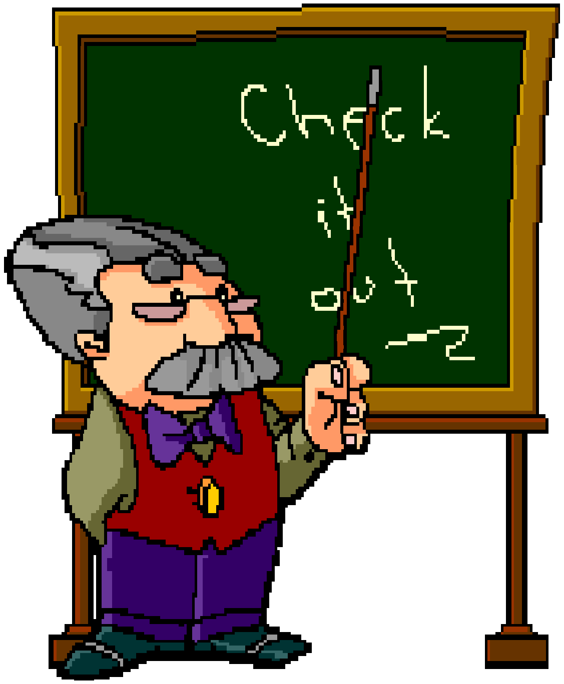
- The efficiency of desalting is dependent on the following parameters:
  1. *Water-crude interface level*. This level should be kept constant; any changes will change electrical field and perturbs electrical coalescence.
  2. *Desalting temperature*. Temperature affects water droplet settling through its effect on oil viscosity; therefore, heavier crude oils require higher desalting temperatures.
  3. *Wash water ratio*. Heavy crudes require a high wash water ratio to increase electrical coalescence. A high wash water ratio acts similarly to raise temperatures.
  4. *Pressure drop in the mixing valve*. A high-pressure-drop operation results in the formation of a fine stable emulsion and better washing. However, if the pressure drop is excessive, the emulsion might be difficult to break.
  5. *Type of demulsifiers*. Demulsifiers are added to aid in comlete electrostatic coalescence and desalting.



Chapter 8

Crude Oil Stabilization and Sweetening

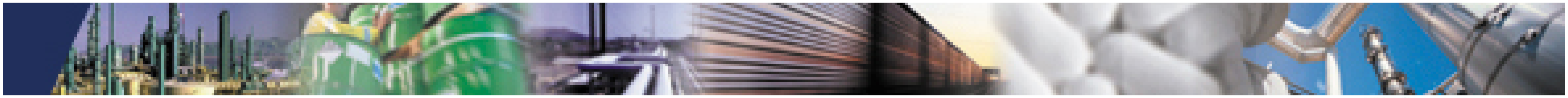
Outline



- Introduction
- Stabilization Operations
  - Stabilization by Flashing
  - Stabilization by Stripping
- Types of Stabilizer
  - Nonrefluxed Stabilizers
  - Main Features and Applications
- Crude Oil Sweetening

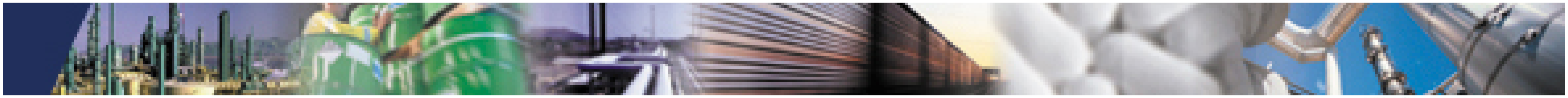
Introduction

- Once degassed and dehydrated-desalted, crude oil is pumped to gathering facilities to be stored in storage tanks.
- However, if there are any dissolved gases that belong to the light or the intermediate hydrocarbon groups, it will be necessary to remove these gases along with hydrogen sulfide (if any) before oil can be stored.
- This process is described as a “dual process” of both stabilizing and sweetening a crude oil.
- In stabilization, adjusting the pentanes and lighter fractions retained in the stock tank liquid can change the crude oil gravity.
- The economic value of the crude oil is accordingly influenced by stabilization.



Introduction

- First, liquids can be stored and transported to the market more profitably than gas.
- Second, it is advantageous to minimize gas losses from light crude oil when stored.
- This chapter deals with methods for stabilizing the crude oil to maximize the volume of production as well as its API gravity, againts two important constraints imposed by its vapor pressure and the allowable hydrogen sulfide content.
- To illustrate the impact of stabilization and sweetening on the quality of crude oil, the properties of oil before and after treatment are compared as follows:



Introduction

- (a) Before treatment (after desalting)

  Water content (B.S.&W.): 0.3% by volume, maximum

  Salt content: 10-20 PTB

  Gas: dissolved gases in varying amounts depending on the GOR

  Vapor pressure: 200-500 psia RVP (Reid vapor pressure)

  H_2S: up to 1000 ppm by weight

- (b) After treatment

  Water content (B.S.&W.): 0.3% by volume, maximum

  Salt content: 10-20 PTB

  Vapor pressure: 5-20 psia RVP

  H_2S: 10-100 ppmw

Introduction

- Sour wet crude must be treated to make it safe and environmentally acceptable for storage, processing, and export.
- Therefore, removing water and salt is mandatory to avoid corrosion; separation of gases and H_2S will make crude oil safe and environmentally acceptable to handle.
- Crude oil is considered “sweet” if the dangerous acidic gases are removed from it.
- On the other hand, it is classified as “sour” if it contains as much as 0.05 ft^3 of dissolved H_2S in 100 gal of oil.
- H_2S gas is a poison hazard because 0.1% in air is toxically fatal in 30 min.

Introduction

- Additional processing is mandatory – via this dual operation – in order to release any residual associated gases along with H_2S present in the crude.
- Prior to stabilization, crude oil is usually directed to a spheroid for storage in order to reduce its pressure to very near atmospheric, as shown in Figure 1.

Introduction

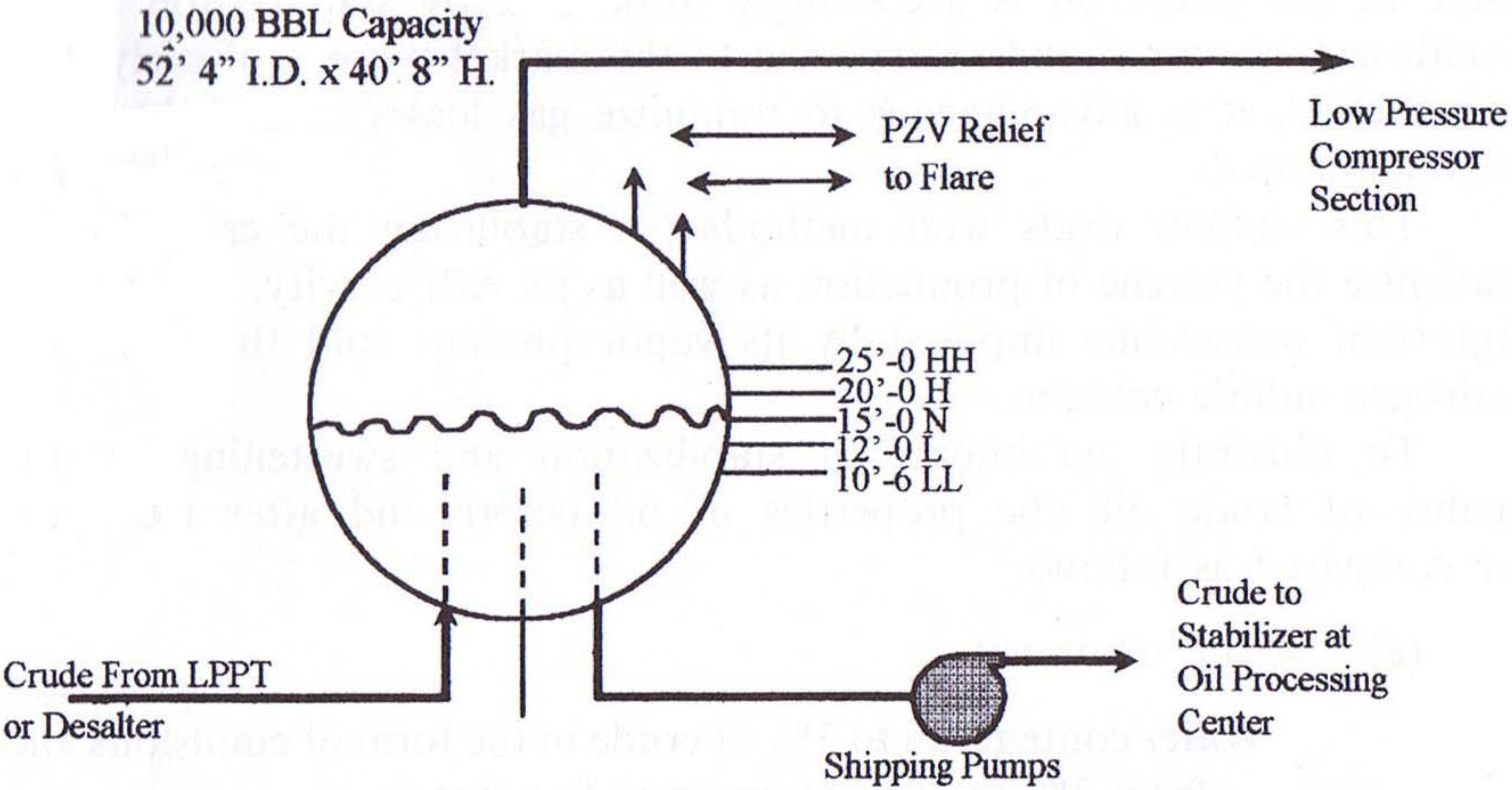
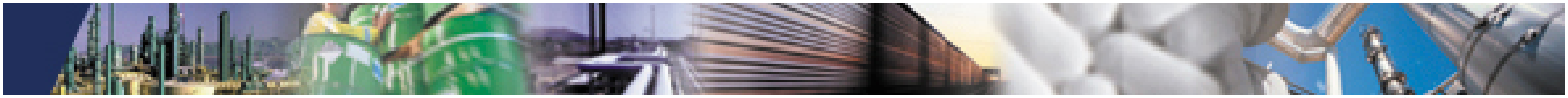


Figure 1 Typical spheroid for oil storage prior to stabilization.



Stabilization Operations

- As was presented in Chapter 4, the traditional process for separating the crude oil-gas mixture to recover oil consists of a series of flash vessels (GOSP) operating over a pressure range from roughly wellhead pressure to nearly atmospheric pressure.
- The crude oil discharged from the last stage in a GOSP or the desalter has a vapor pressure equal to the total pressure in the last stage.
- Usually, operation of this system could lead to a crude product with a RVP in the range of 4 to 12 psia.
- Most of the partial pressure of a crude comes from the low-boiling compounds, which might be present only in small quantities – in particular H_2S and low-molecular-weight hydrocarbons such as methane and ethane.

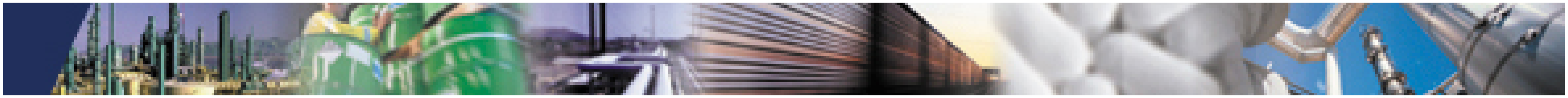
Stabilization Operations

- Now, stabilization is directed to remove these low-boiling compounds without losing the more valuable components.
- This is particularly true for hydrocarbons lost due to vent losses during storage.
- In addition, high vapor pressure exerted by low-boiling-point hydrocarbons imposes a safety hazard.
- Gases evolved from unstable crude are heavier than air and difficult to disperse with a greater risk of explosion.
- The stabilization mechanism is based on removing the more volatile components by (a) flashing using stage separation and (b) stripping operations.

Stabilization Operations

- As stated earlier, the two major specifications set for stabilized oil are as follows:
  - The Reid vapor pressure (RVP)
  - Hydrogen sulfide content
- Based on these specifications, different cases are encountered:

Case 1: sweet oil (no H_2S); no sweetening is needed. For this case and assuming that there is a gasoline plant existing in the facilities (i.e., a plant designed to recover pentane plus), stabilization could be eliminated, allowing the stock tank vapors to be collected (via the VRU) and sent directly to the gasoline plant, as shown in Figure 2.



Stabilization Operations

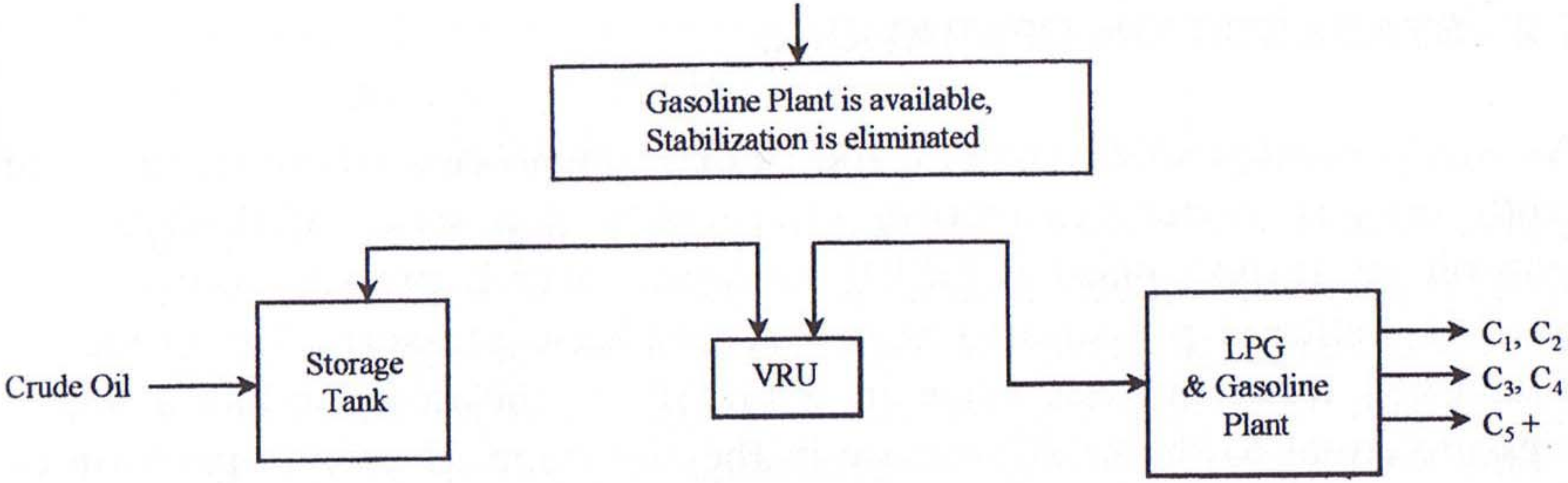


Figure 2 Field operation with no stabilization.

Stabilization Operations

Case 2: Sour crude; sweetening is a must. For this case, it is assumed that the field facilities did not include a gasoline plant. Stabilization of the crude oil could be carried out using one of the approaches outlined in Figure 3. Basically, either flashing or stripping stabilization is used.

- It can be concluded from the above that H_2S content in the well stream can have a bearing effect on the method of stabilization.
- Therefore, the recovery of liquid hydrocarbon can be reduced when the stripping requirement to meet the H_2S specifications is more stringent than that to meet the RVP specified.

Stabilization Operations

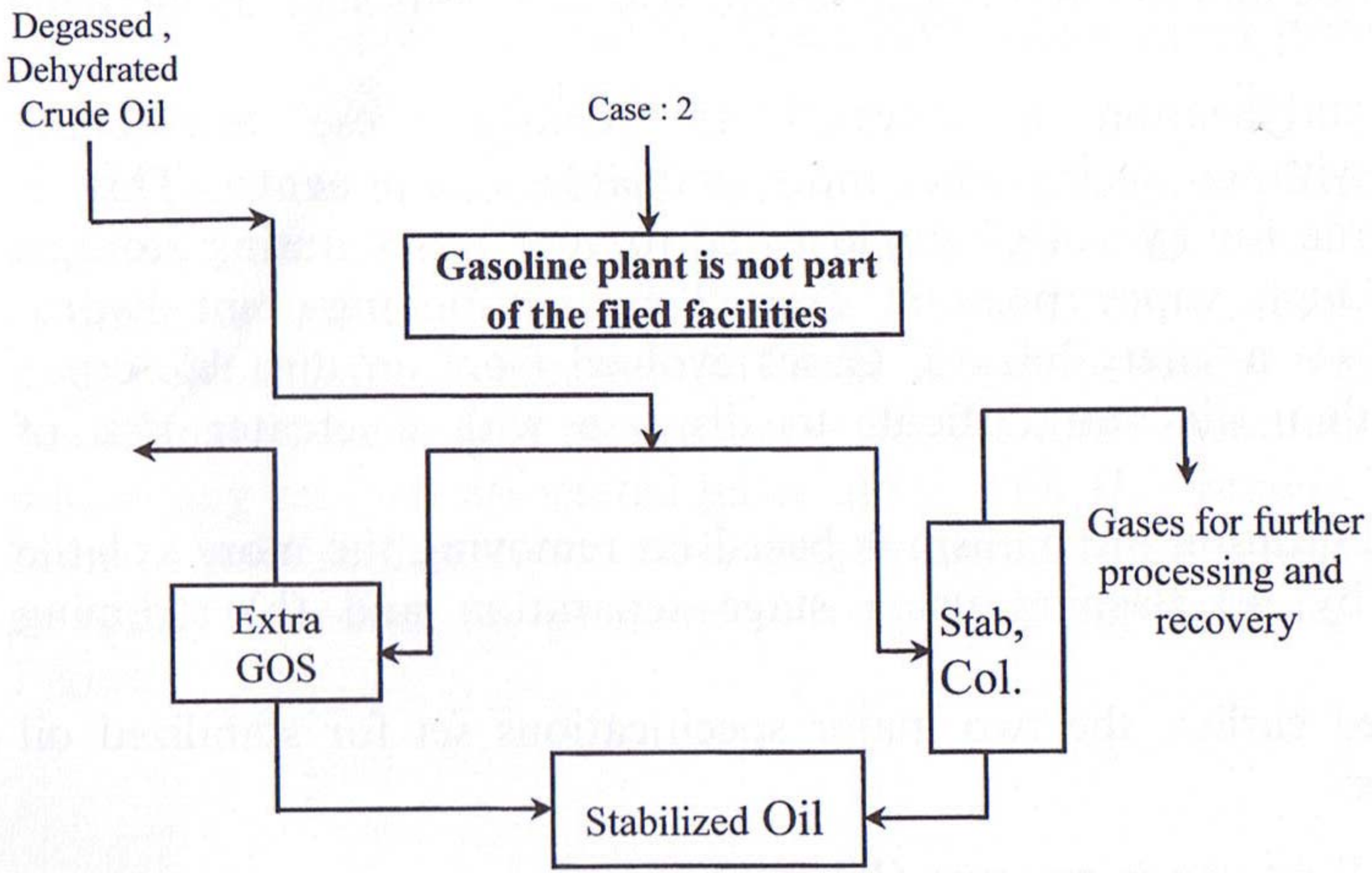


Figure 3 Alternatives for stabilizing crude oil.

Stabilization by Flashing

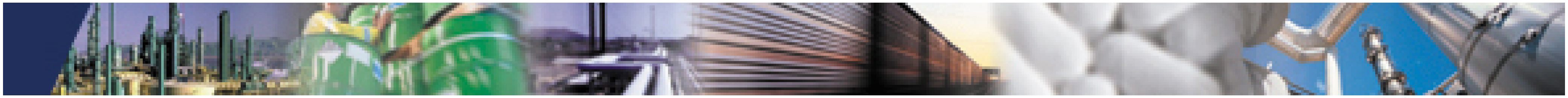
- The method utilizes an inexpensive small vessel to be located above the storage tank.
- The vessel is operated at atmospheric pressure.
- Vapors separated from the separator are collected using a VRU.
- This approach is recommended for small-size oil leases handling small volume of fluids to be processed.
- The principles underlying the stabilization process are the same for gas-oil separation covered in Chapter 4.

Stabilization by Stripping

- The stripping operation employs a stripping agent, which could be either energy or mass, to drive the undesirable components (low-boiling hydrocarbons and H_2S gas) out of the bulk of crude oil.
- This approach is economically justified when handling large quantities of fluid and in the absence of a VRU.
- It is also recommended for dual-purpose operations for stabilizing sour crude oil, where stripping gas is used for stabilization.
- Stabilizer-column installations are used for the stripping operations.

Types of Stabilizer

- Two basic types of stabilizer are commonly used:
    1. Conventional reflux types normally operate from 150 to 300 psia. This type of stabilizer is not common in field installations. It is more suitable for large central field processing plants.
    2. Nonrefluxed stabilizers generally operate between 55 to 85 psia. These are known as “cold feed” stabilizers. They have some limitations, but they are commonly used in field installations because of their simplicity in design and operation.



Nonrefluxed Stabilizers

- When hydrocarbon liquids are removed from the separators, the liquid is at its vapor pressure or bubble point.
- With each subsequent pressure reduction, additional vapors are liberated.
- Therefore, if the liquids were removed directly from a high-pressure separator into a storage tank, vapors generated would cause loss of lighter as well as heavier ones.
- This explains the need for many stages in a GOSP.
- Nevertheless, regardless of the number of stages used, some valuable hydrocarbons are lost with the overhead vapor leaving the last stage of separation or the stock tank.

Nonrefluxed Stabilizers

- A maximum volume of hydrocarbon liquid could be obtained under stock tank conditions with a minimum loss of solution vapors by fractionating the last-stage separator liquid.
- This implies using a simple fractionating column, where the vapors liberated by increasing the bottom temperature are counterflowed with the cool feed introduced from the top.
- Interaction takes place on each tray in the column.
- The vapors act as a stripping agent and the process is described as stabilization.
- Figure 4 depicts a stabilizer in its simplest form.

Nonrefluxed Stabilizers

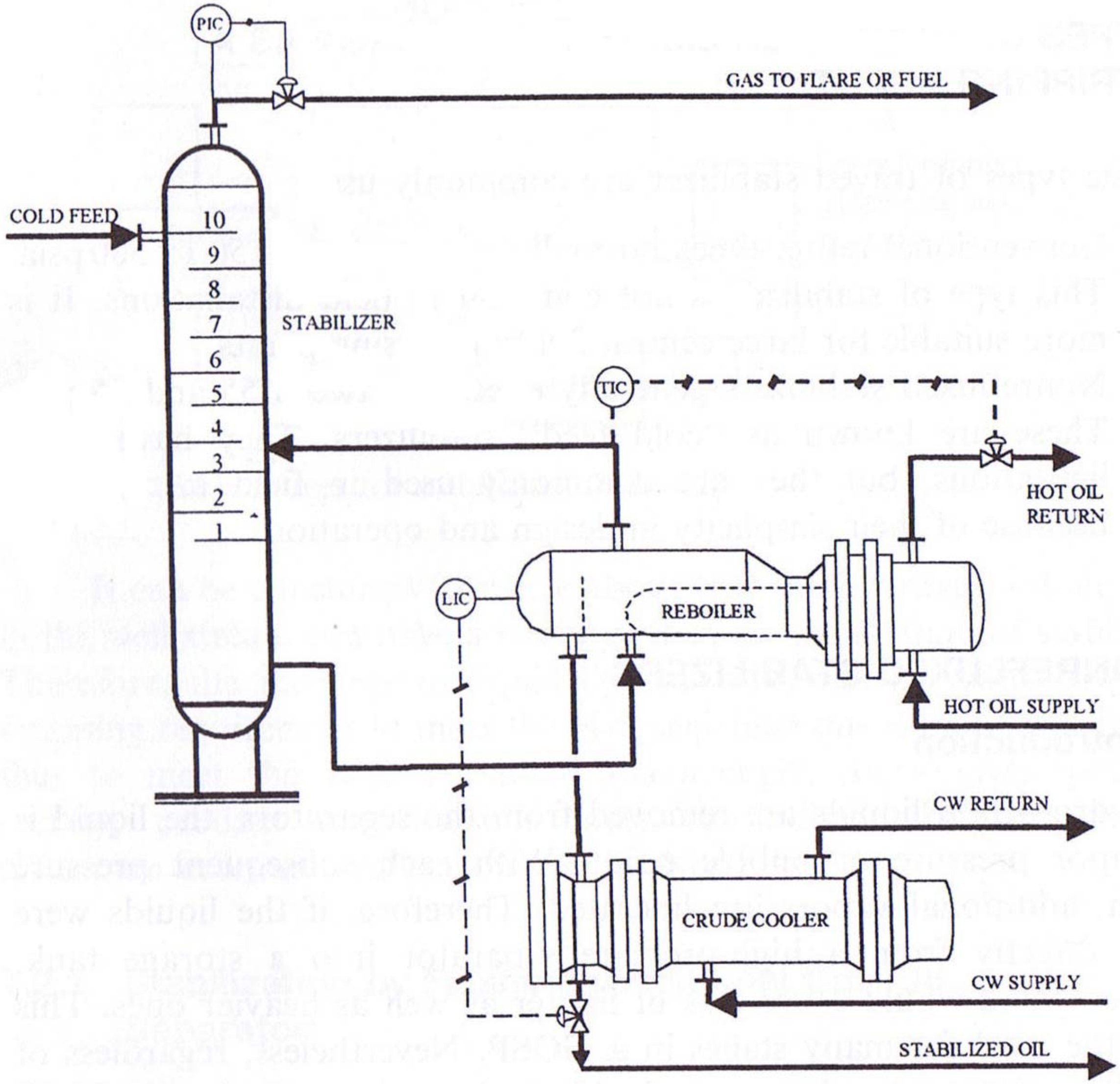


Figure 4 Typical trayed stabilizer.

Nonrefluxed Stabilizers

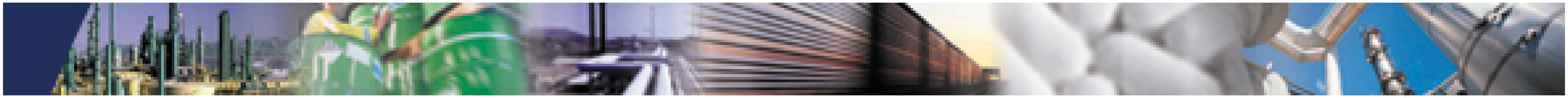
- Relatively cool liquid (oil) exiting the GOSP is fed to the top plate of the column where it contacts the vapor rising from below.
- The rising vapors strip the lighter ends from the liquid (i.e., acting as a stripping agent).
- At the same time, the cold liquid (acting as an internal reflux) will condense and dissolve heavier ends from the rising vapor, similar to a rectification process.
- The net separation is very efficient as compared to stage separation (3-7% more).
- In general, as the tower pressure is increased, more light ends will condense in the bottom.
- In normal operation, it is best to operate the tower at the lowest possible pressure without losing too much of the light ends.

Main Features and Applications

- Stabilizers used for oil production field operations should have the following features:
  - They must be self-contained and require minimum utilities that are available in the field, such as natural gas for fuel.
  - Stabilizers must be capable of unattended operation and to stand fail-safe operation.
  - Stabilizers must be equipped with simple but reliable control system.
  - They should be designed in a way to make them accessible for easy dismantling and reassembly in the field.
  - Maintenance of stabilizers should be made simple and straight-forward.

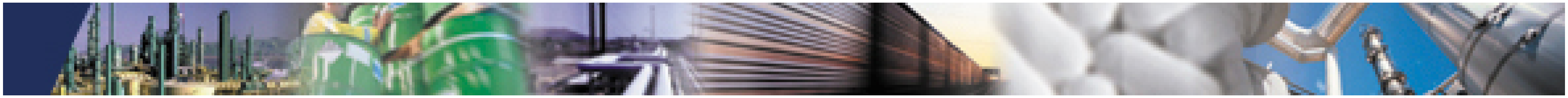
Main Features and Applications

- Stabilizer's applications, on the other hand, are justified over simple stage separation under the following operating conditions:
  - The first-stage separation temperature is between 0°F and 40°F.
  - The first-stage separation pressure is greater than 1200 psig.
  - The liquid gravity of the stock tank oil is greater than 45° API.
  - Oil to be stabilized contains significant quantities of pentanes plus, even though the oil gravity is less than 45° API.
  - Specifications are set by the market for product compositions – obtained from an oil – that require minimum light ends.



Crude Oil Sweetening

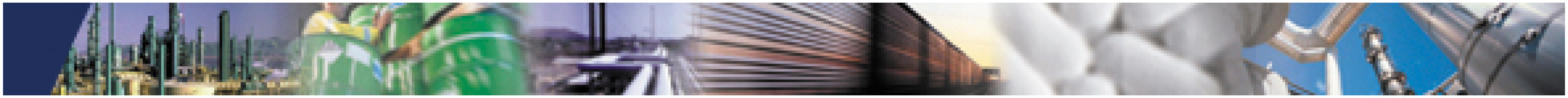
- Apart from stabilization problems of “sweet” crude oil, “sour” crude oils containing H_2S, mercaptans, and other sulfur compounds present unusual processing problems in oil field production facilities.
- The presence of H_2S and other sulfur compounds in the well stream impose many constraints.
- Most important are the following:
  - Personnel safety and corrosion considerations require that H_2S concentration be lowered to a safe level.
  - Brass and copper materials are particularly reactive with sulfur compounds; their use should be prohibited.
  - Sulfides stress cracking problems occur in steel structures.
  - Mercaptans compounds have an objectionable odor.



Crude Oil Sweetening

- Along with stabilization, crude oil sweetening brings in what is called a “dual operation”, which permits easier and safe downstream handling and improves and upgrades the crude marketability.
- Three general schemes are used to sweeten crude oil at the production facilities:

Process	Stripping Agent
1. Stage vaporization with stripping gas	Mass (gas)
2. Trayed stabilization with stripping gas	Mass (gas)
3. Reboiled tray stabilization	Energy (heat)



Stage Vaporization with Stripping Gas

- This process utilizes stage separation along with a stripping agent.
- H_2S is normally the major sour component having a vapor pressure greater than propane but less than ethane.
- Normal stage separation will, therefore, liberate ethane and propane from the stock tank liquid along with H_2S.
- Stripping efficiency of the system can be improved by mixing a lean (sweet) stripping gas along with the separator liquid between each separation stage.
- Figure 5 represent typical stage vaporization with stripping gas for crude oil sweetening/stabilization.
- The effectiveness of this process depends on the pressure available at the first-stage separator, well stream composition, and the final specifications set for the sweet oil.

Stage Vaporization with Stripping Gas

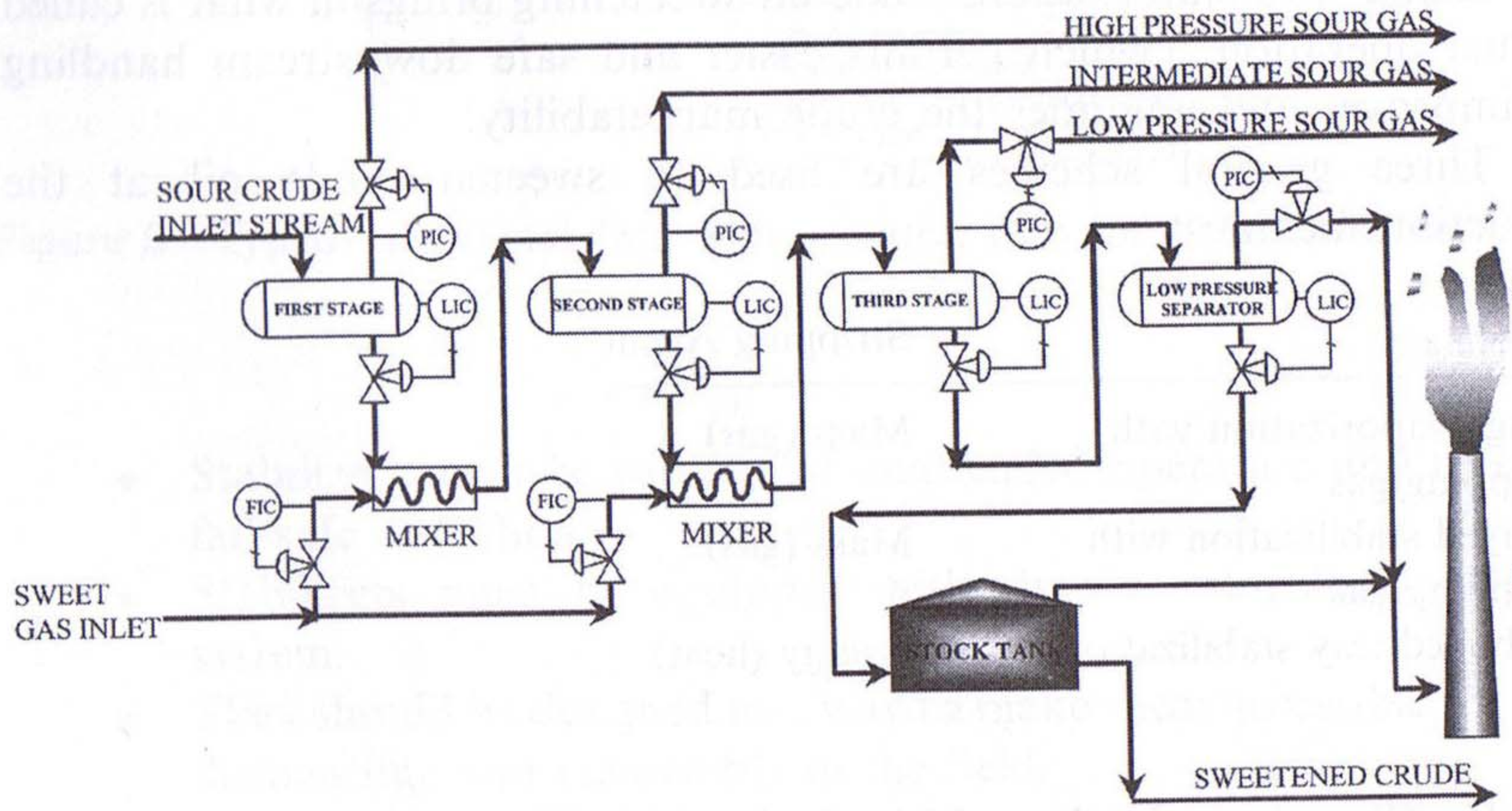


Figure 5 Crude sweetening by stage vaporization with stripping gas.

Trayed Stabilization with Stripping Gas

- In this process, a tray stabilizer (nonreflux) with sweet gas as a stripping gas as a stripping agent is used as shown in Figure 6.
- Oil leaving a primary separator is fed to the top tray of the column countercurrent to the stripping sweet gas.
- The tower bottom is flashed in a low-pressure stripper.
- Sweetened crude is sent to stock tanks, whereas vapors collected from the top of the gas separator and the tank are normally incinerated.
- These vapors cannot be vented to the atmosphere because of safety considerations.
- This process is more efficient than the previous one.
- However, tray efficiencies cause a serious limitation on the column height.

Trayed Stabilization with Stripping Gas

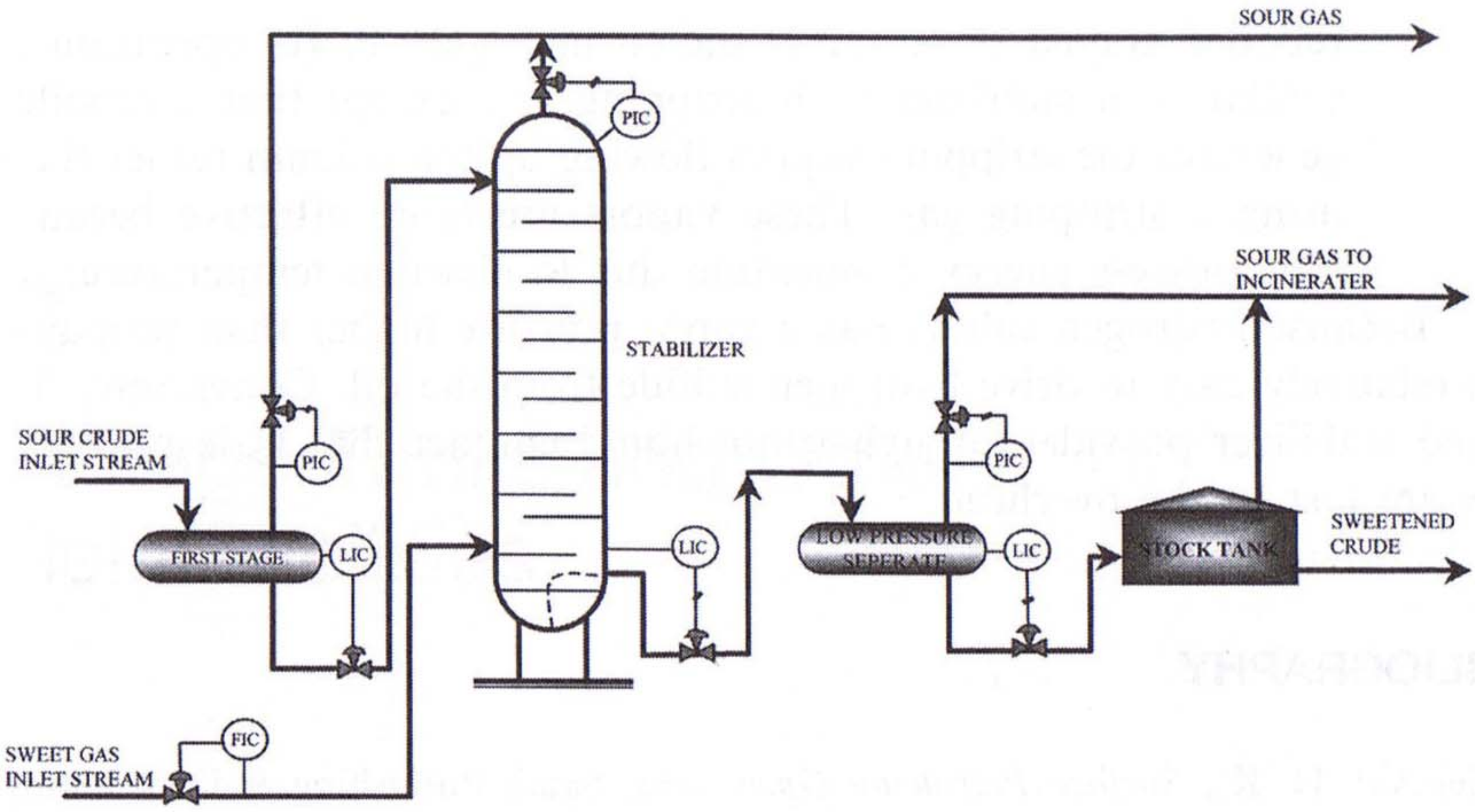
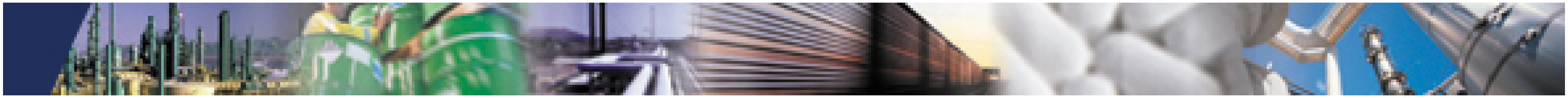


Figure 6 Crude sweetening by trayed stabilization with stripping gas.



Reboiled Trayed Stabilization

- The reboiled trayed stabilizer is the most effective means to sweeten sour crude oils.
- A typical reboiled trayed stabilizer is shown in Figure 7.
- Its operation is similar to a stabilizer with stripping gas, except that a reboiler generates the stripping vapors flowing up the column rather than using a stripping gas.
- These vapors are more effective because they posses energy momentum due to elevated temperature.
- Because H_2S has a vapor pressure higher than propane, it is relatively easy to drive H_2S from the oil.
- Conversely, the trayed stabilizer provides enough vapor/liquid contact that little pentanes plus are lost to the overhead.

Reboiled Trayed Stabilization

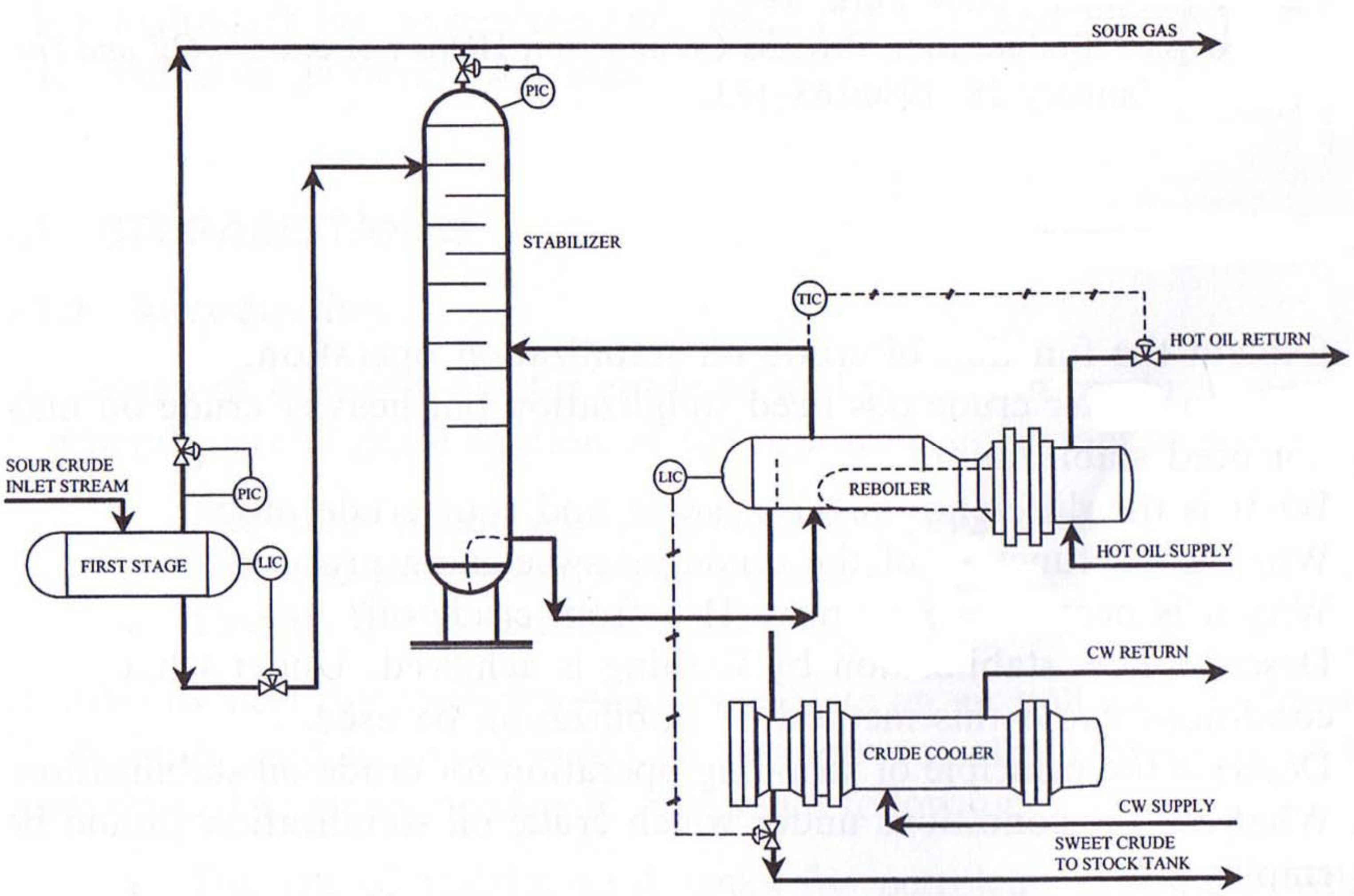
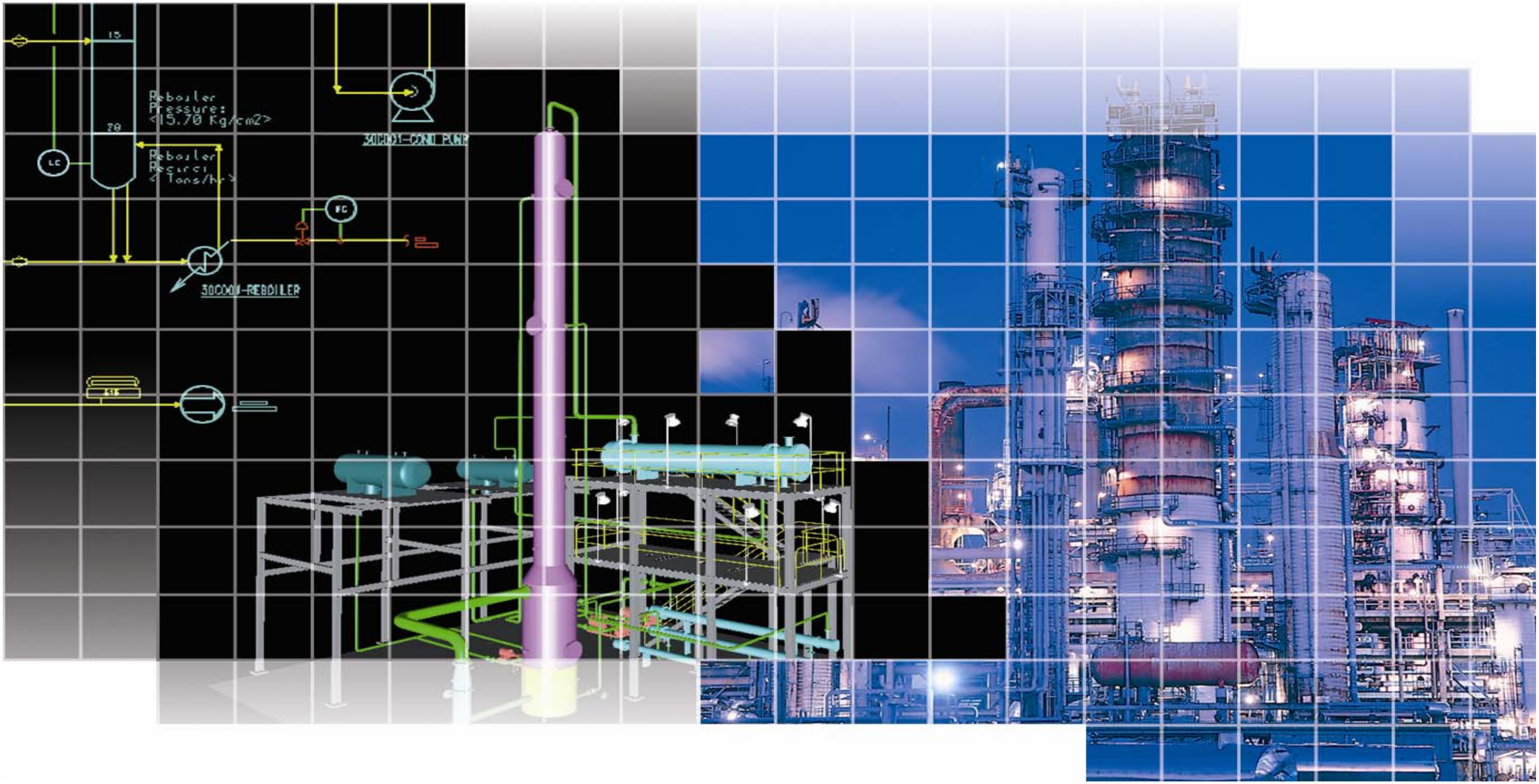
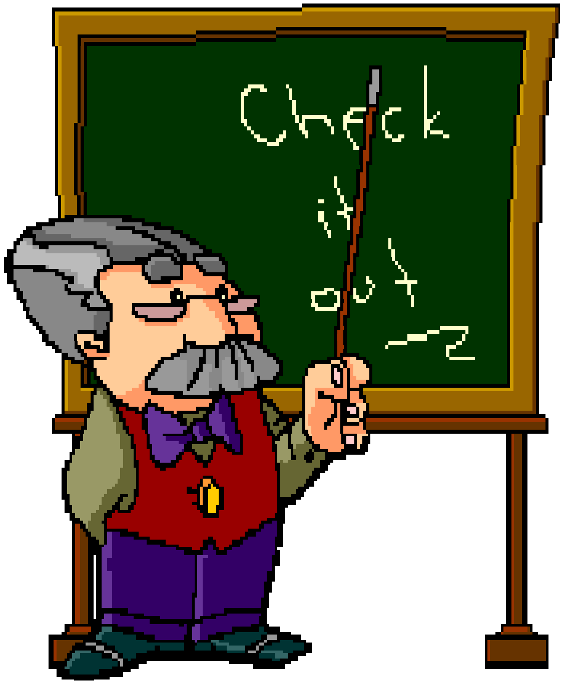


Figure 7 Crude sweetening by reboiled trayed stabilization.



Chapter 9
Overview of Gas Field Processing

Outline



- Planning the System
- Background
  - What is Natural Gas?
  - Why Field Processing?
  - Types of Gas Reservoir
  - Gas Specifications
- Effect of Impurities Found in Natural Gas

Planning the System

- This chapter and the next three are devoted to field treatment and processing operations of natural gas and other associated products.
- These include dehydration, acidic gas removal (H_2S and CO_2), and the separation and fractionation of liquid hydrocarbons (natural gas liquid; NGL).
- Sweetening of natural gas almost always precedes dehydration and other gas plant processes carried out for the separation of NGL.
- Dehydration, on the other hand, is usually required before the gas can be sold for pipeline marketing and it is necessary step in the recovery of NGL from natural gas.
- For convenience, a system involving field treatment of a gas project could be divided into two main stages, as shown in Figure 1.

Planning the System

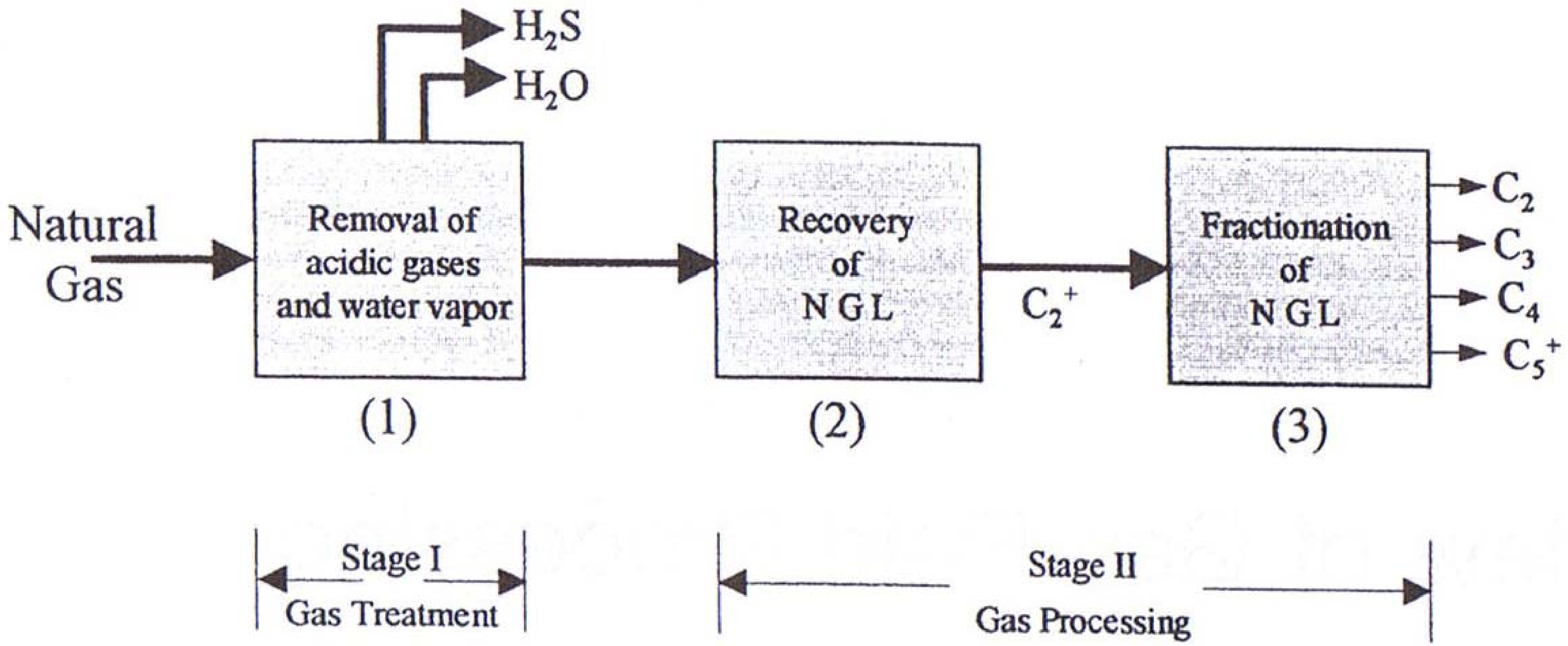


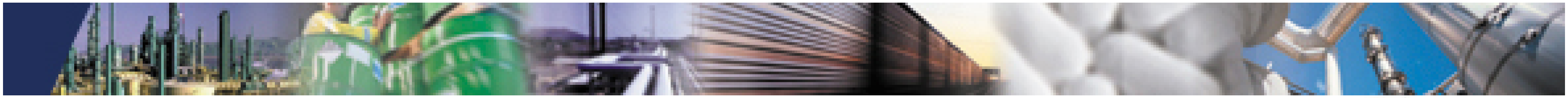
Figure 1 Operations involved in the treatment and processing of natural gas.

Planning the System

- Natural gas field processing and the removal of various components from it tend to involve the most complex and expensive processes.
- Natural gas leaving the field can have several components which will require removal before the gas can be sold to a pipeline gas transmission company.
- All of the H_2S and most of the water vapor, CO_2, and N_2 must be removed from the gas.
- Gas compression is often required during these various processing steps.
- To illustrated this point, a sour gas leaving a GOSP might require first the use of an amine unit (MEA) to remove the acidic gases, a glycol unit (TEG) to dehydrate it, and a gas compressor to compress it before it can be sold.

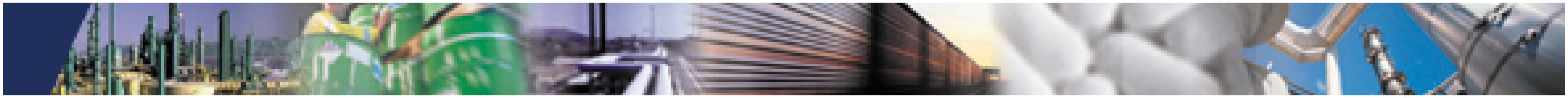
Planning the System

- It is also generally desirable to recover NGL present in the gas in appreciable quantities.
- This normally includes the hydrocarbons known as C_3+.
- In some cases, ethane (C_2) could be separated and sold as a petrochemical feed stock.
- NGL recovery is the first operation in Stage II.
- To recover and separate NGL from a bulk of a gas stream would require a change in phase; that is, a new phase has to be developed fro separation to take place by using one of the following:
  1. An energy-separating agent; examples are refrigeration for partial or total liquefaction and fractionation.
  2. A mass-separating agent: examples are adsorption and absorption (using selective hydrocarbons, 100-180 MW).



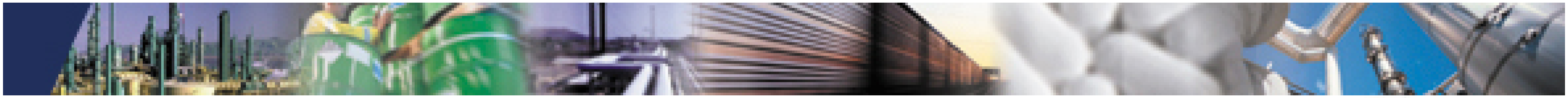
Planning the System

- The second operation in Stage II is concerned with the fractionation of NGL product into specific cuts such as LPG (C_3/C_4) and natural gasoline.
- In designing a system for gas field processing, the following parameters should be evaluated and considered in the study:
  1. Estimated gas reserve (both associated and free).
  2. The gas flow rate and composition of the feed gas.
  3. Market demand, both local and export, for the products
  4. Geographic location and methods of shipping of finished products.
  5. Environmental factors.
  6. Risks involved in implementing the project and its economics.
- Of these factors, the gas/oil reserve might be the paramount factor.



What is Natural Gas?

- Natural gas is the gas obtained from natural underground reservoirs either as free gas or gas associated with crude oil.
- It generally contains large amount of methane (CH_4) along with decreasing amounts of other hydrocarbons.
- Impurities such as H_2S, N_2, and CO_2 are often found with the gas.
- It also generally comes saturated with water vapor.



Why Field Processing?

- The principal market for natural gas is achieved via transmission lines, with distribute it to different consuming centers, such as industrial, commercial, and domestic.
- Field processing operations are thus enforced to treat the natural gas in order to meet the requirements and specifications set by the gas transmission companies.
- The main objective is to simply obtain the natural gas as a main product free from impurities.
- In addition, it should be recognized that field processing units are economically justified by the increased liquid product (NGL) recovery above that obtained by conventional separation.

Types of Gas Reservoir

- At one end, some fields produce saturated associated gas (gas associated with crude oil); on the other end, a dry gas (free gas) is produced from some fields.
- In between these two ends, one can find numerous types of reservoir in which the hydrocarbons vary in composition and, hence, the gas produced.
- Some of the factors contributing to these changes are as follows:
  1. The contents of heavier components.
  2. The percentage of acidic gases.
  3. The presence of inert gases.
- For discussion purposes, Figure 2 illustrates some diversified processing operations involved in the treatment of natural gas produced by different reservoirs.

Types of Gas Reservoir

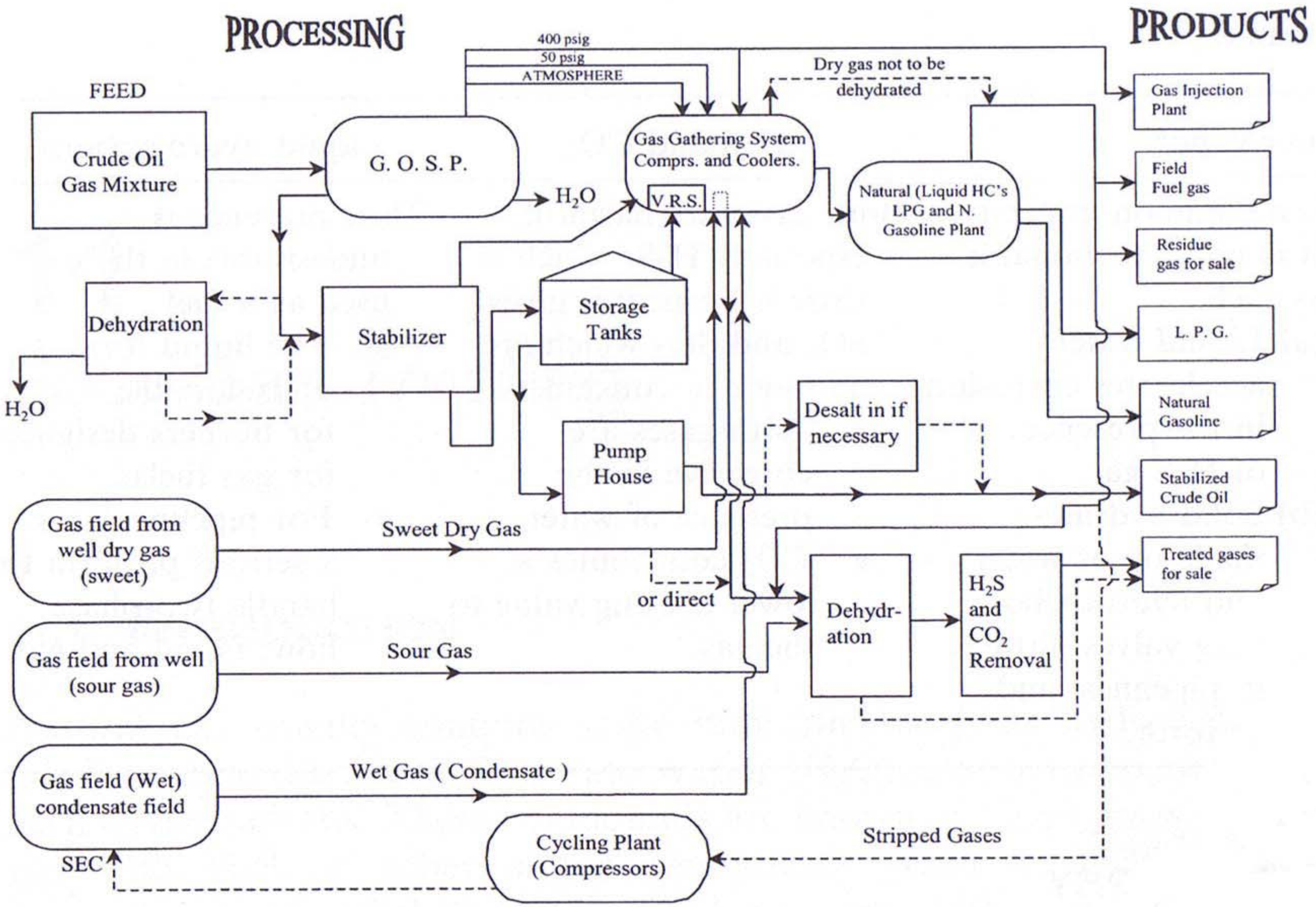
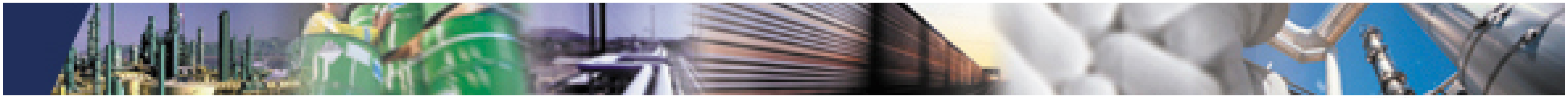


Figure 2 Schematic presentation of processing operations



Gas Specifications

- Market sales of natural gas require some specifications set by the consumers regarding the maximum contents allowable for the following: acidic gases and sulfur, oxygen and carbon dioxide, water vapor, and liquefiable hydrocarbons.

H_2S	0.25-0.3 grain per 100 ft^3
Total sulfur	20 grains per 100 ft^3
Oxygen (air)	0.2% by volume
Carbon dioxide	2% by volume
Liquefiable hydrocarbons	0.2 gal per 1000 ft^3
Water content	7 lbs/MMSCF (in a 1000-psia gas line)
Thermal heating value	1150 Btu/ft^3

Effect of Impurities Found in NG

- Field processing operations of natural gas, which is classified as a part of gas engineering, generally include the following:
  1. Removal of water vapor, dehydration.
  2. Removal of acidic gases (H_2S and CO_2).
  3. Separation of heavy hydrocarbons.
- Before these processes are detailed in the following chapters, the effect each of these impurities has on the gas industry, as end user, is briefly outlined:
  1. Water vapor:
     - Liquid water accelerates corrosion in the presence of H_2S gas.
     - Solid hydrates, made up of water and hydrocarbons, plug valves, fittings in pipelines, and so forth.

Effect of Impurities Found in NG

2. H_2S and CO_2:

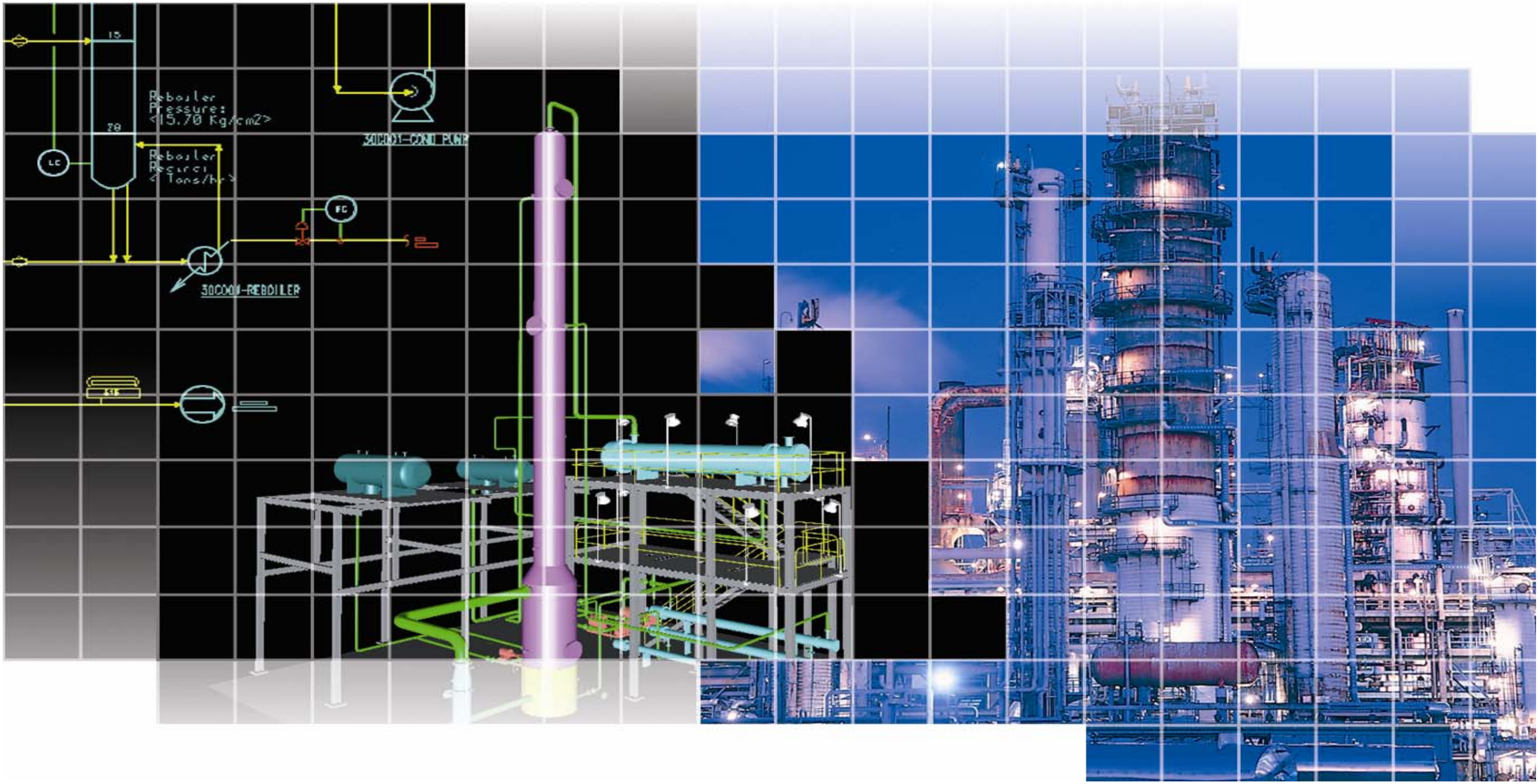
   Both gases are harmful, especially H_2S, which is toxic if burned; it gives SO_2 and SO_3 which are irritant to consumers.

   - Both gases are corrosive in the presence of water.
   - CO_2 contributes a lower heating value to the gas.

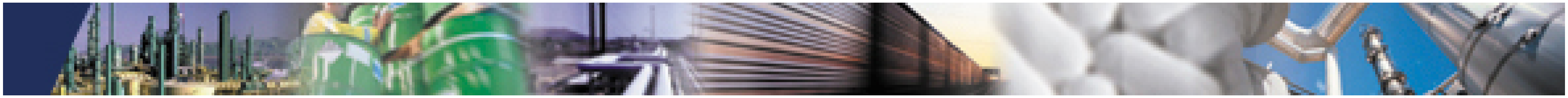
3. Liquid hydrocarbons:

   Their presence in undesirable in the gas used as a fuel.

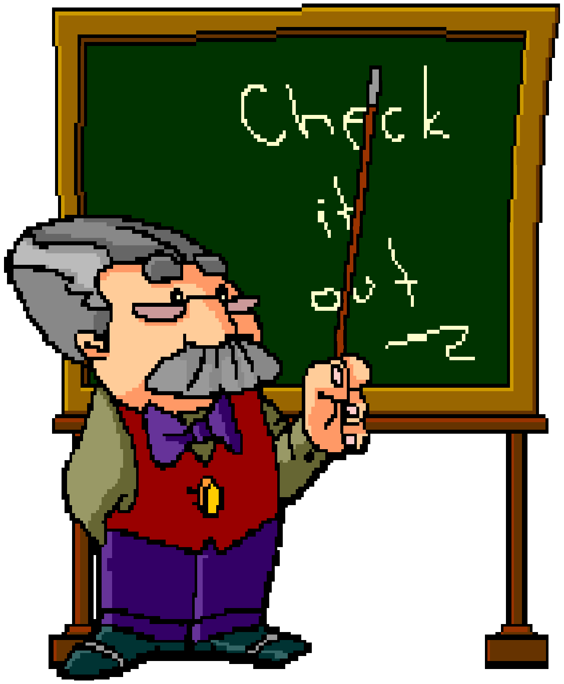
   - The liquid form is objectionable for burners designed for gas fuels.
   - For pipelines, it is a serious problem to handle two-phase flow: liquid and gas.



Chapter 10
Sour Gas Treating



Outline



- Introduction
- Gas-Sweetening Processes
- Selection of Sweetening Process
- Batch Processes (*Iron Sponge, Zinc Oxide, Molecular Sieves*)
- Liquid-Phase Processes (*Amine Processes, Potassium Carbonate, Physical Solvent*)
- Direct Conversion Processes (*Stretford, LOCAT, Sulferox*)

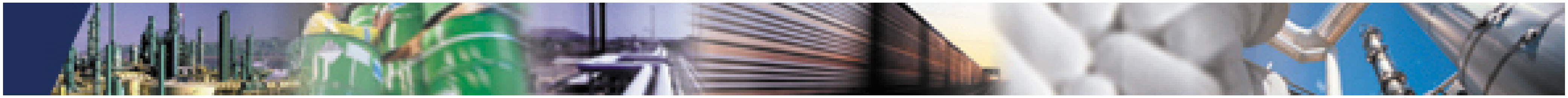
Introduction

- Natural gas usually contains some impurities such as H_2S, CO_2, $H_2O_{(g)}$, and heavy hydrocarbons.
- These compounds are known as “acid gases”
- Natural gas with H_2S or other sulfur compounds (e.g. COS, CS_2 and merchaptans) is called “sour gas”.
- It is usually desirable to remove H_2S and CO_2 to prevent corrosion problems and to increase heating value of the gas.
- Sweetening of natural gas is one of the most important steps in gas processing for the following reasons:

  1. **Health hazards**. At 0.13 ppm, H_2S can be sensed by smell. At 4.6 ppm, the smell is quire noticeable. As the concentration increases beyond 200 ppm, the sense of smell fatigues, and the gas can no longer be detected by odor. At 500 ppm, breathing problems are observed and death can be expected in minutes. At 1000 ppm, death occurs immediately.

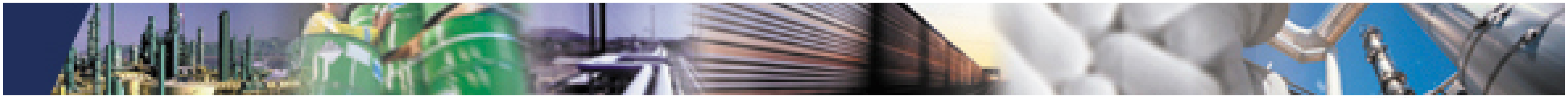
Introduction

2. **Sales contracts**. Three of the most important natural gas pipeline specification are related to sulfur content. Such contracts depend on negotiations, but they are quite strict about H_2S content.
3. **Corrosion problems**. If the partial pressure of CO_2 exceeds 15 psia, inhibitors usually can only be used to prevent corrosion. The partial pressure of CO_2 depends on the mole fraction of CO_2 in the gas and the natural gas pressure. Corrosion rates will also depend on temperature. Special metallurgy should be used if CO_2 partial pressure exceeds 15 psia. The presence of H_2S will cause metal embrittlement due to the stresses formed around sulfides formed.



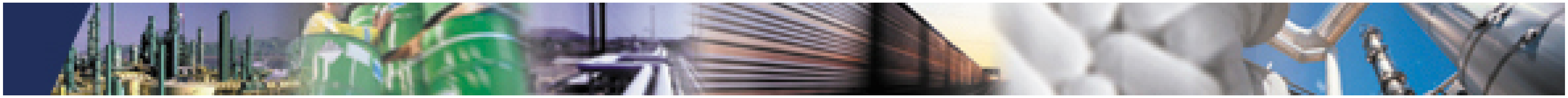
Gas-Sweetening Processes

- There are more than 30 processes for natural gas sweetening. The most important of these processes can be classified as follows:
  1. **Batch solid bed absorption**. For complete removal of H_2S at low concentration, the following materials can be used: iron sponge, molecular sieve, and zinc oxide. If the reactants are discarded, then this method is suitable for removing a small amount of sulfur when gas flow rate is low and/or H_2S concentration is also low.
  2. **Reactive solvents**. MEA (monoethanol amine), DEA (diethanol amine), DGA (diglycol amine), DIPA (di-isopropanol amine), hot potassium carbonate, and mixed solvents. These solutions are used to remove large amounts of H_2S and CO_2 and the solvents are regenerated.
  3. **Physical solvents**. Selexol, Recitisol, Purisol, and Flour solvent. They are mostly used to remove CO_2 and are regenerated.



Gas-Sweetening Processes

4. **Direct oxidation to sulfur**. Stretford, Sulferox LOCAT, and Claus. These processes eliminate H_2S emissions.
5. **Membranes**. This is used for very high CO2 concentrations. AVIR, Air Products, Cynara (Dow), DuPont, Grace, International Permeation, and Monsanto are some of these processes.

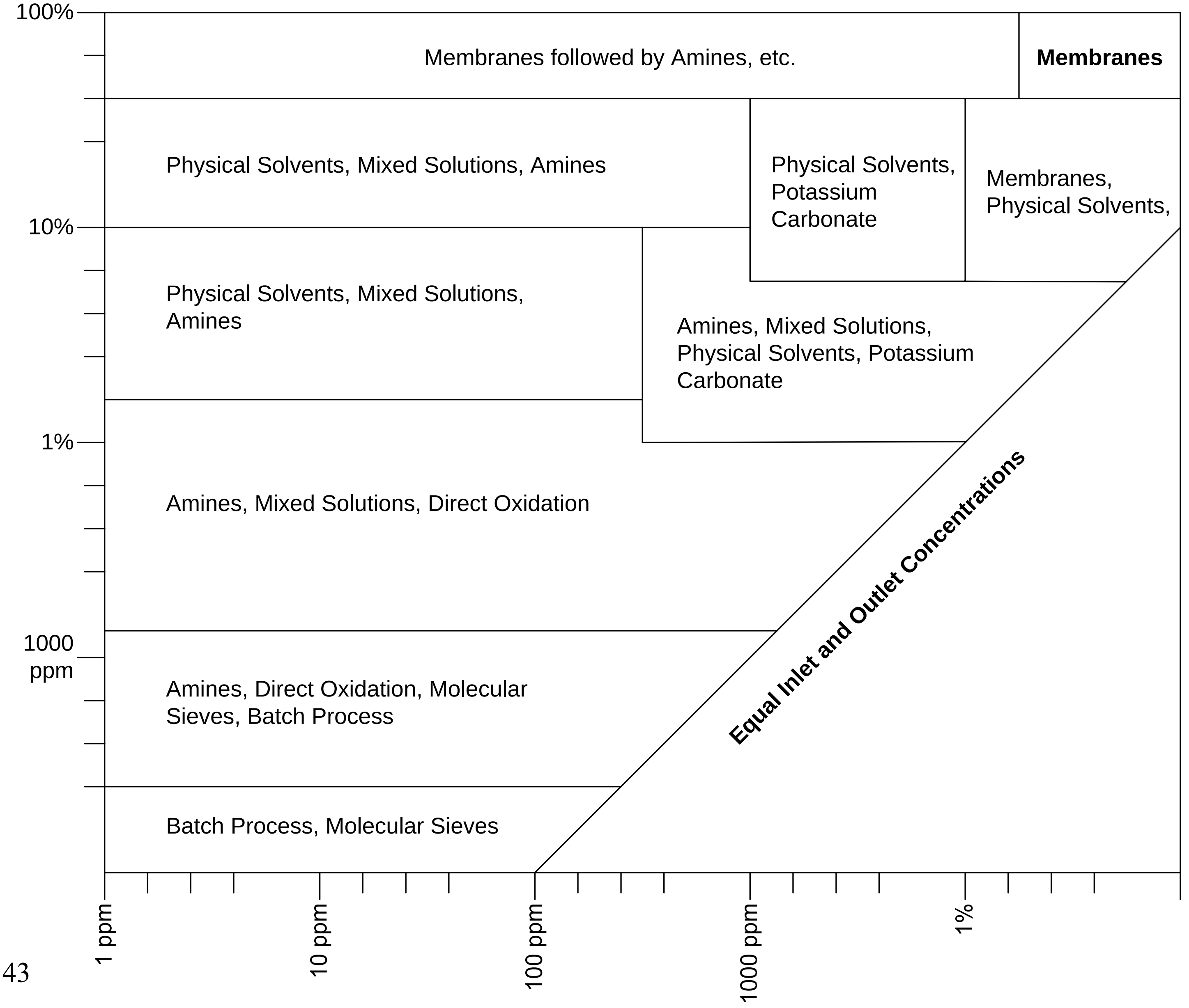


Selection of Sweetening Process

There are many factors to be considered in the selection of a given sweetening process. These include the following:

1. Type of impurities to be removed (H_2S, CO_2, merchaptans, etc.)
2. Inlet and outlet acid gas concentrations
3. Gas flow rate, temperature, and pressure
4. Feasibility of sulfur recovery
5. Acid gas selectivity required
6. Presence of heavy aromatic in the gas
7. Well location
8. Environmental consideration
9. Relative economics

Selection of Sweetening Process



Membranes followed by Amines, etc.

Membranes

Physical Solvents, Mixed Solutions, Amines

Physical Solvents, Potassium Carbonate

Membranes, Physical Solvents,

Physical Solvents, Mixed Solutions, Amines

Amines, Mixed Solutions, Physical Solvents, Potassium Carbonate

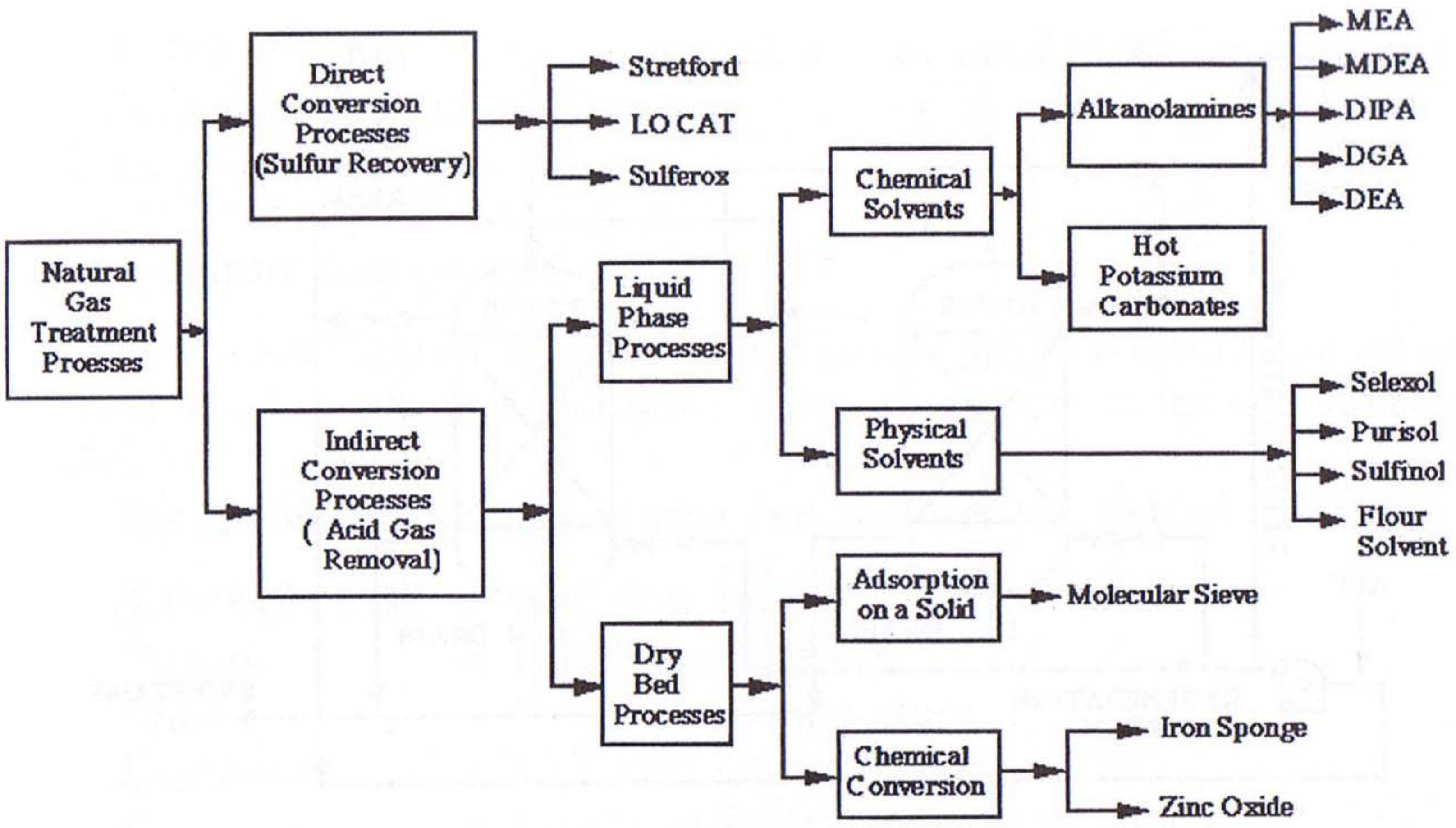
Amines, Mixed Solutions, Direct Oxidation

Amines, Direct Oxidation, Molecular Sieves, Batch Process

Batch Process, Molecular Sieves

Figure 1 Selection of gas-Sweetening processes.

Selection of Sweetening Process



Natural Gas Treatment Proesses

Direct Conversion Processes (Sulfur Recovery)
- Stretford
- LO CAT
- Sulferox

Indirect Conversion Processes (Acid Gas Removal)
- Liquid Phase Processes
  - Chemical Solvents
    - Alkanolamines
      - MEA
      - MDEA
      - DIPA
      - DGA
      - DEA
    - Hot Potassium Carbonates
  - Physical Solvents
    - Selexol
    - Purisol
    - Sulfinol
    - Flour Solvent
- Dry Bed Processes
  - Adsorption on a Solid
    - Molecular Sieve
  - Chemical Conversion
    - Iron Sponge
    - Zinc Oxide

Figure 2 Alternatives for natural gas sweetening.

Batch Processes

In this case, H_2S is basically removed and the presence of CO_2 does not affect the processes. Usually, batch processes are used for low-sulfur-content feeds.

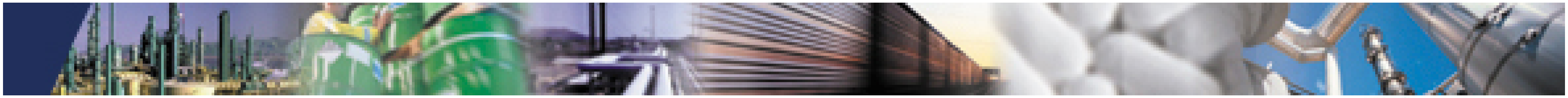
1. Iron Sponge
2. Zinc Oxide
3. Molecular Sieves

Iron Sponge

- Iron sponge fixed-bed chemical absorption is the most widely used batch process.
- This process is applied to sour gases with low H_2S concentrations (300 ppm) operating at low to moderate pressures (50-500 psig).
- CO_2 is not removed by this treatment.
- The inlet gas is fed at the top of the fixed-bed reactor filled wiith hydrated iron oxide and wood chips.
- The basic reaction is the formation of ferric sulfide when H_2S reacts with ferric oxide:

$$2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O \qquad (1)$$

- The reaction requires an alkalinity pH level 8-10 with controlled injection of water.



Iron Sponge

- The bed is regenerated by controlled oxidation as

  $2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 3S_2$ (2)

- Some of the sulfur produced might cake in the bed and oxygen should be introduced slowly to oxide this sulfur

  $S_2 + 2O_2 \rightarrow 2SO_2$ (3)

- Repeated cycling of the process will deactivate the iron oxide and the bed should be changed after 10 cycles.
- The process can be run continuously, in this case, small amounts of air or oxygen are continuously added to the inlet sour gas so that the produced sulfur is oxidized as it forms.
- The advantage of this process is the large savings in labor cost for loading and unloading of the batch process.

Iron Sponge

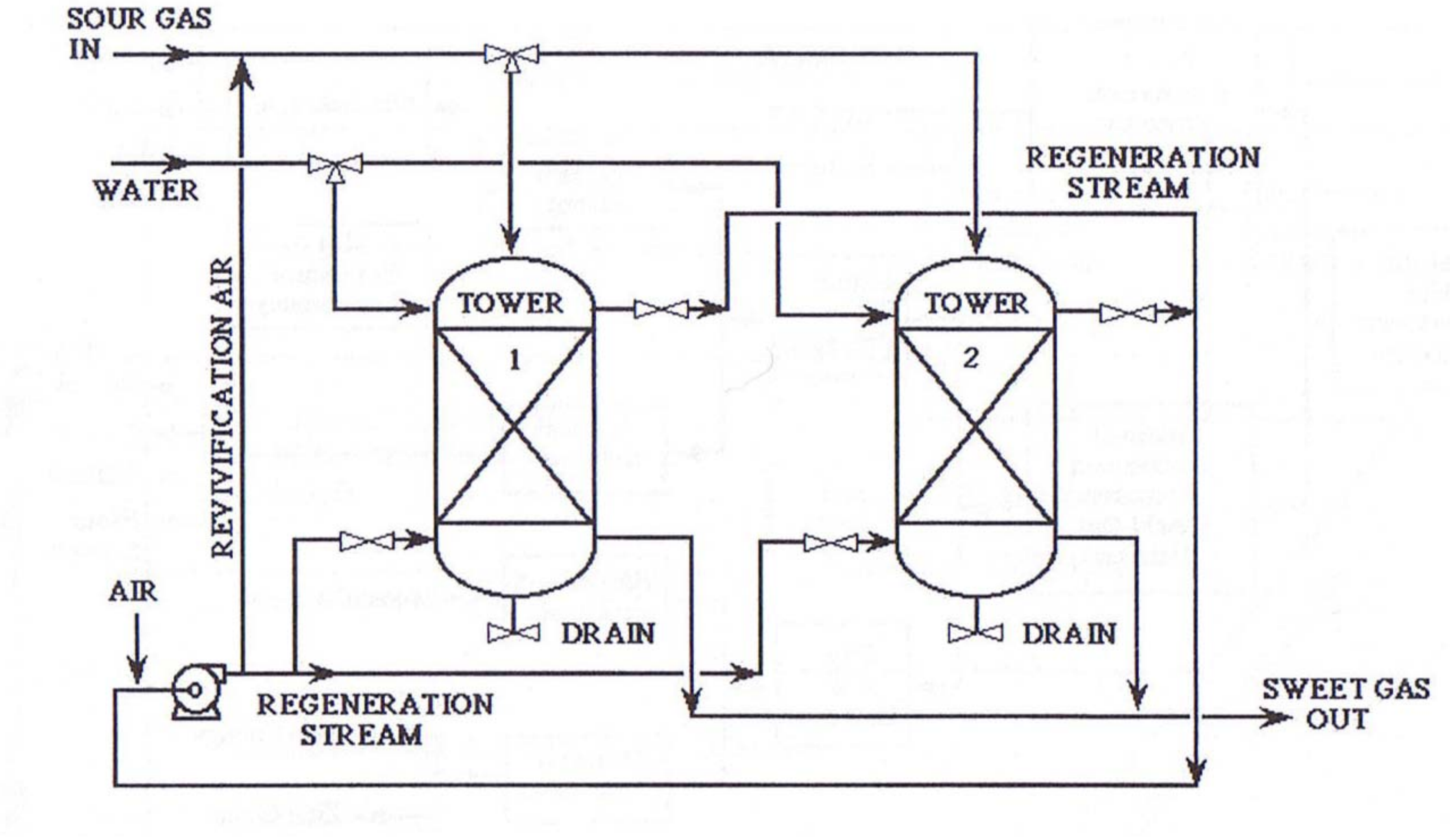


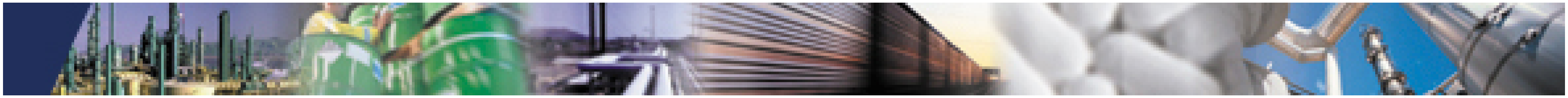
Figure 3 Typical iron oxide process flowsheet.

Zinc Oxide

- Zinc oxide can be used instead of iron oxide for the removal of H_2S, COS, CS_2, and merchaptans.
- However, this material is a better sorbent and the exit H_2S can be as low as 1 ppm at a temperature of about 300 ^{o}C.
- The zinc oxide reacts with H_2S to form water and zinc sulfide:

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad (4)$$

- A major drawback of zinc oxide is that it is not possible to regenerate it to zinc oxide on site.
- The process has been decreasing is use due to the above problem and the difficulty of disposing of zinc sulfide; Zn is considered a heavy metal.



Molecular Sieves

- Molecular sieves (MS) are crystalline sodium alumino silicates and have very large surface areas and a very narrow range of pore sizes.
- They posses highly localized polar charges on their surface that act as adsorption site for polar materials at even very low concentrations.
- This is why the treated natural gas could have very low H_2S concentrations (4 ppm).
- Commercial applications require at least two beds so that one is always on line while the other is being regenerated.
- The schematic diagram of the process is shown in Figure 4.
- The sulfur compounds are adsorbed on a cool, regenerated bed in the sweetening.
- The saturated bed is regenerated by passing a portion of the sweetened gas, preheated to about 400-600 ^{o}F or more, for about 1.5h to heat the bed.

Molecular Sieves

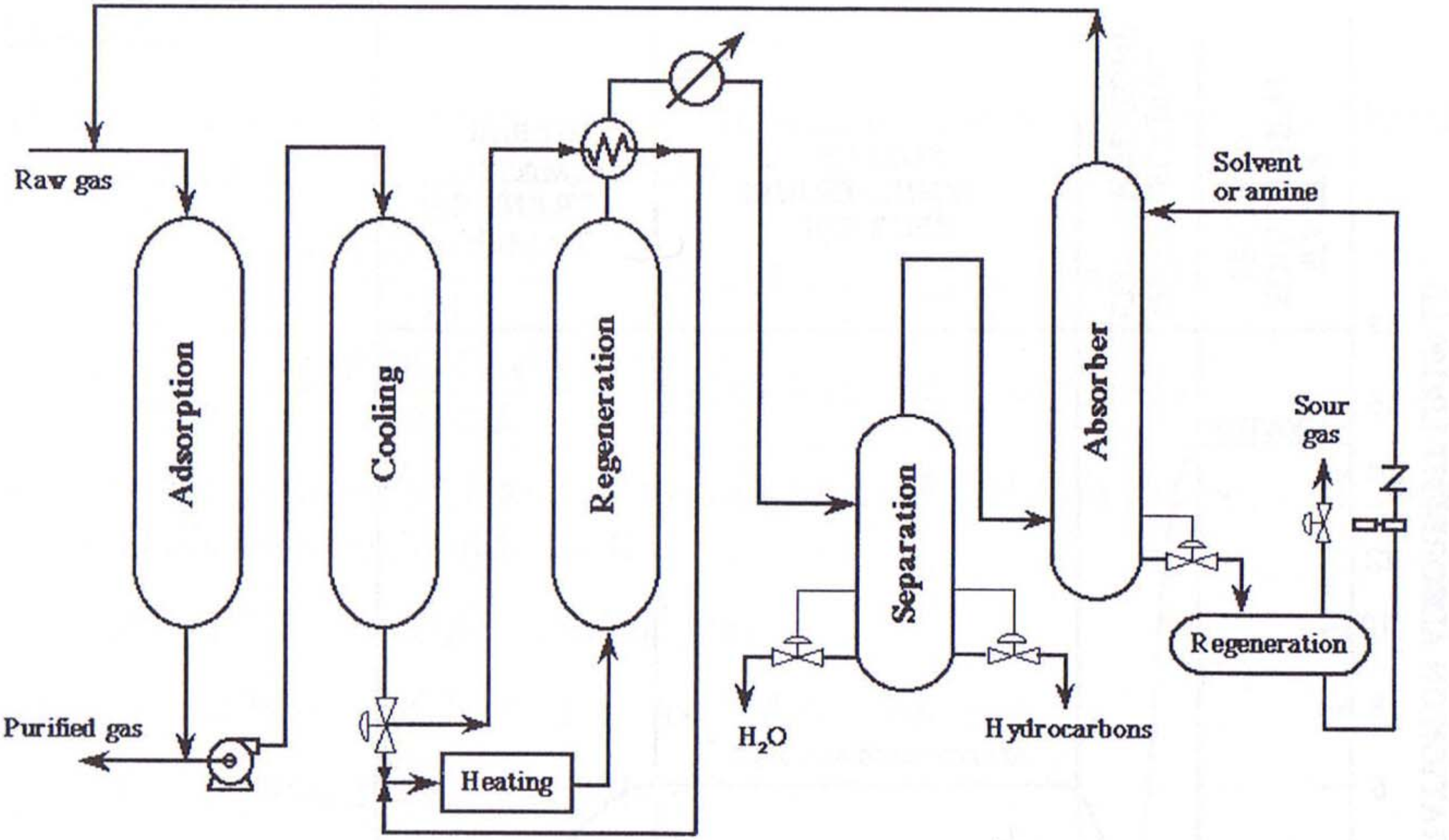


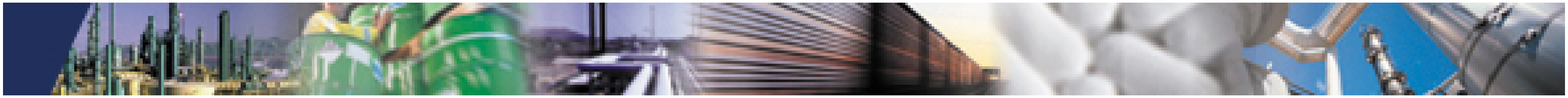
Figure 4 Sweetening of natural gas by molecular sieves.

Molecular Sieves

- As the temperature of the bed increases, it releases the adsorbed H_2S into the generation gas stream.
- The sour effluent gas is flared off, with about 1-2% of the treated gas lost.
- An amine unit can be added to this process to recover this loss; in this case, H_2S will be flared off from the regenerator of the amine unit.
- In case this flaring is prohibited environmentally, the H_2S can be sent to a gathering center for the sulfur recovery unit, if it exists on site.

Liquid-Phase Processes

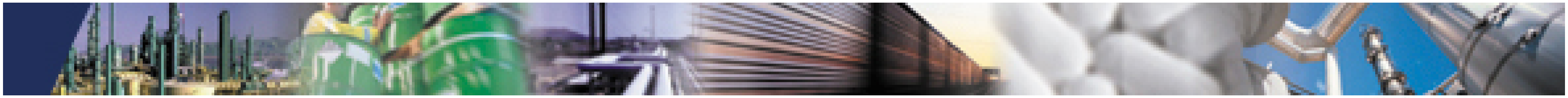
- This is one of the most commonly used processes for acid gas treatment.
- Chemical solvents are used in the form of aqueous solution to react with H_2S and CO_2 reversibly and form products which can be regenerated by a change of temperature or pressure or both.
- Physical solvents can be utilized to selectively remove sulfur compounds.
- They are regenerated at ambient temperature by reducing the pressure.
- A combination of physical and chemical solvents can be used.
- A comparison of chemical solvents (amines, carbonates) and physical solvents is shown in Table 1.



Process Control & Safety

Liquid-Phase Processes

Feature	Amine	Carbonate	Physical
Absorbents	MEA, DEA, DGA, MDEA	K_2CO_3, K_2CO_3+ MEA, K_2CO_3+DEA	Selexol, Purisol, Rectisol
Operating P (psi)	Insensitive to pressure	➢200	250-1000
Operating T (°F)	100-400	200-250	Ambient T
Recovery of absorbents	Reboiled stripping	Stripping	Flashing, reboiled or stream stripping
Utility cost	High	Medium	Low/ Medium
Selectivity $H2_S$, CO_2	Selective for some amines (MDEA)	May be selective	Selective to H_2S
Effect of O_2 in the feed	Formation of degradation products	None	Sulfur precipitation at low T
COS and CS_2 removal	MEA: not removed, DEA: slightly removed, DGA: removed	Converted to CO_2 and H_2S and removed	Removed
Operating problems	Solution degradation; foaming; corrosion	Column instability; erosion; corrosion	Absorption of heavy hydrocarbons



Amine Processes

- The most widely used for sweetening of natural gas are aqueous solutions of alkanoamines.
- They are generally used for bulk removal of CO2 and H2S.
- The low operating cost and flexibility of tailoring solvent composition to suit gas compositions make this process one of most commonly selected.
- A liquid physical solvent can be added to the amine to improve selectivity.
- A typical amine process is shown in Figure 5.
- The acid gas is fed into a scrubber to remove entrained water and liquid hydrocarbons.
- The gas then enters the bottom of absorption tower which is either a tray (for high flow rates) or packed (for lower flow rate).

Amine Processes

Process Control & Safety

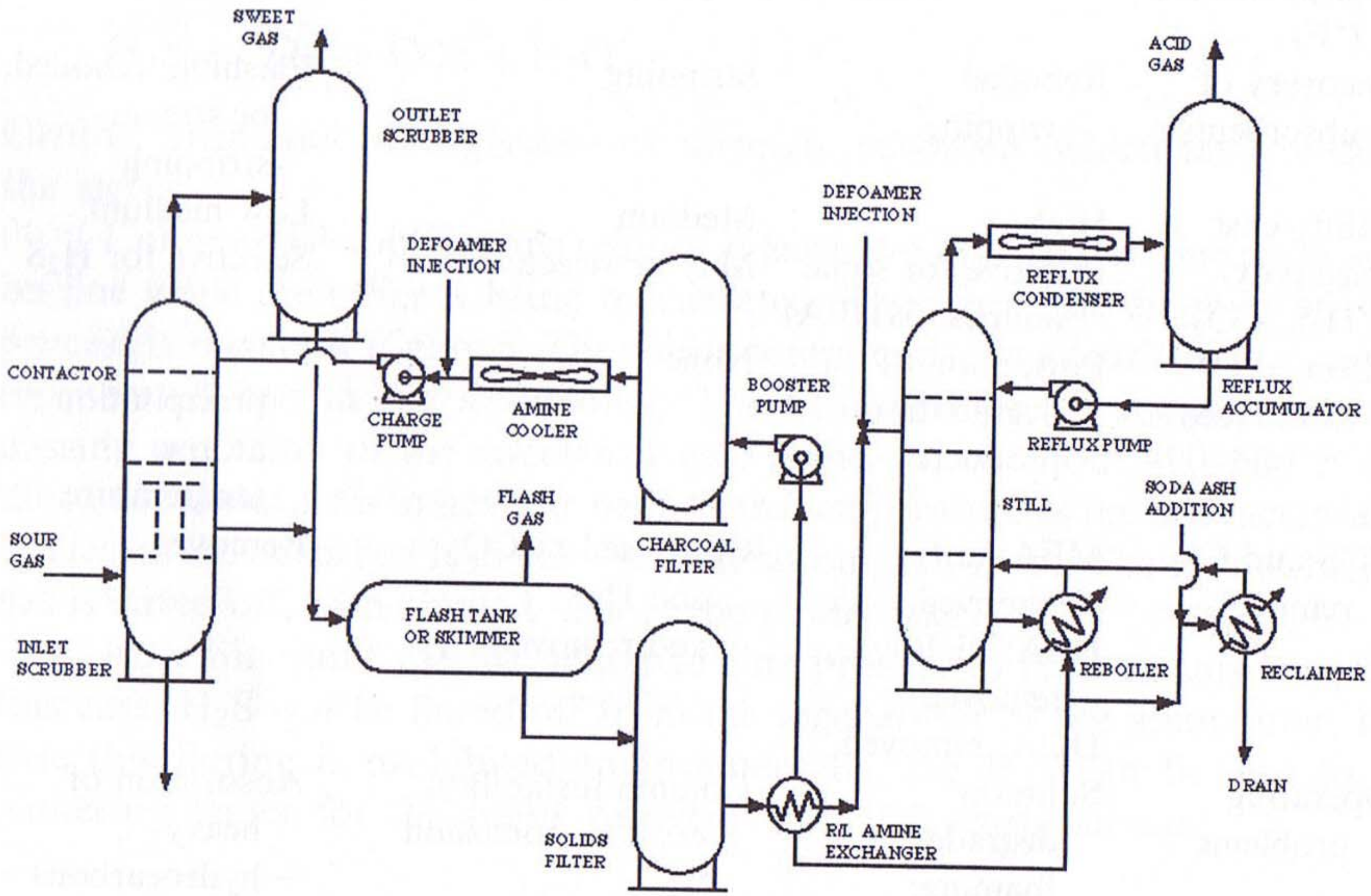


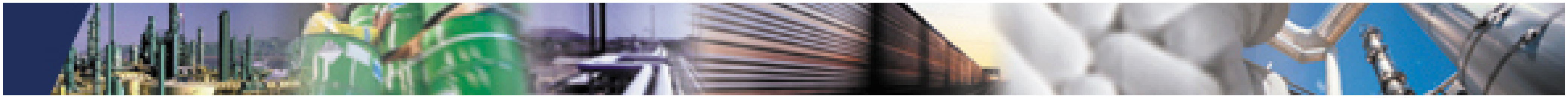
Figure 5 Flowsheet for the amine process.

Amine Processes

- The sweet gas exits at the top of tower.
- The regenerated amine (lean amine) enters at the top of this tower and the two streams are contacted countercurrently.
- In this tower, CO_2 and H_2S are absorbed with the chemical reaction into the amine phase.
- The exit amine solution, loaded with CO_2 and H_2S, is called rich amine.
- This stream is flashed, filtered, and then fed to the top of a stripper to recover the amine, and acid gases (CO_2 and H_2S) are stripped and exit at the top of the tower.
- The refluxed water helps in steam stripping the rich amine solution.
- The regenerated amine (lean) is recycled back to the top of the absorption tower.

Amine Processes

- The operating conditions of the process depends on the type of the amine used.
- Primary amines (MEA, DGA) are the strongest to react with acid gases, but the stable bonds formed make it difficult to recover by stripping.
- Secondary amines (DEA, DIPA) have a reasonable capacity for acid gas absorption and are easily recovered.
- Tertiary amines (MDEA) have a lower capacity, but they are more selective for H_2S absorption.
- Among the amines, DEA is the most common.
- This is may be due to the fact it is less expensive to install and operate.



Potassium Carbonate Process

- In this process, hot potassium carbonate (K_2CO_3) is used to removed both CO_2 and H_2S.
- It can also remove (reversibly) COS and CS.
- It works best when the CO_2 partial pressure is in the range 30-90 psi.
- The following reaction occur in this case:

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3 \qquad (5)$$

$$K_2CO_3 + H_2S \leftrightarrow KHS + KHCO_3 \qquad (6)$$

- It can be seen from reaction (5) that a high partial pressure of CO_2 is required to keep $KHCO_3$ in solution, and in Eq. (6), H_2S will no react if the CO_2 pressure is not high.
- For this reason, this process cannot achieve a low concentration of acid gases in the exit stream and a polishing process is needed (molecular sieve).

Potassium Carbonate Process

- An elevated temperature is also necessary to ensure that potassium carbonate and reaction products ($KHCO_3$ and KHS) remain in solution.
- Thus, this process cannot be used for gases containing H_2S only.
- The hot carbonate process which is given in Figure 6 is referred to as the "hot" process because both the absorber and the regenerator operate at elevated temperatures, usually in the range (230-240 ^oF).
- In Figure 6, the sour gas enters at the bottom of the absorber and flows countercurrently to the carbonate liquid stream.
- The sweet gas exits at the top of the absorber.
- The absorber is operated at 230 ^oF and 90 psia.

Potassium Carbonate Process

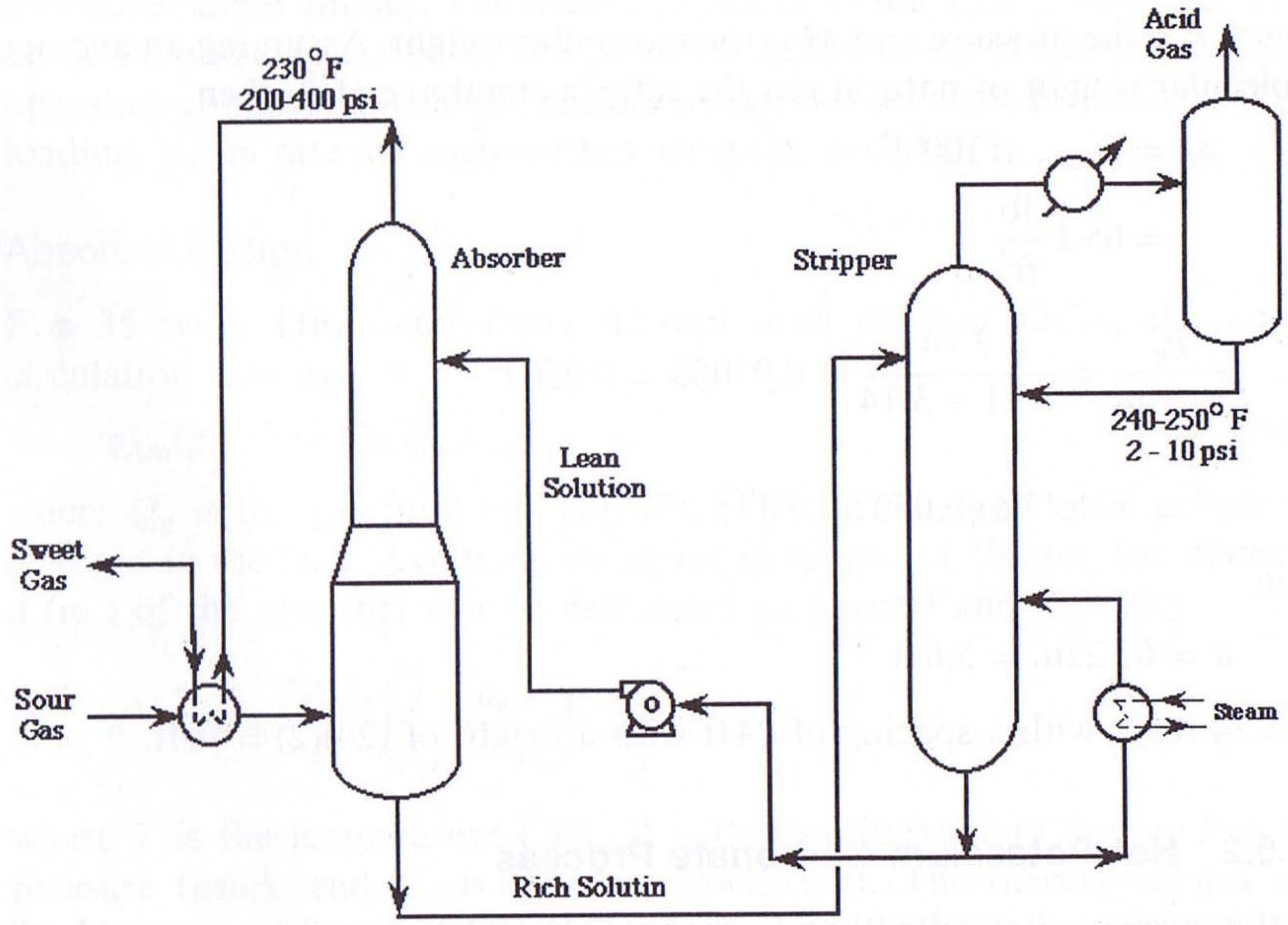


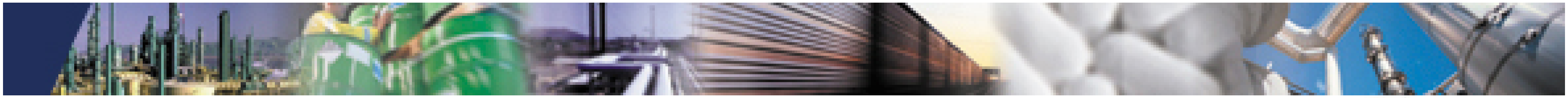
Figure 6 Hot carbonate process.

Potassium Carbonate Process

- The rich carbonate solution exits from the bottom of the absorbed and is flashed in the stripper, which operates at 245 ^{o}F and atmospheric pressure, where acid gases are driven off.
- The lean carbonate solution is pumped back to the absorber.
- The strength of the potassium carbonate solution is limited by the solubility of potassium bicarbonate ($KHCO_3$) in the rich stream.
- The high temperature of the system increases $KHCO_3$ solubility, but the reaction with CO_2 produces 2 mol of $KHCO_3$ per mole of K_2CO_3 reacted. For this reason, $KHCO_3$ in the rich stream limits the lean solution of K_2CO_3 concentration to 20-35% (wt).

Physical Solvent Processes

- Organic liquid (solvents) are used in these processes to absorb H_2S (usually) preferentially over CO_2 at high pressure and low temperatures.
- Regeneration is carried out by releasing the pressure to the atmosphere and sometimes in vacuum with no heat.
- This means that at high pressure, acid gases will dissolve in solvents, and as the pressure is released, the solvent can regenerated.
- The properties of four of the important solvents used in natural gas processing are given in Table 2.



Physical Solvent Processes

Process	Flour	Purisol	Selexol	Sulfinol
Solvent	Propylene carbonate	N-Methyl pyrrilidone	Diethylene dimethyl ether	Sulfolane
Molecular weight	102.09	99.13	134.17	120.17
Freezing (°F)	-56	-12	-83	77
Boiling (°F)	467	396	324	546
Gas solubility (cm^3 gas at 1 atm, 75 °F/cm^3 solvent)				
H_2S	13.3	43.3	25.5	
CO_2	3.3	3.8	3.6	
COS	6.0	10.6	9.8	
C_3	2.1	3.5	4.6	

Physical Solvent Processes

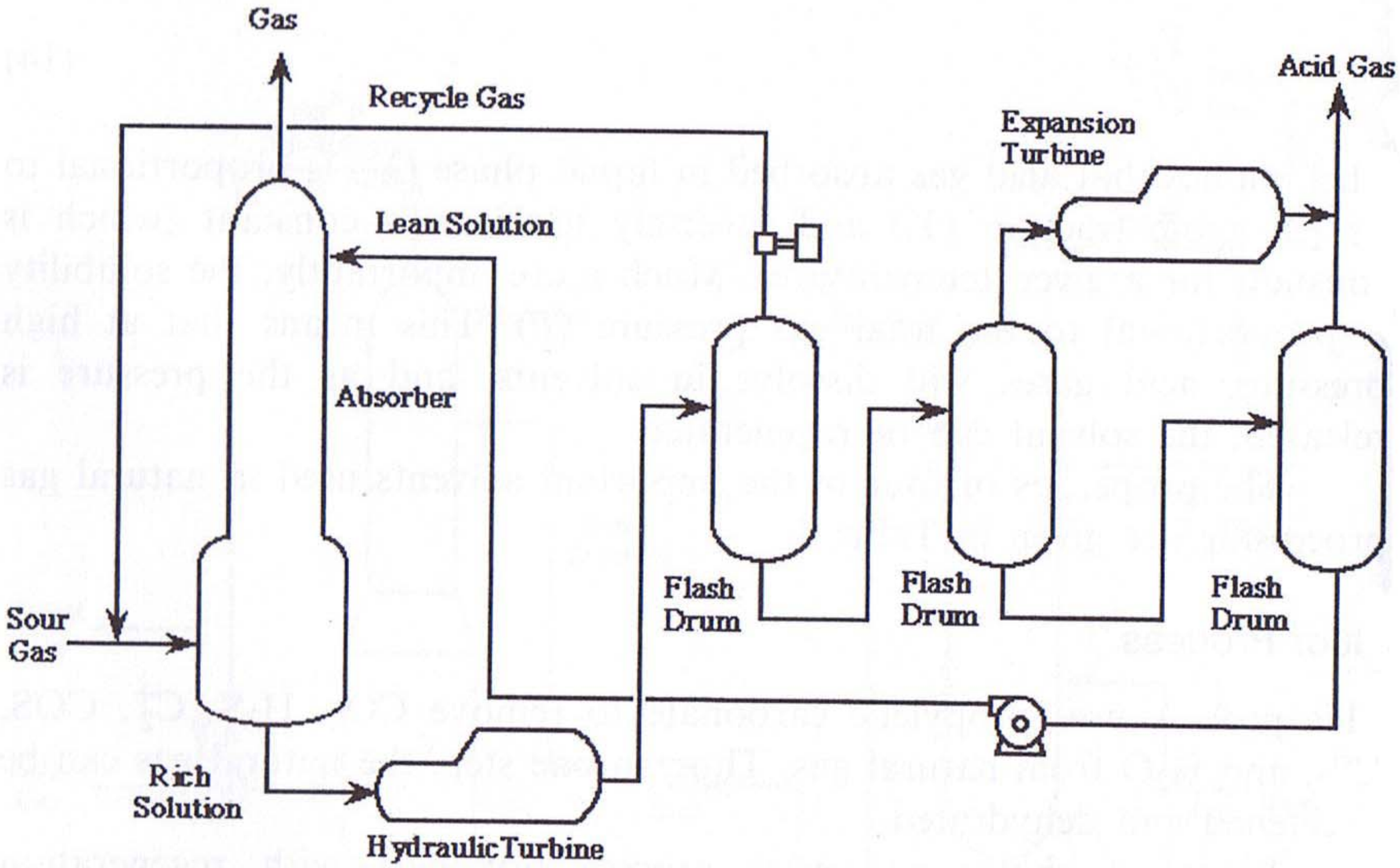


Figure 7 Flour process.

Physical Solvent Processes

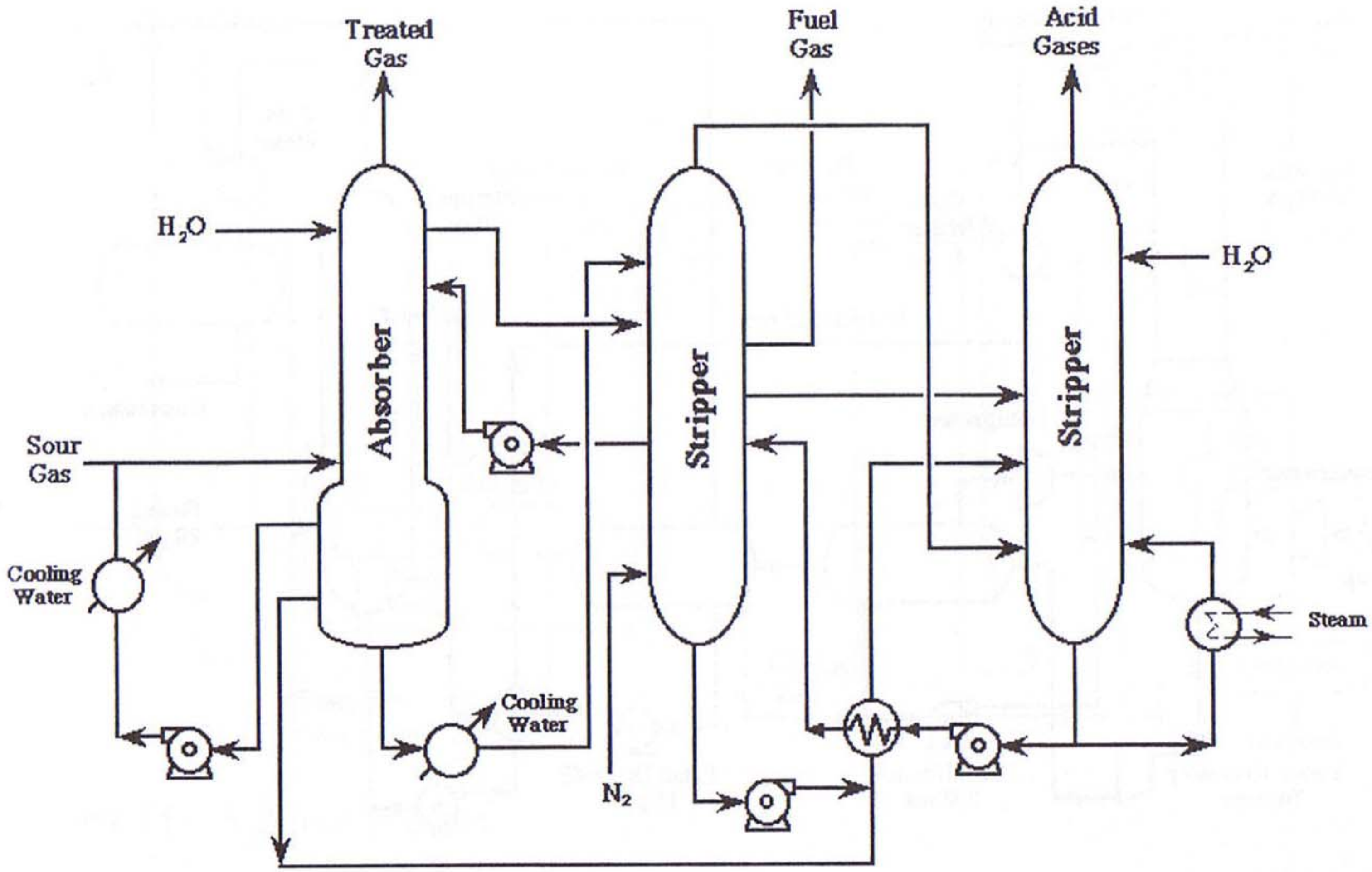


Figure 8 Purisol process.

Physical Solvent Processes

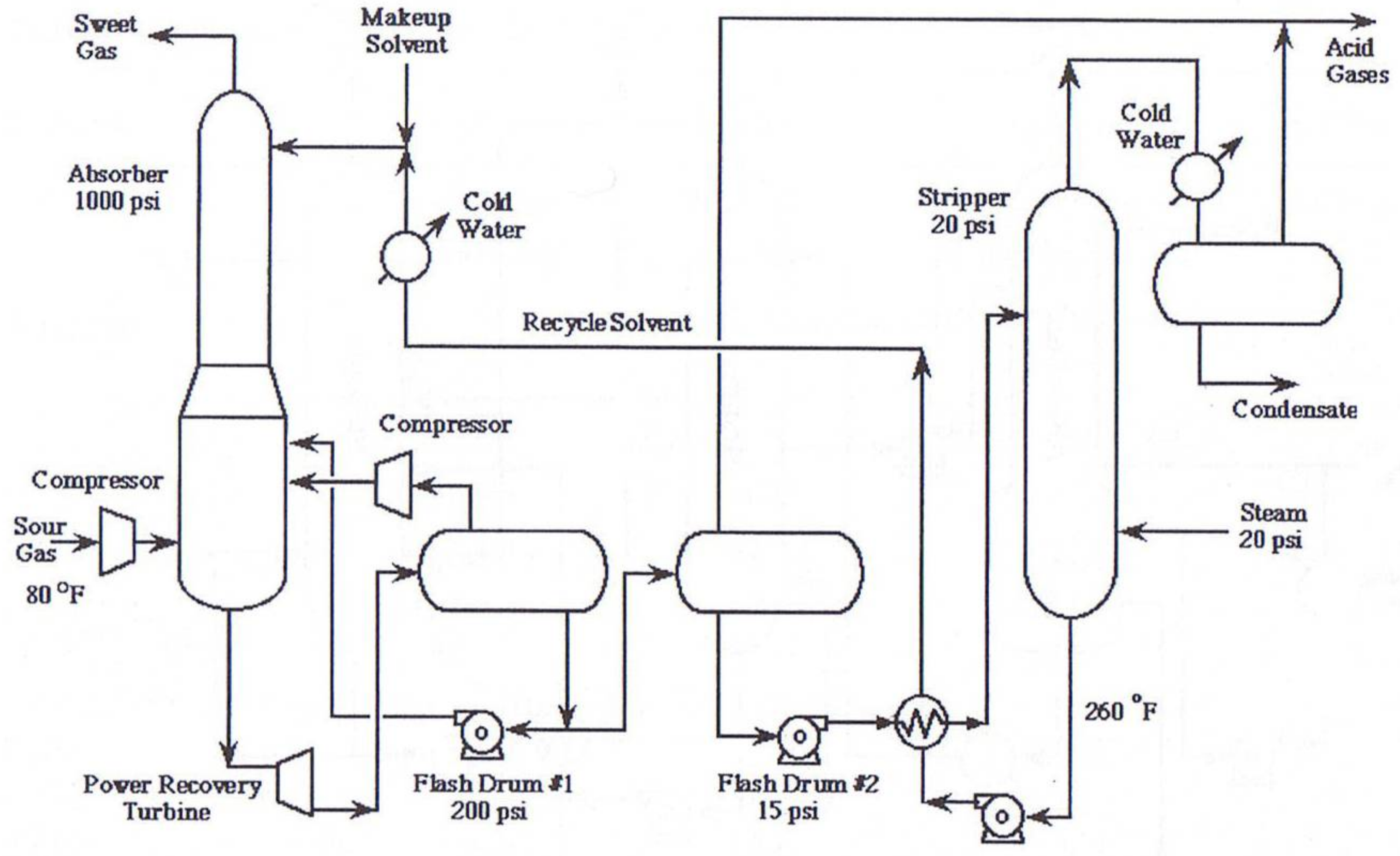


Figure 9 Selexol process.

Physical Solvent Processes

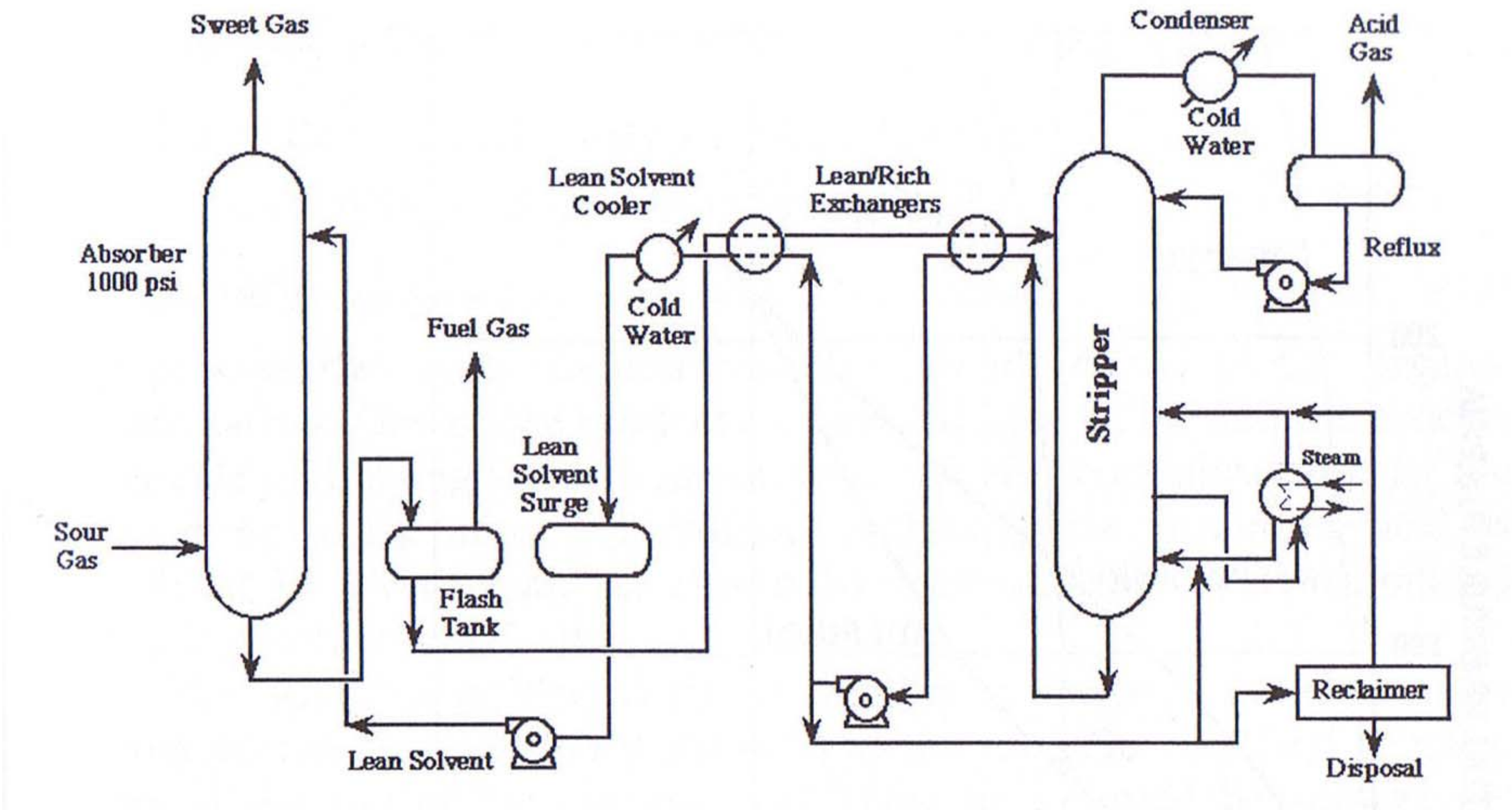


Figure 10 Sulfinol process.

Direct Conversion Processes

- There are many processes used to convert H_2S to sulfur; however, our discussion here is limited to those processes applied to natural gas.
- Generally, H_2S is absorbed in an alkine solution containing an oxidizing agent which converts it to sulfur.
- The solution is regenerated by air in a flotation cell (oxidizer).
- The following processes are used for this purpose:
  1. Stretford Process.
  2. LOCAT Process.
  3. Sulferox Process.

Stretford Process

- The absorbing solution is dilute Na_2CO_3, $NaVO_3$, and anthraquinone disulfonic acid (ADA). The reaction occurs in four steps:

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3 \qquad (7)$$

$$4NaVO_3 + 2NaHS + H_2O \rightarrow Na_2V_4O_9 + NaOH + 2S \qquad (8)$$

$$Na_2V_4O_9 + 2NaOH + H_2O + ADA(quinone)$$

$$\rightarrow 4NaVO_3 + 2ADA(hydroquinone) \qquad (9)$$

$$ADA(hydroquinone) + 1/2O_2 \rightarrow ADA(quinone) \qquad (10)$$

- The Stretford process is shown in Figure 11.
- Sour gas enters the bottom of absorber and sweet gas exits at the top.
- The Stretford solution enters at the top of the absorber and some time should be allowed for reaction to take place in the bottom part of the absorber, where H_2S is selectively absorbed.

Stretford Process

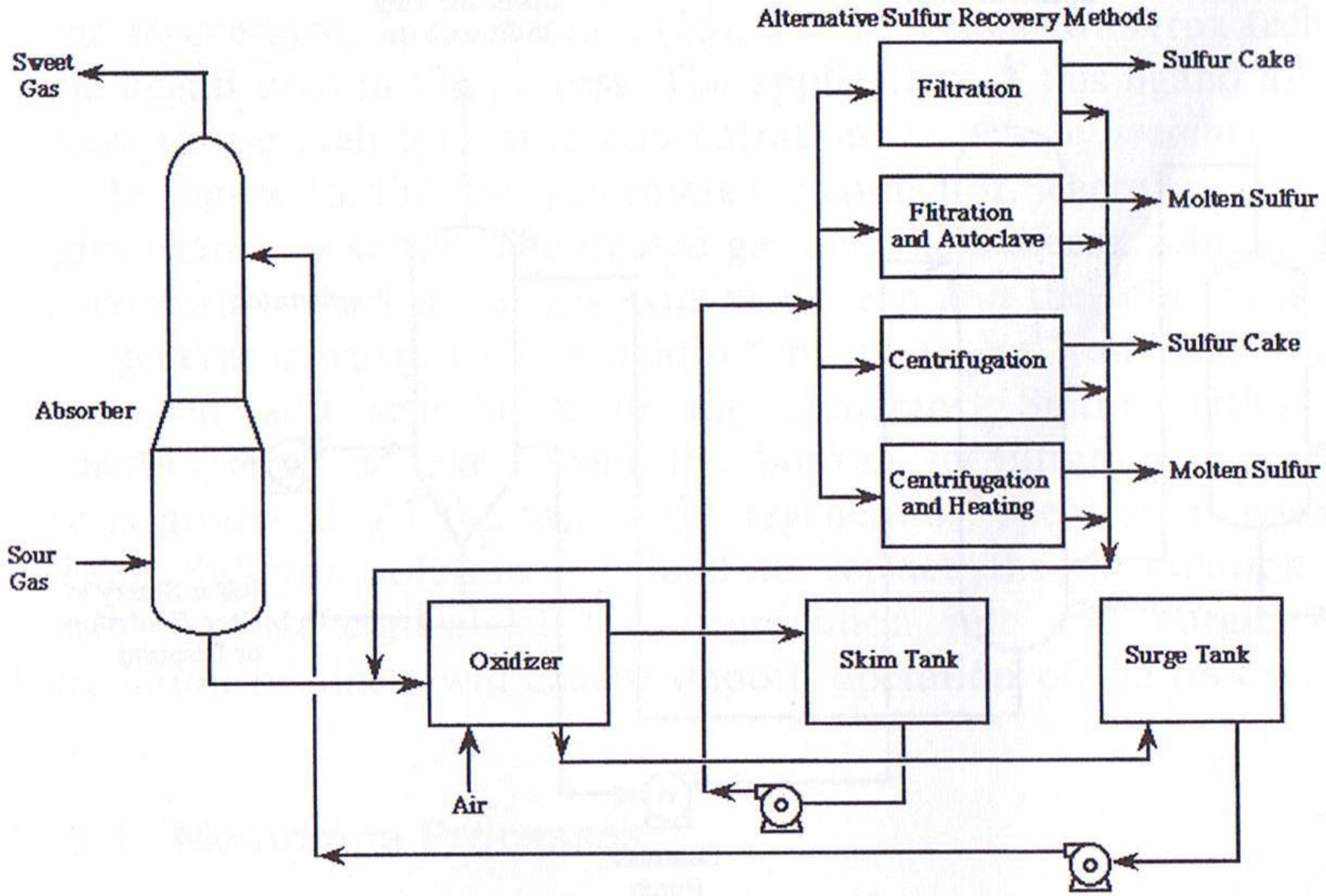


Figure 11 Stretford process.

Stretford Process

- The reaction products are fed to the oxidizer, where air is blown to oxidize ADA(hydroquinone) back to ADA(quinone).
- The sulfur froth is skimmed and sent to either a filtration or centrifugation unit.
- If heat is used, molten sulfur is produced; otherwise a filter sulfur cake is obtained.
- The filtrate of these units along with the liquid from the oxidizer are sent back to the absorber.

LOCAT Process

- This process uses as extremely dilute solution of iron chelates.
- A small portion of the chelating agent is depleted in some side reactions and is lost with precipitated sulfur.
- In this process (Figure 12), sour gas is contacted with the chelating reagent in the absorber and H_2S reacts with the dissolved iron to form elemental sulfur.
- The reactions involved are the following:

$$H_2S + 2Fe^{3+} \rightarrow 2H^+ + S + 2Fe^{2+} \qquad (11)$$

- The reduced iron ion is regenerated in the generator by blowing are as

$$1/2O_2 + H_2O + 2Fe^{2+} \rightarrow 2(OH)^- + 2Fe^{3+} \qquad (12)$$

- The sulfur is removed from the regenerator to centrifugation and melting.

LOCAT Process

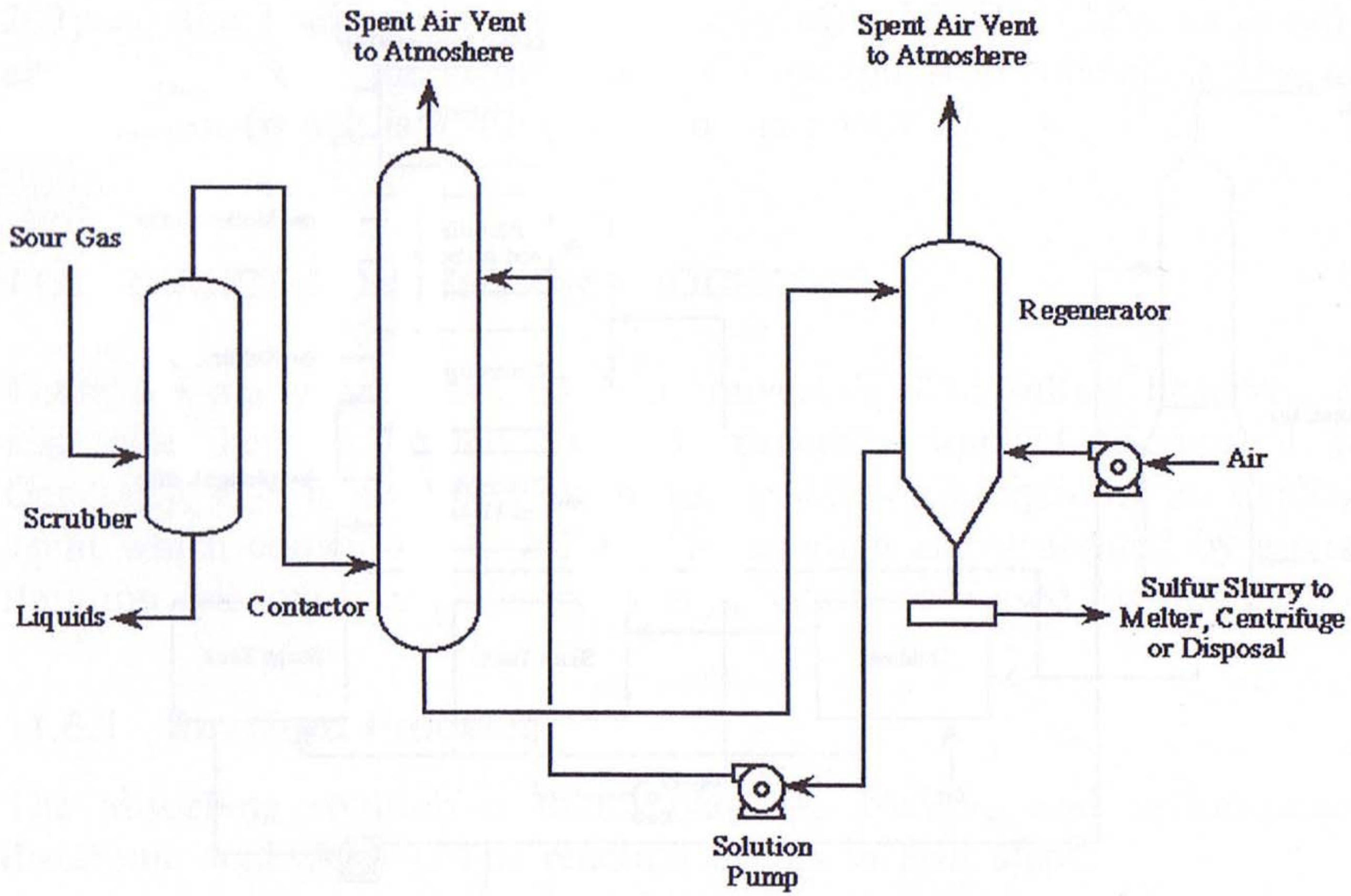
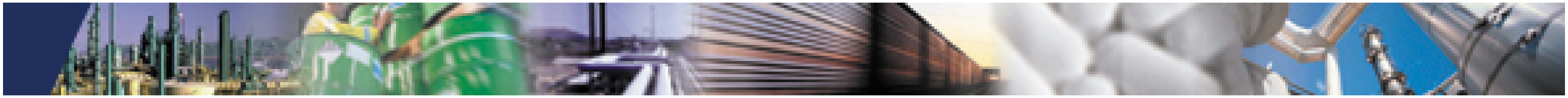


Figure 12 LOCAT process.



Sulferox Process

- Chelating iron compounds are also the heart of the sulferox process.
- Sulferox is a redox technology, as is the LOCAT; however, in this case, a concentrated iron solution is used to oxidize H_2S to elemental sulfur.
- Patented organic liquids or chelating agents are used to increase the solubility of iron in the operating solution.
- As a result of high iron concentrations in the solution, the rate of liquid circulation can be kept low and, consequently, the equipment is small.
- As in LOCAT process, there are two basic reactions; the first takes place in the absorber, as in reaction (11), and the second takes place in the regenerator, as in reaction (12).

Sulferox Process

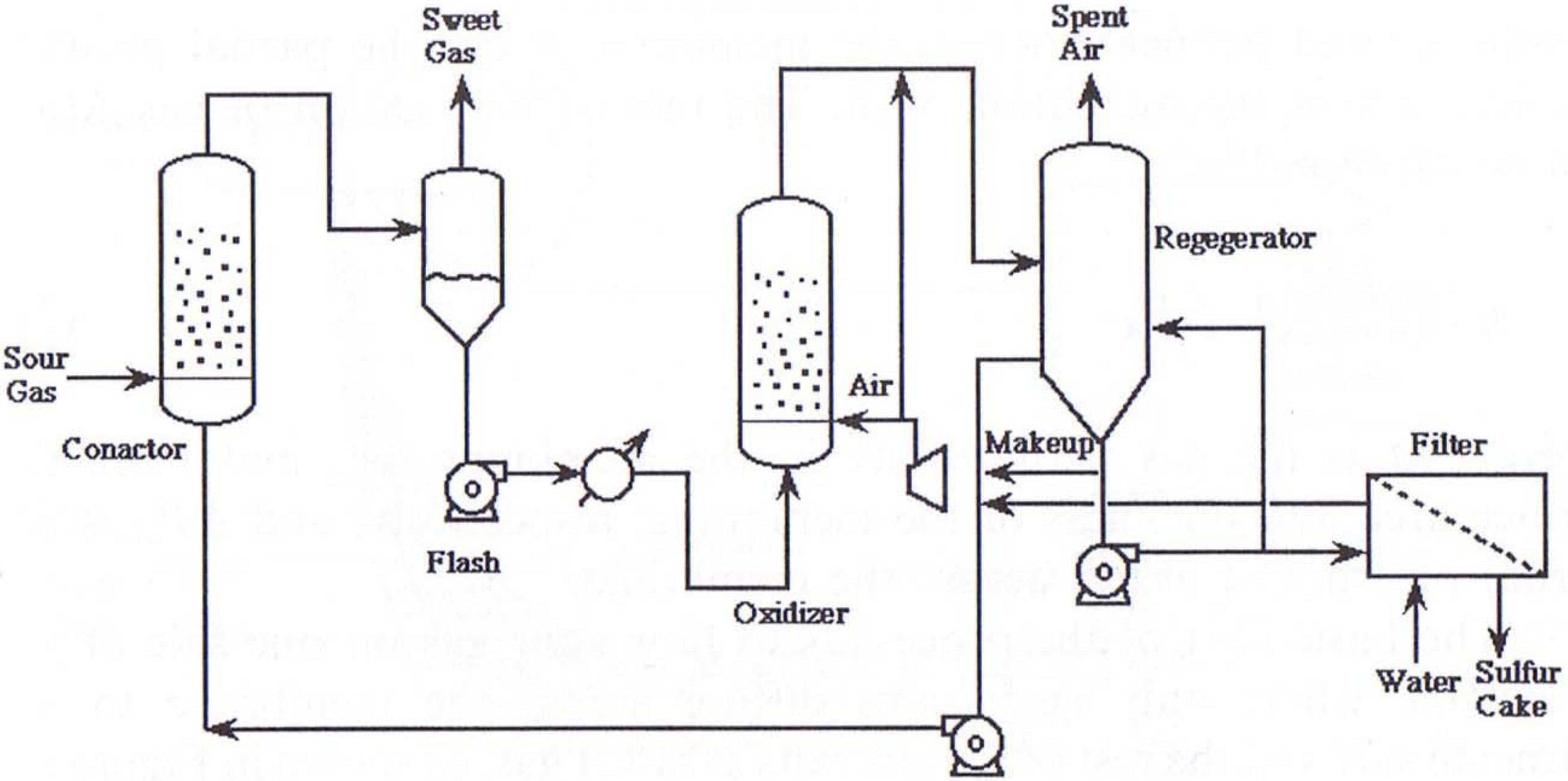
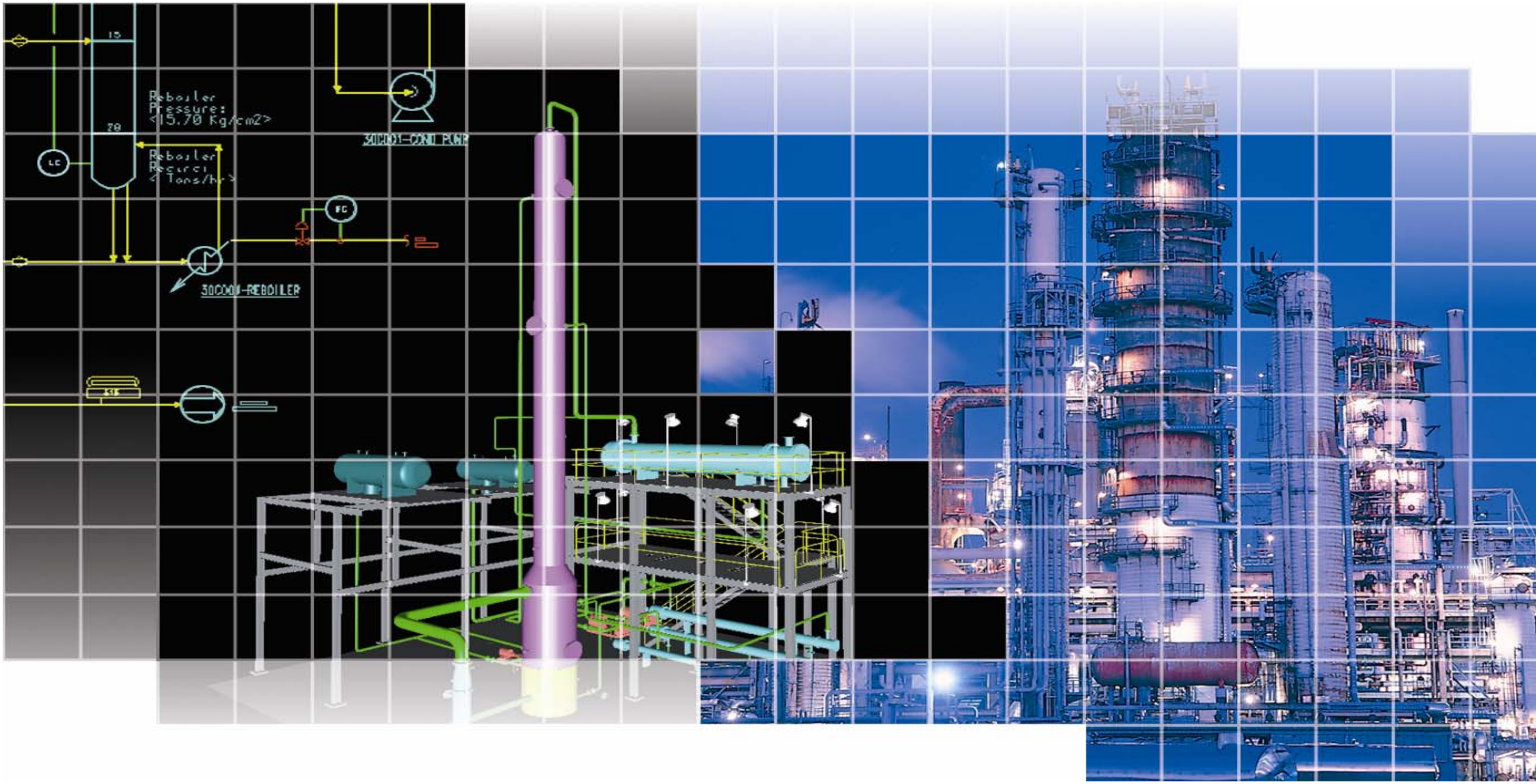


Figure 13 Sulferox process.

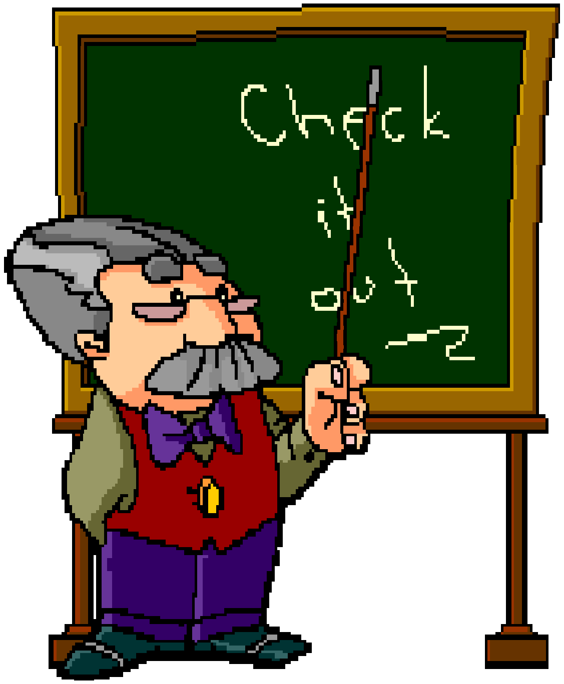
Sulferox Process

- In Figure 13, the sour gas enters the contactor, where H_2S is oxidized to give elemental sulfur.
- The treated gas and the Sulferox solution flow to the separator, where sweet gas exits at the top and the solution is sent to the regenerator where Fe^{2+} is oxidized by air to Fe^{3+} and the solution is regenerated and sent back to the contactor.
- Sulfur settles in the regenerator and is taken from the bottom to filtration, where sulfur cake is produced.
- At the top of the regenerator, spent air is released.

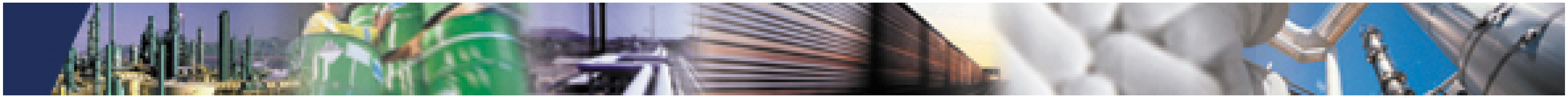


Chapter 11
Natural Gas Dehydration

Outline



- Introduction
- Methods Used to Inhibit Hydrate Formation
  - Temperature/Pressure Control
  - Chemical Injection (*Methanol*, *Glycol*)
  - Dehydration Methods (*Absorption: Glycol Dehydration*, *Adsorption: Solid-Bed Dehydration*)



Introduction

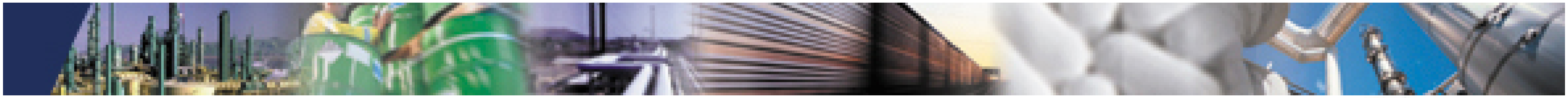
- Natural gas dehydration is the process of removing water vapor from the gas stream to lower the dew point of that gas.
- Water is the most common contaminant of hydrocarbons.
- It is always present in the gas-oil mixtures produced from wells.
- The dew point is defined as the temperature at which water vapor condenses from the gas stream.
- The sale contracts of natural gas specify either its dew point or the maximum amount of water vapor present.
- There are three basic reasons for the dehydration of natural gas streams:

Introduction

1. **To prevent hydrate formation**. Hydrates are solids formed by the physical combination of water and other small molecules of hydrocarbons. They are icy hydrocarbon compounds of about 10% hydrocarbons and 90% water. Hydrates grow as crystals and can build up in orifice plates, valves, and other areas not subjected to full flow. Thus, hydrates can plug lines and retard the flow of gaseous hydrocarbon streams. The primary conditions promoting hydration formation are the following:
    - Gas must be at or below its water (dew) point with “free” water present.
    - Low temperature.
    - High pressure.

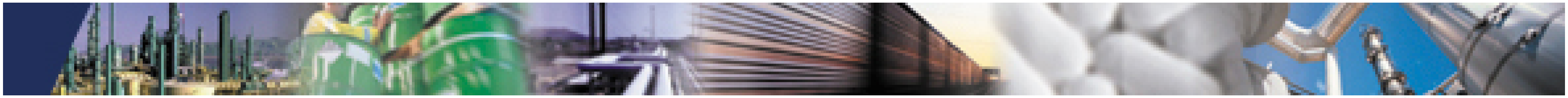
Introduction

2. **To avoid corrosion problems**. Corrosion often occurs when liquid water is present along with acidic gases, which tend to dissolve and disassociate in the water phase, forming acidic solutions. The acidic solutions can be extremely corrosive, especially for carbon steel, which is typically used in the construction of most hydrocarbon processing facilities.
3. **Downstream processing requirements**. In most commercial hydrocarbon processes, the presence of water may cause side reactions, foaming, or catalyst deactivation. Consequently, purchasers typically require that gas and liquid petroleum gas (LPG) feedstocks meet certain specifications for maximum water content. This ensures that water-based problems will not hamper downstream operations.



Methods Used to Inhibit Hydrate Formation

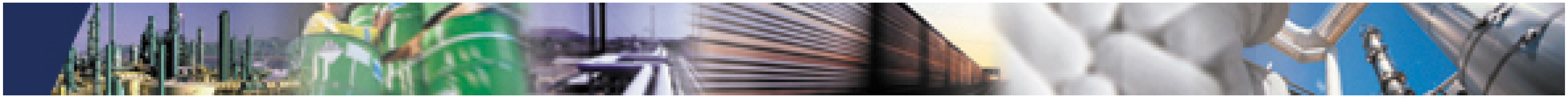
- Hydrate formation in natural gas is promoted by high-pressure, low-temperature conditions and the presence of liquid water.
- Therefore, hydrates can be prevented by the following:
  1. Raising the system temperature and/or lowering the system pressure (temperature/pressure control).
  2. Injecting a chemical such as methanol or glycol to depress the freezing point of liquid water (chemical injection).
  3. Removing water vapor form the gas liquid-water drop out that is depressing the dew point (dehydration).



Temperature/Pressure Control

Methods recommended for temperature control of natural gas streams include the following:

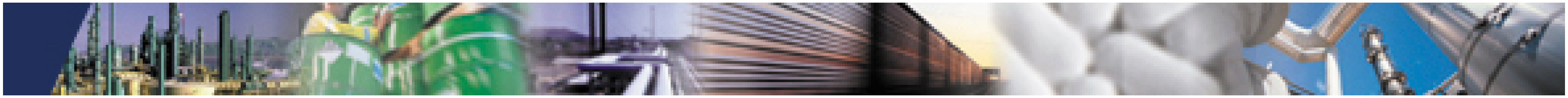
1. **Downhole regulators or chokes**. In this method, a pressure regulator (choke) is installed downhole (in the well). This causes the largest portion of the desired pressure drop from the bottom-hole flowing pressure to the surface flow line pressure to occur where the gas temperature is still high. The bottom-hole temperature will be sufficiently high to prevent hydrate formation as the pressure is reduced. At surface, little or no pressure reduction may required, thus hydrate formation is also avoided at the surface.



Temperature/Pressure Control

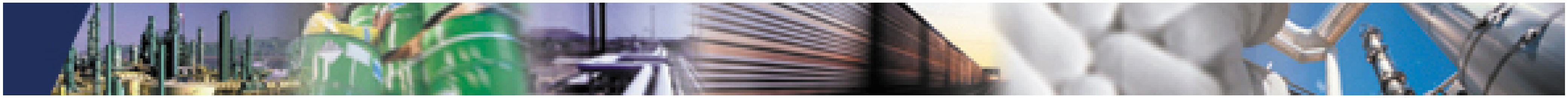
Process Control & Safety

2. **Indirect heaters**. Both wellhead and flow line indirect heaters are commonly used to heat natural gas to maintain the flowing temperature above the hydrate formation temperature. The primary purpose of the wellhead heater is to heat the flowing gas stream at or near the wellhead, where choking or pressure reduction frequently occurs. Flow line heaters, on the other hand, provide additional heating if required. They are particularly used for cases where the conditions neccesitate a substantial reduction in pressure between the wellhead stream and the next field facility.



Chemical Injection

- Methanol and glycols are the most commonly used chemicals, although others (such as ammonia) have been applied to lower the freezing point of water, thus reducing (or preventing) hydrate formation.
- The application of hydrate inhibitors should be considered for such cases:
  - A system of gas pipelines, where the problem of hydrate formation is of short duration.
  - A system of gas pipelines which operate at a few degrees below the hydrate formation temperature.
  - Gas gathering systems found in pressure-declining fields.
  - Gas lines characterized by hydrate formation in localized points.
- The principle underlying the use of hydrate inhibitors is to lower the formation of the hydrate by causing a depression of the hydrate formation temperature.



Methanol Injection

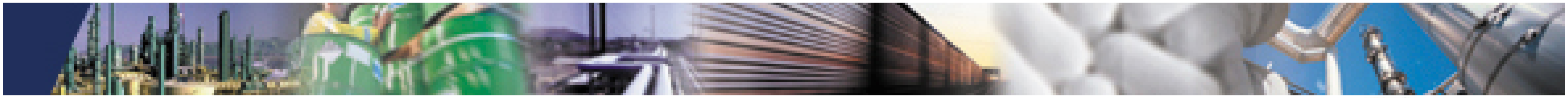
- Methanol is the most commonly used nonrecoverable hydrate inhibitor.
- It has the following properties:
  1. It is noncorrosive.
  2. It is chemically inert; no reaction with the hydrocarbons.
  3. It is soluble in all proportions with water.
  4. It is volatile under pipeline conditions, and its vapor pressure is greater than that of water.
  5. It is not expensive.
- Methanol is soluble in liquid hydrocarbons (about 0.5% by weight).
- Therefore, if the gas stream has high condensate contents, a significant additional volume of methanol will be required.

Methanol Injection

- This makes this method of hydrate inhibition unattractive economically because methanol is nonrecoverable.
- In such a situation, it will be necessary to first separate the condensate from the gas.
- Some methanol would also vaporize and goes into the gas.
- The amount of methanol that goes into the gas phase depends on the operating pressure and temperature.
- In many applications, it is recommended to inject methanol some distance upstream of the point to be protected by inhibition, in order to allow time for the methanol to vaporize before reaching that point.

Glycol Injection

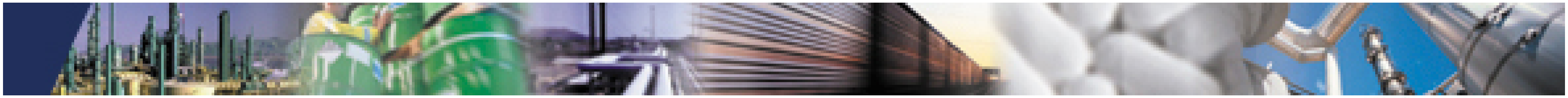
- Glycol functions in the same way as methanol; however, glycol has a lower vapor pressure and does not evaporate into vapor phase as readily as methanol.
- It is also less soluble in liquid hydrocarbons than methanol.
- This, together with the fact that glycol could be recovered and reused for the treatment, reduces the operating costs as compared to the methanol injection.
- Three types of glycols can be used: ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG).
- The following specific applications are recommended:



Glycol Injection

1. For natural gas transmission lines, where hydrate protection is of importance, EG is the best choice. It provides the highest hydrate depression, although this will be at the expense of its recovery because of its high vapor pressure.
2. Again, EG is used to protect vessels or equipment handling hydrocarbon compounds, because of its low solubility in multicomponent hydrocarbons.
3. For situations where vaporization losses are appreciable, DEG or TEG should be used, because of their lower vapor pressure.

Removing of the free water from the gas stream ahead of the injection point will cause a significant savings in the amount of the inhibitor used.



Dehydration Methods

- The most common dehydration methods used for natural gas processing are as follows:
  1. Absorption, using the liquid desiccants (e.g., glycol and methanol)
  2. Adsorption, using solid desiccants (e.g., alumina and silica gel)
  3. Cooling/condensation below the dew point, by expansion and/or refrigeration.

- This is in addition to the hydrate inhibition procedures described earlier.
- Classification of dehydration methods is given in Figure 1.

Dehydration Methods

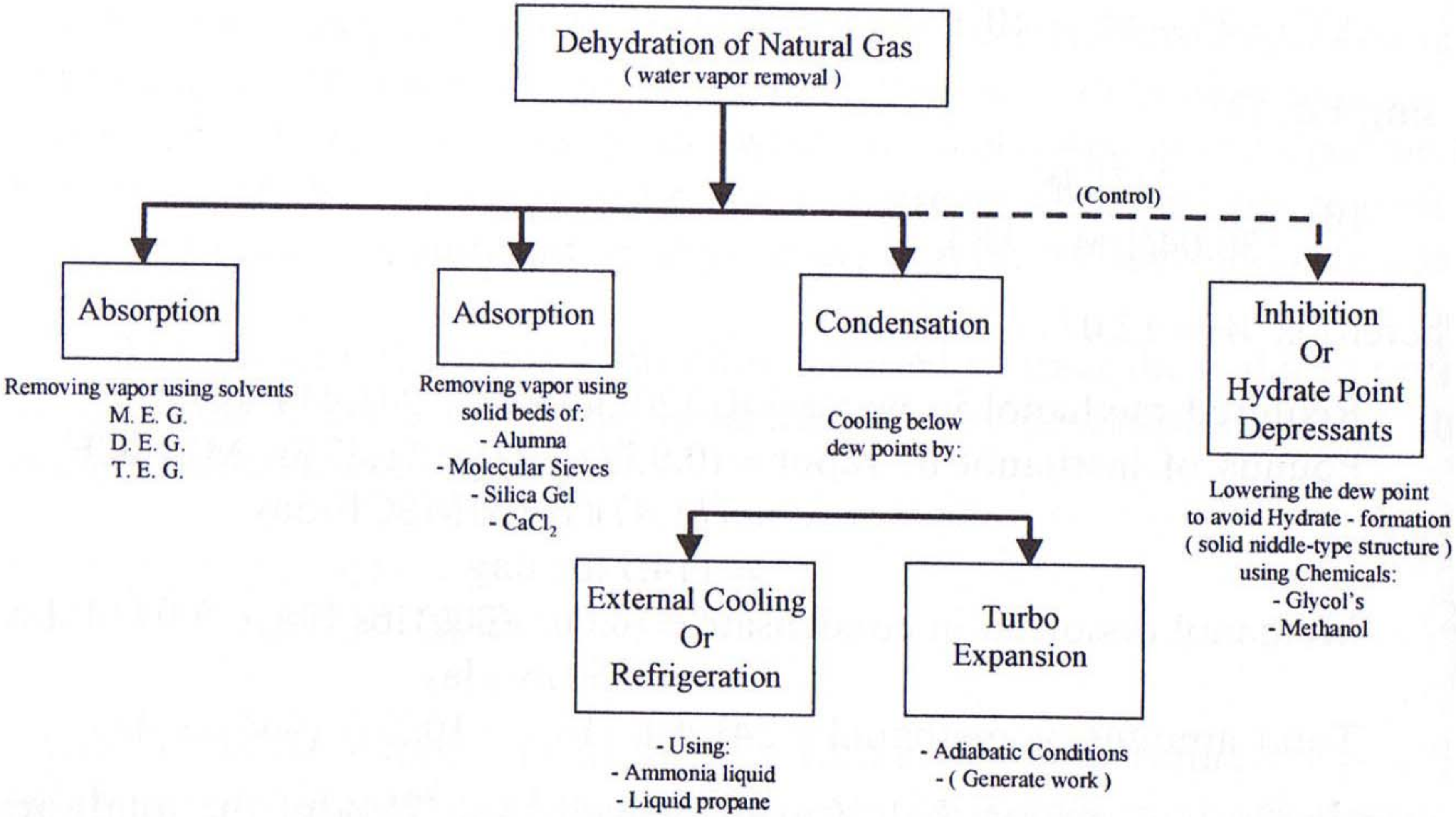


Figure 1 Classification of natural gas dehydration methods.

Absorption: Glycol Dehydration

- The absorption process is shown in Figure 2.
- The wet natural gas enters the absorption column (glycol contactor) near its bottom and flows upward through the bottom tray to the top tray and out at the top of the column.
- Usually, six to eight trays are used.
- Lean (dry) glycol is fed at the top of the column and it flows down from tray to tray, absorbing water vapor from the natural gas.
- The rich (wet) glycol leaves from the bottom of the column to the glycol regeneration unit.
- The dry natural gas passes through mish mesh to the sales line.

Absorption: Glycol Dehydration

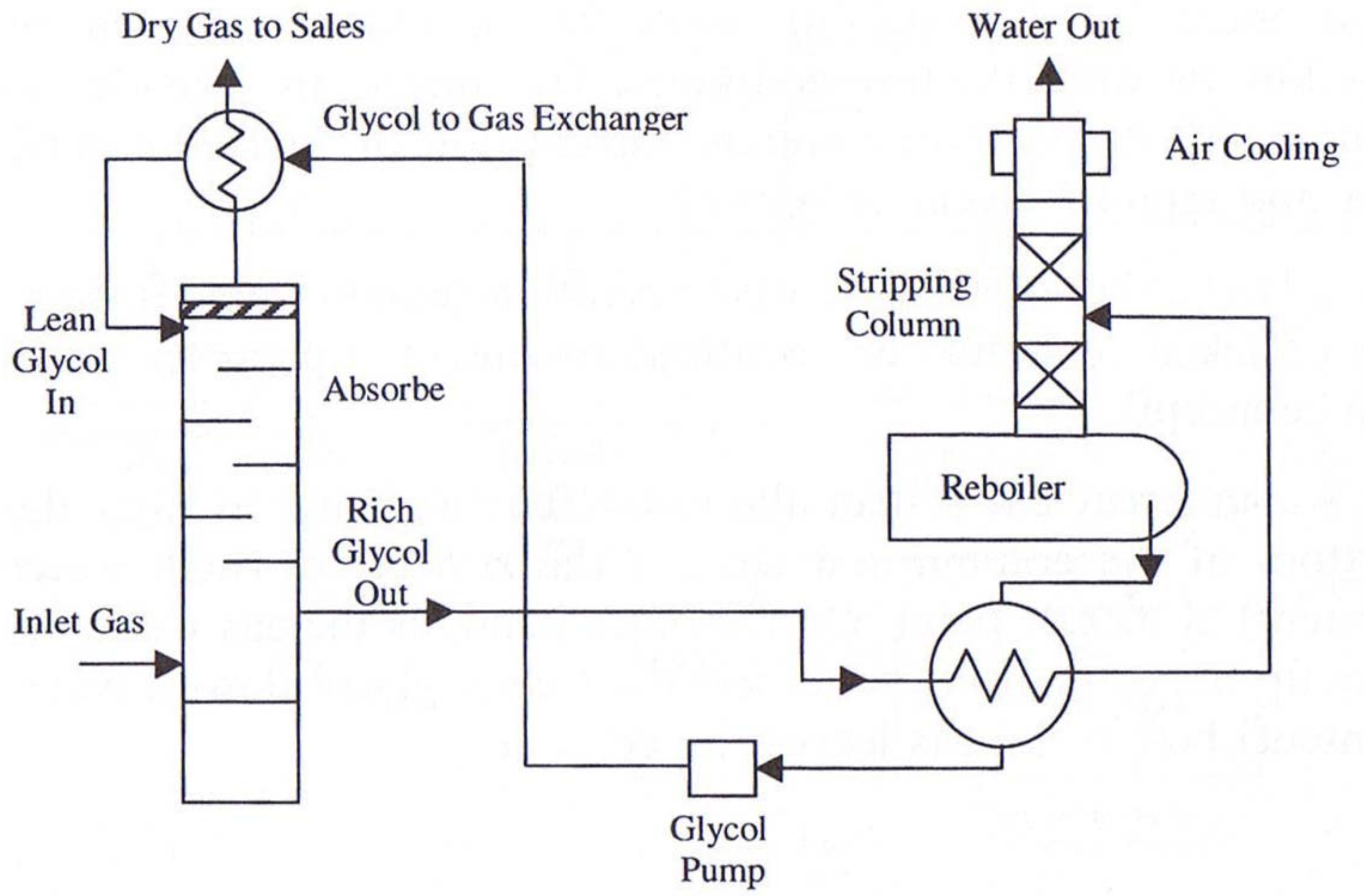


Figure 2 Flow diagram of TEG dehydration.

Absorption: Glycol Dehydration

- The glycol regeneration unit is composed of a reboiler where steam is generated from the water in the glycol.
- The steam is circulated through the packed section to strip the water from glycol.
- Stripped water and any lost hydrocarbons are vented at the top of the stripping column.
- The hydrocarbons losses are usually benzene, toluene, xylene, and ethyl benzene and it is important to minimize these emissions.
- The rich glycol is preheated in heat exchangers, using the hot lean glycol, before it enters the still column of the glycol reboiler.
- This cools down the lean glycol to the desired temperature and saves the energy required for heating the rich glycol in the reboiler.

Adsorption:Solid-Bed Dehydration

- When very low dew points are required, solid-bed dehydration becomes the logical choice.
- It is based on fixed-bed adsorption of water vapor by a selected desiccant.
- A number of solid desiccants could be used such as silica gel, activated alumina, or molecular sieves.
- The system may consist of two-bed (as shown in Figure 3), three-bed, or multi-bed operation.
- In the three-bed operation, if two beds are loading at different stages, the third one would be regenerated.
- The feed gas in entering the bed from the top and the upper becomes saturated first.

Adsorption:Solid-Bed Dehydration

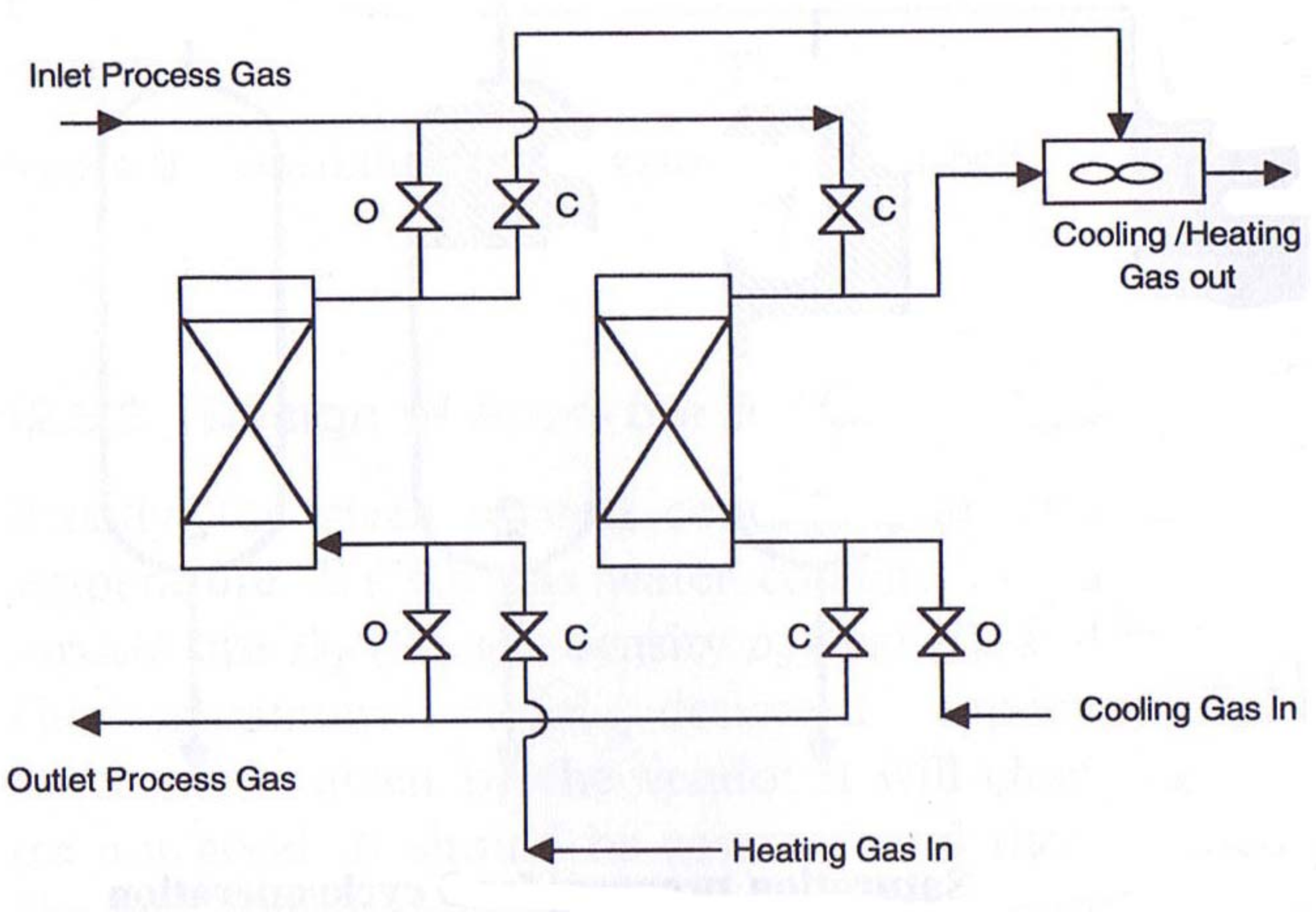
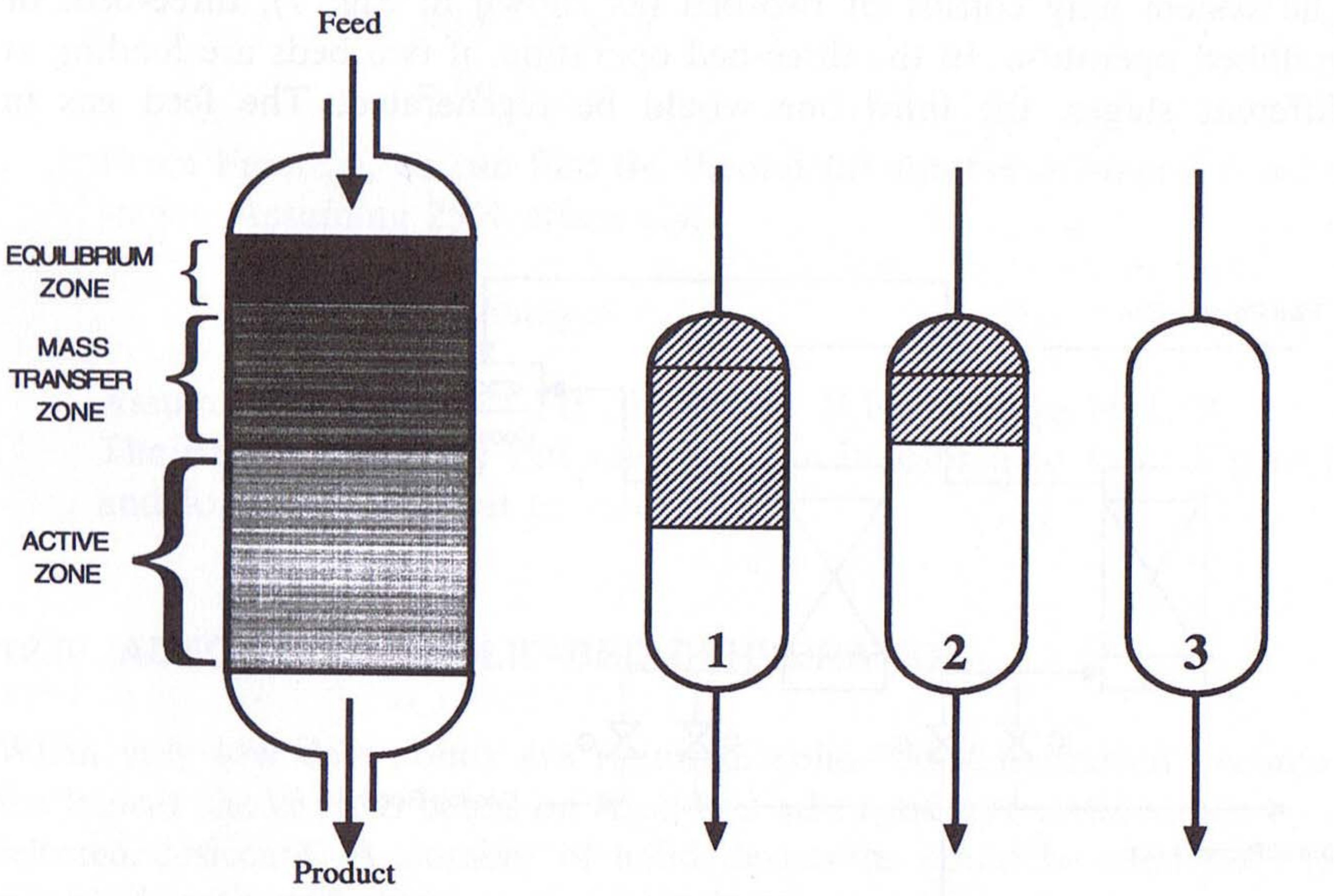


Figure 3 Solid-bed dehydration process.

Adsorption:Solid-Bed Dehydration

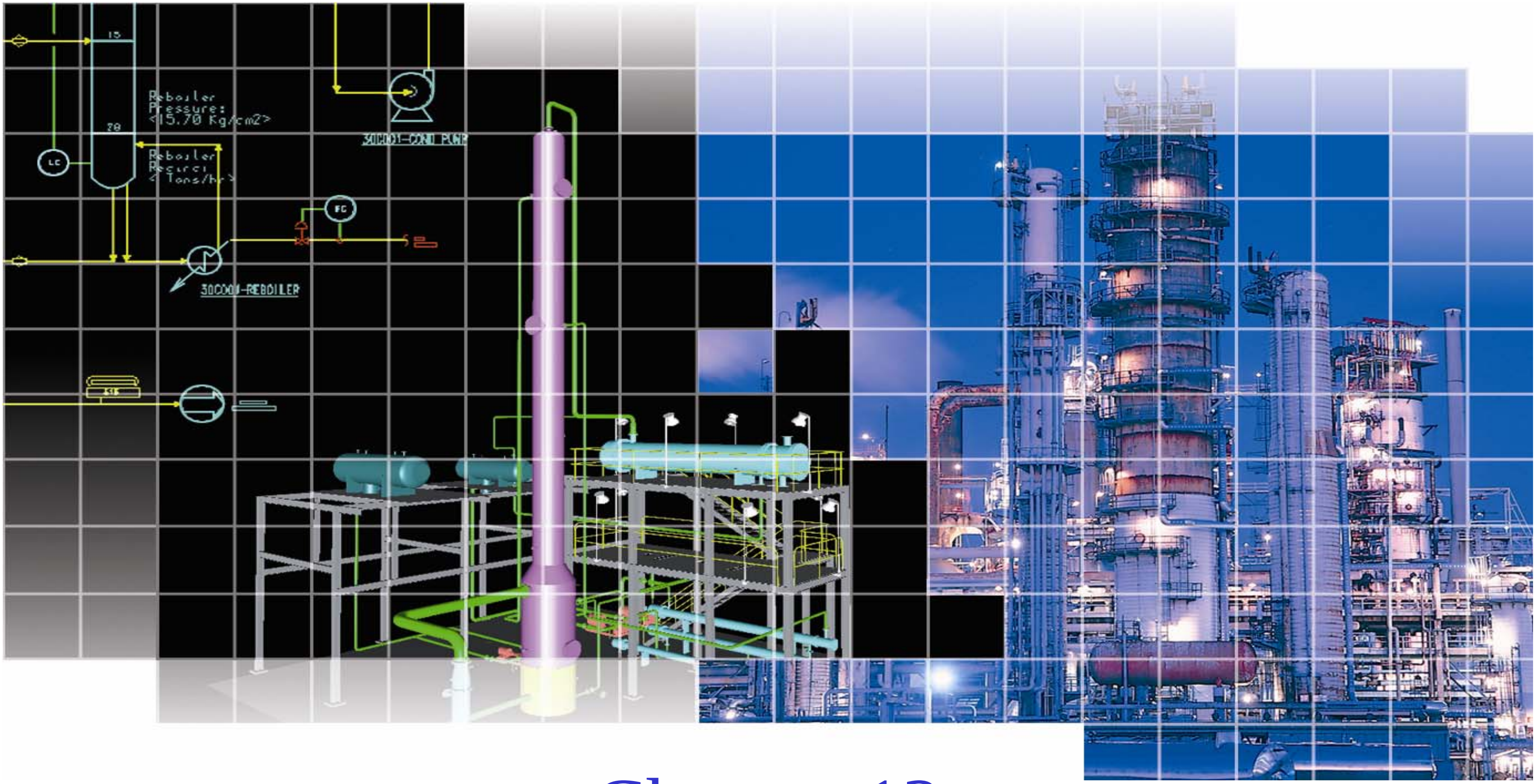
- The second zone is the mass transfer zone (MTZ) and is being loaded.
- The third zone is still not used and active.
- The different saturation progress and representation of different zones is shown in Figure 4.
- While the bed is in operation, the outlet concentration has very low water concentration and the MTZ moves downward.
- At a certain point, the outlet water content rises to the point that is equivalent to the initial wet gas content as if bed is not present.
- After the bed has been used and loaded with water, then it is regenerated by hot gas and then cooled by switching to cold gas.

Adsorption:Solid-Bed Dehydration



Operating zones **Saturation progress for 3 cycle operation**

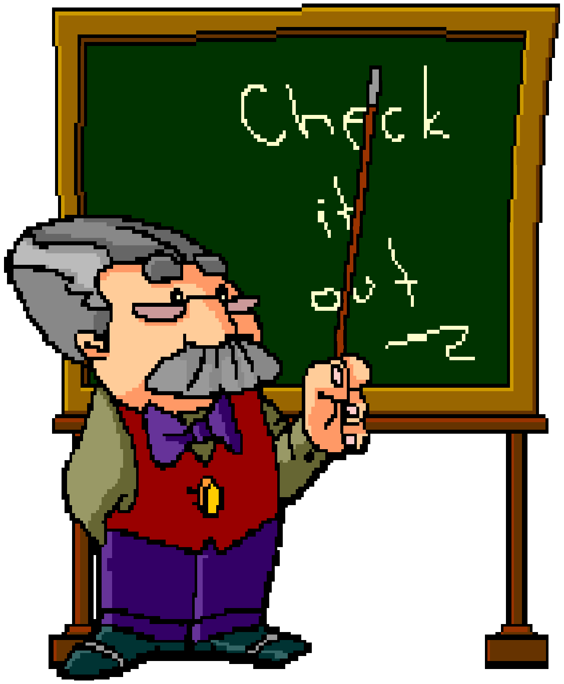
Figure 4 Mode operation.



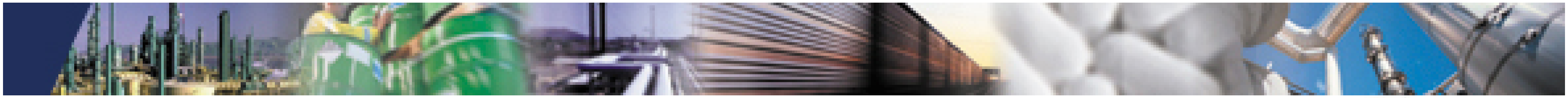
Chapter 12

Recovery, Separation, and Fractionation of Natural Gas Liquids

Outline

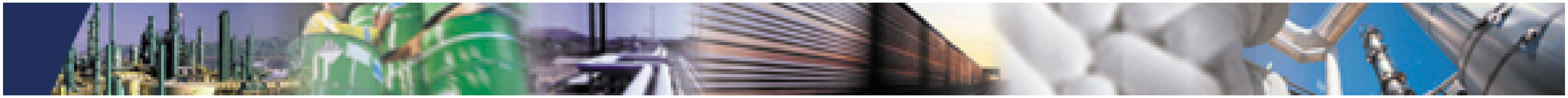


- Introduction
- Recovery and Separation of NGL
  - Parameters Controlling NGL Separation
  - Selected Separation Processes
- Fractionation of NGL



Introduction

- The material presented in this chapter includes two parts: the recovery and separation of natural gas liquid (NGL) constituents, and methods of fractionation into finished product streams suitable for sale.
- In the first part, several alternatives for the separation and recovery of NGL are detailed.
- They are essentially based on phase change either by using energy separating agent (ESA) or mass separating agent (MSA).
- Thus, partial liquefaction or condensation of some specific NGL constituents will lead to their separation from the bulk of the gas stream.
- Total condensation is also a possibility.
- The second part covers materials on fractionation facilities that are recommended to produce specification quality products from NGL.



Recovery and Separation of NGL

- To recover and separate NGL from a bulk of gas stream, a change in phase has to take place.
- In other words, a new phase has to be developed for separation to occur.
- Two distinctive options are in practice depending on the use of ESA or MSA.

Energy Separating Agent

- The distillation process best illustrates a change in phase using ESA.
- To separate, for example, a mixture of alcohol and water heat is applied.
- A vapor phase is formed in which alcohol is more concentrated, and then separated by condensation.
- This case of separation is expresses as follows:

A mixture of liquids + Heat → Liquid + Vapor

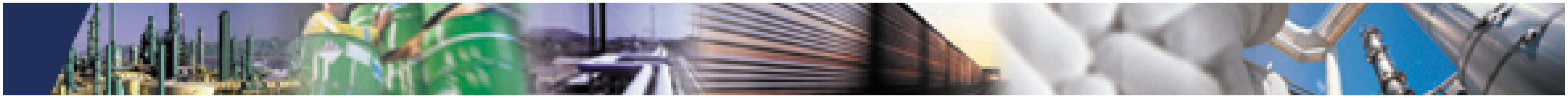
- For the case of NGL separation and recovery in a gas plant, removing heat (by refrigeration) on the other hand, will allow heavier components to condense, hence, a liquid phase is formed.

A mixture of hydrocarbon vapor – Heat → Liquid + Vapor

- Partial liquefaction is carried out for a specific cut, whereas total liquefaction is done for the whole gas stream.

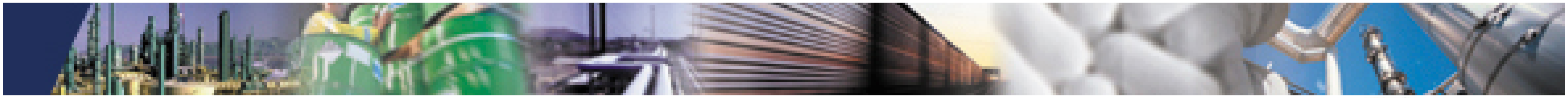
Mass Separating Agent

- To separate NGL, a new phase is developed by using either a solid material in contact with the gas stream (adsorption) or a liquid in contact with the gas (absorption).
- These two cases are represented later in this chapter.



Parameters Controlling NGL Separation

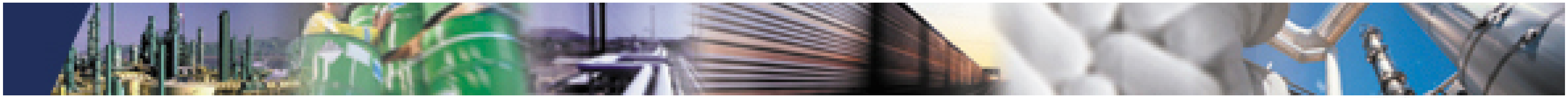
- A change in phase for NGL recovery and separation always involves control of one or more of the following three parameters:
  - Operating pressure, P
  - Operating temperature, T
  - System composition or concentration, x and y
- To obtain the right quantities of specific NGL constituents, a control of the relevant parameters has to be carries out:
  1. For separation using ESA, pressure is maintained by direct control. Temperature, on the other hand, is reduced by refrigeration using one of the following techniques:
     - Compression refrigeration
     - Cryogenic separation; expansion across a turbine
     - Cryogenic separation; expansion across a valve



Parameters Controlling NGL Separation

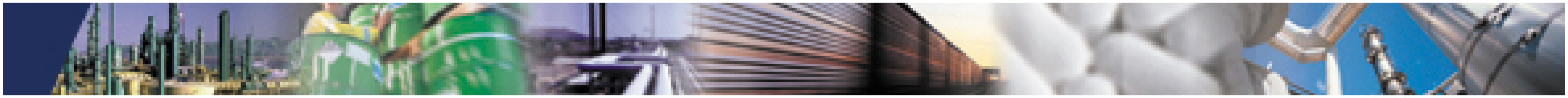
2. For separation using MSA, a control in the composition or the concentration of the hydrocarbons to be recovered (NGL); y and x is obtained by using adsorption or absorption methods.

- Adsorption is defined as a concentration (or composition) control process that precedes condensation.
- Therefore, refrigeration methods, may be coupled with adsorption to bring in condensation and liquid recovery.
- Absorption, on the other hand, presents a similar function of providing a surface or “contact” are of liquid-gas interface.
- The efficiency of condensation, hence NGL recovery, is a function of P, T, gas and oil flow rates, and contact time.
- Again, absorption could be coupled with refrigeration to enhance condensation.



Selected Separation Processes

- In this section a brief description is given for the absorption, refrigeration, and cryogenic (Joule-Thomson turbo expansion) processes recommended to separate NGL constituents from a gas stream.



Absorption Process

- The absorption unit consists of two sections: the absorption and regeneration as illustrated in Figure 1.
- An upflow natural gas stream is brought in direct contact, countercurrently with the solvent (light oil in the kerosene boiling range) in the absorber.
- The column – a tray or packed one – operates at about 400-1000 psia and ambient or moderately subambient temperatures.
- The rich oil (absorbed NGL plus solvent) is directed to a distillation unit to separate and recover the NGL, whereas the lean oil is recycled back to the absorber.
- In addition to natural gasoline, C_3/C_4 could be recovered as well.
- Provision is made to separate ethane from rich oil using a deethanizer column.

Absorption Process

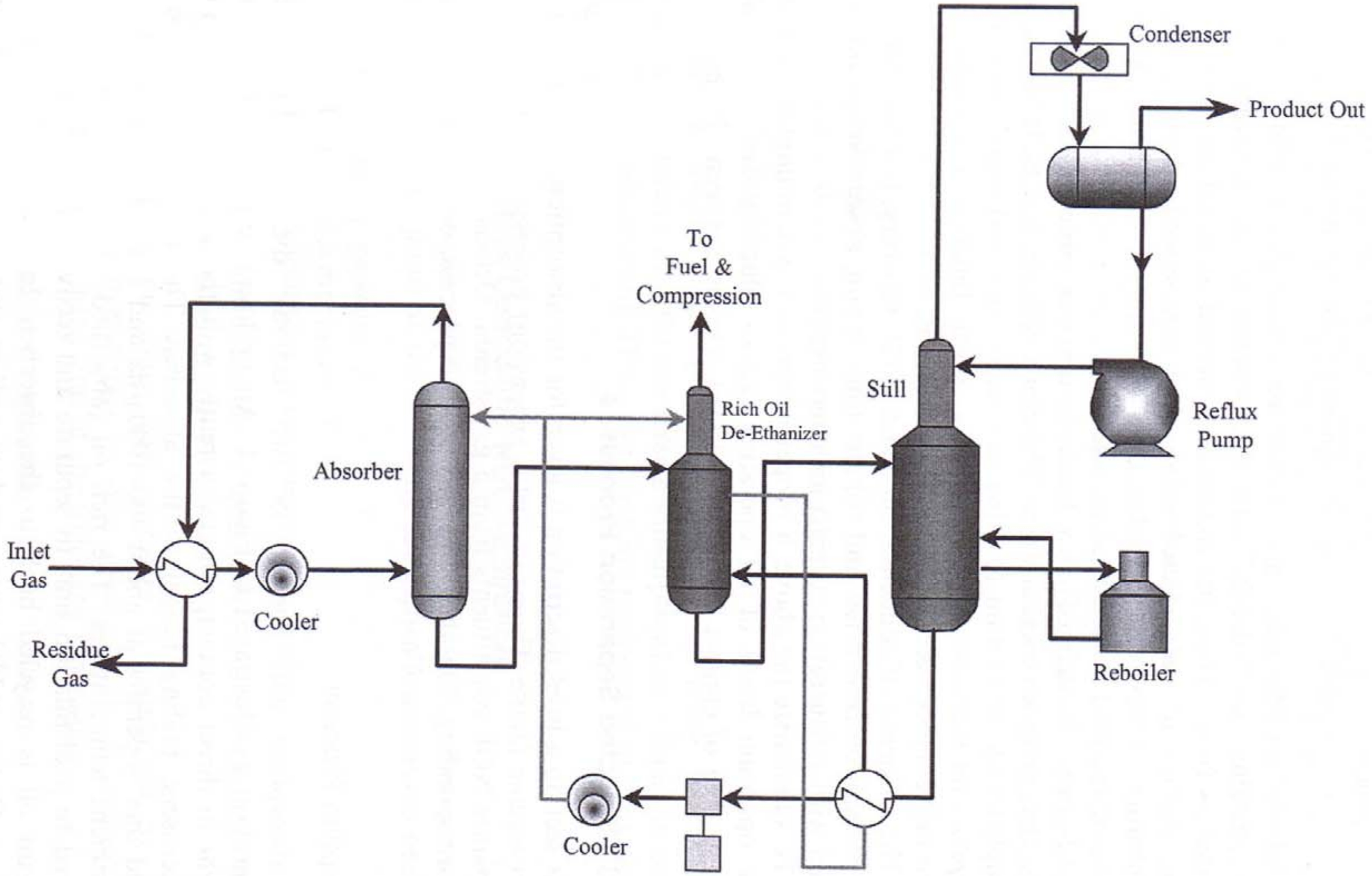
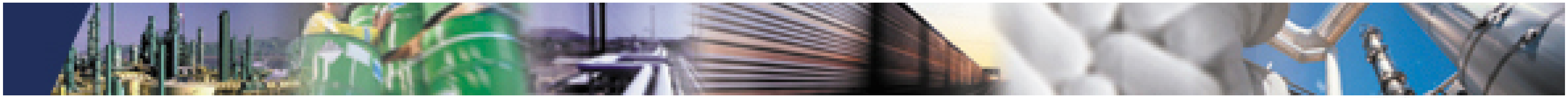


Figure 1 Separation of NGL by absorption.



Refrigeration Process

- The production of NGL at low temperature is practiced in many gas processing plants in order to condense NGL from gas streams.
- As indicated in Figure 2, using nontoxic and noncorrosive refrigerants to chill the feed natural gas to a temperature between 0°F and -40°F using a low-level one-component refrigerant system provides external refrigeration.
- For a given selected separation pressure the corresponding operating temperature is chosen based on the type of product:
  - If the liquid product is to be sold as “crude oil”, then the separation temperature is between 0°C and 5°C.
  - If the liquid product contains propane as the lightest component, temperature is about -30°C to -18°C.
  - If the operating temperature is set below -30°C, a cryogenic range of ethane recovery is encountered.

Refrigeration Process

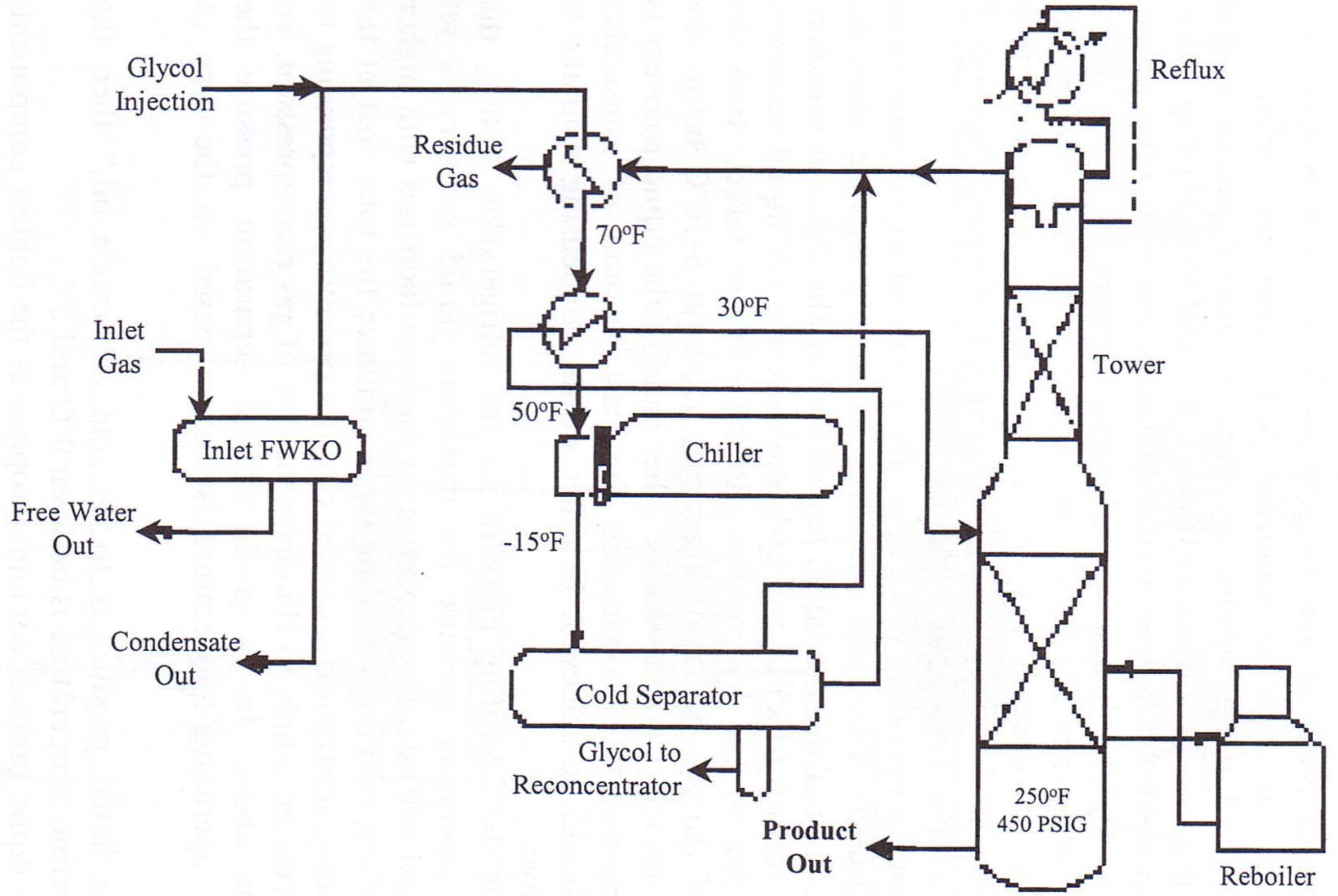


Figure 2 Separation of NGL using refrigeration plant.

Cryogenic Processes

- Natural gas liquid could be separated from natural gas using two approaches based on cryogenic expansion (autorefrigeration):
  - An expander plant produces refrigeration to condense and recover the liquid hydrocarbons contained in the natural gas by using a turboexpander. In this process, the enthalpy of the natural gas is converted into useful work, behaving thermodynamically as an approximate isentropic process.
  - Expansion across the valve will lead to a similar result. However, the expansion is described in this case as “isenthalpic”.
- Temperatures produced by turboexpansion are much more lower than those of valve expansion.

Cryogenic Processes

- A schematic presentation for the turboexpansion process is presented in Figure 3.
- The process operates at -100oF to -160oF and 1000 psia.
- The process represents a new development in the gas processing industry.
- Increased liquid recovery (especially ethane) is an advantage of this process.
- Figure 5 illustrates the condensation process using ethane/propane, followed by demethanization to produce NGL as a final product.
- Figure 5, on the other hand, presents a typical gas plant for the recovery and separation of NGL.

Cryogenic Processes

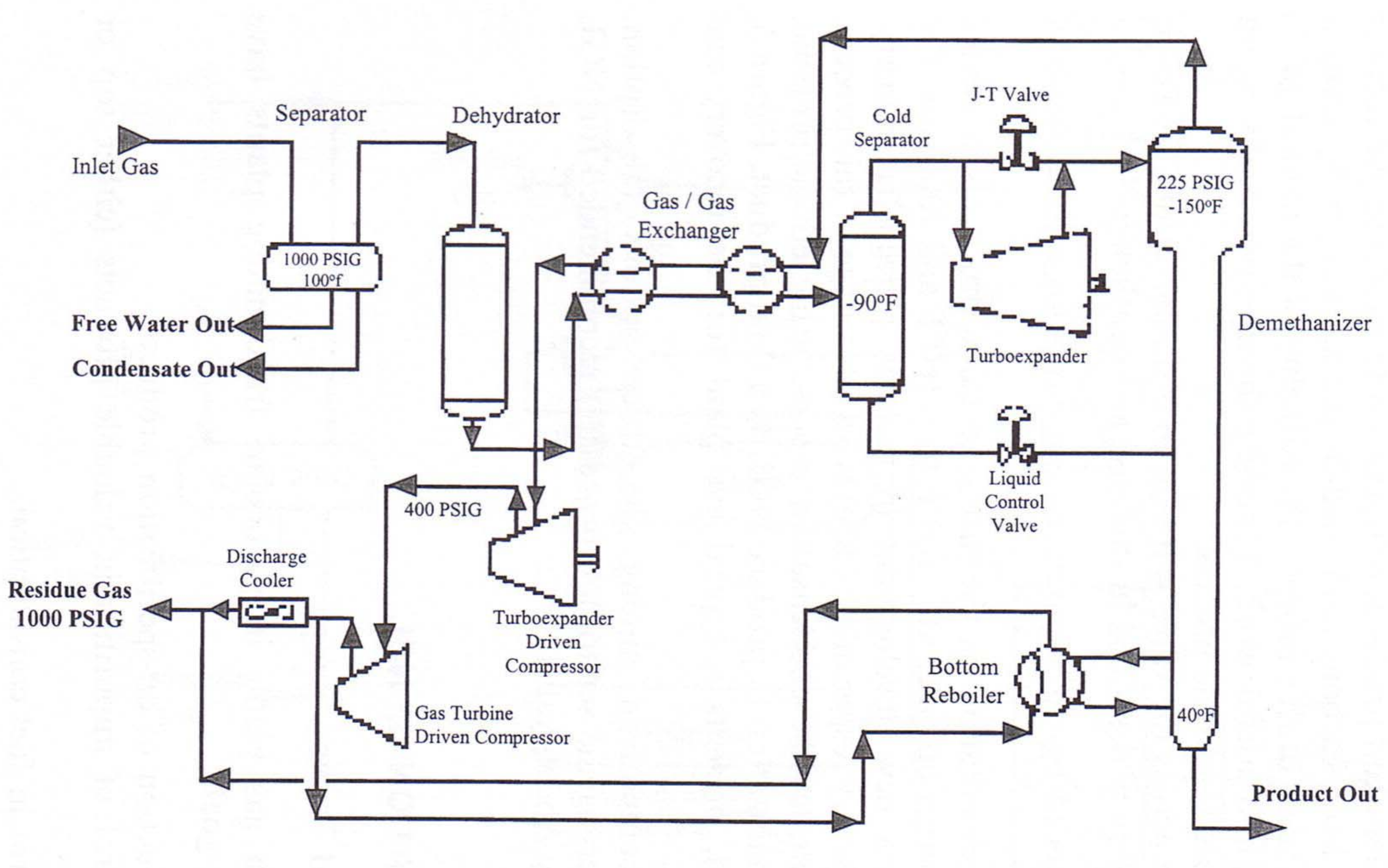


Figure 3 Cryogenic separation of NGL.

Cryogenic Processes

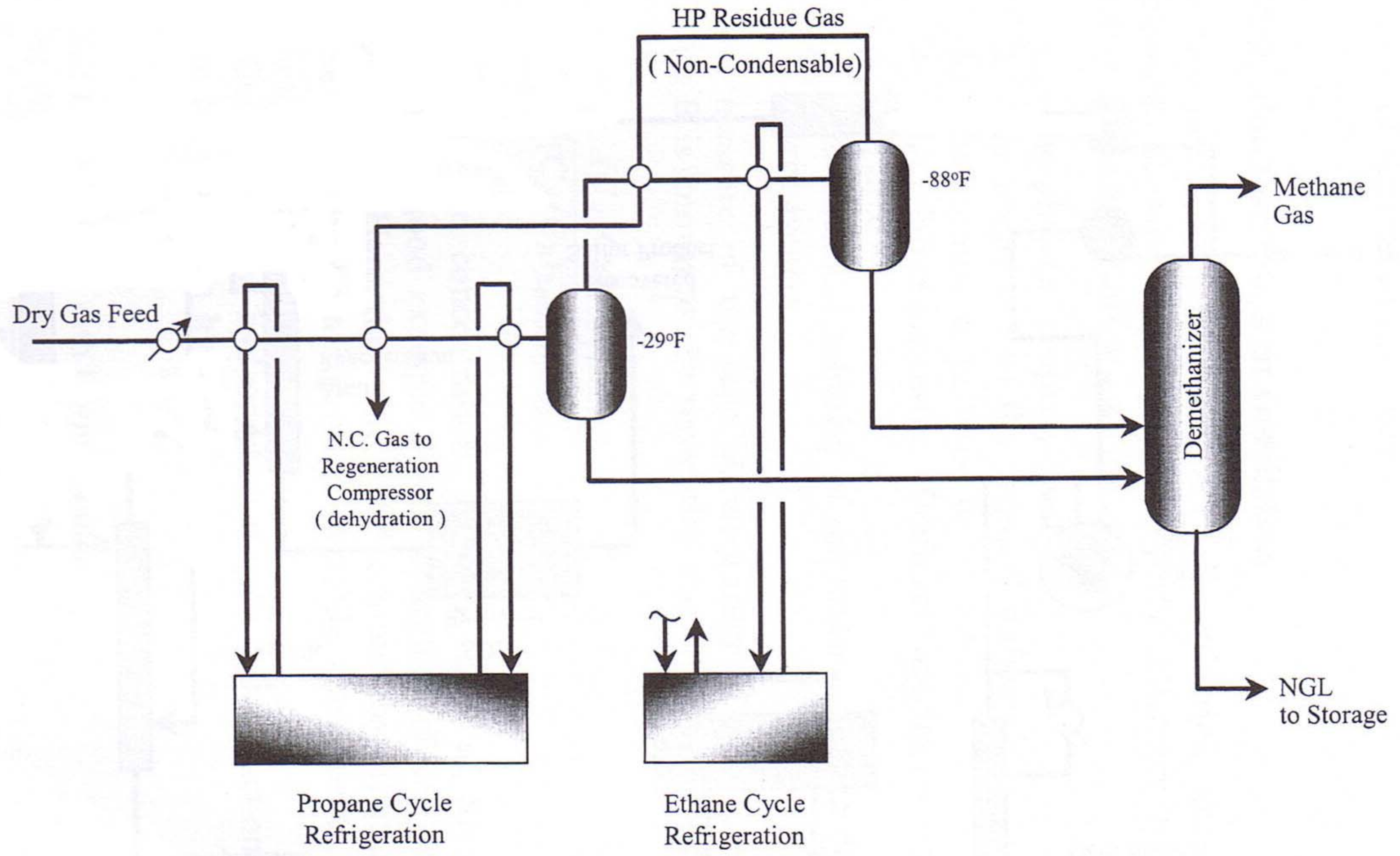


Figure 4 NGL condensation/demethanization.

Cryogenic Processes

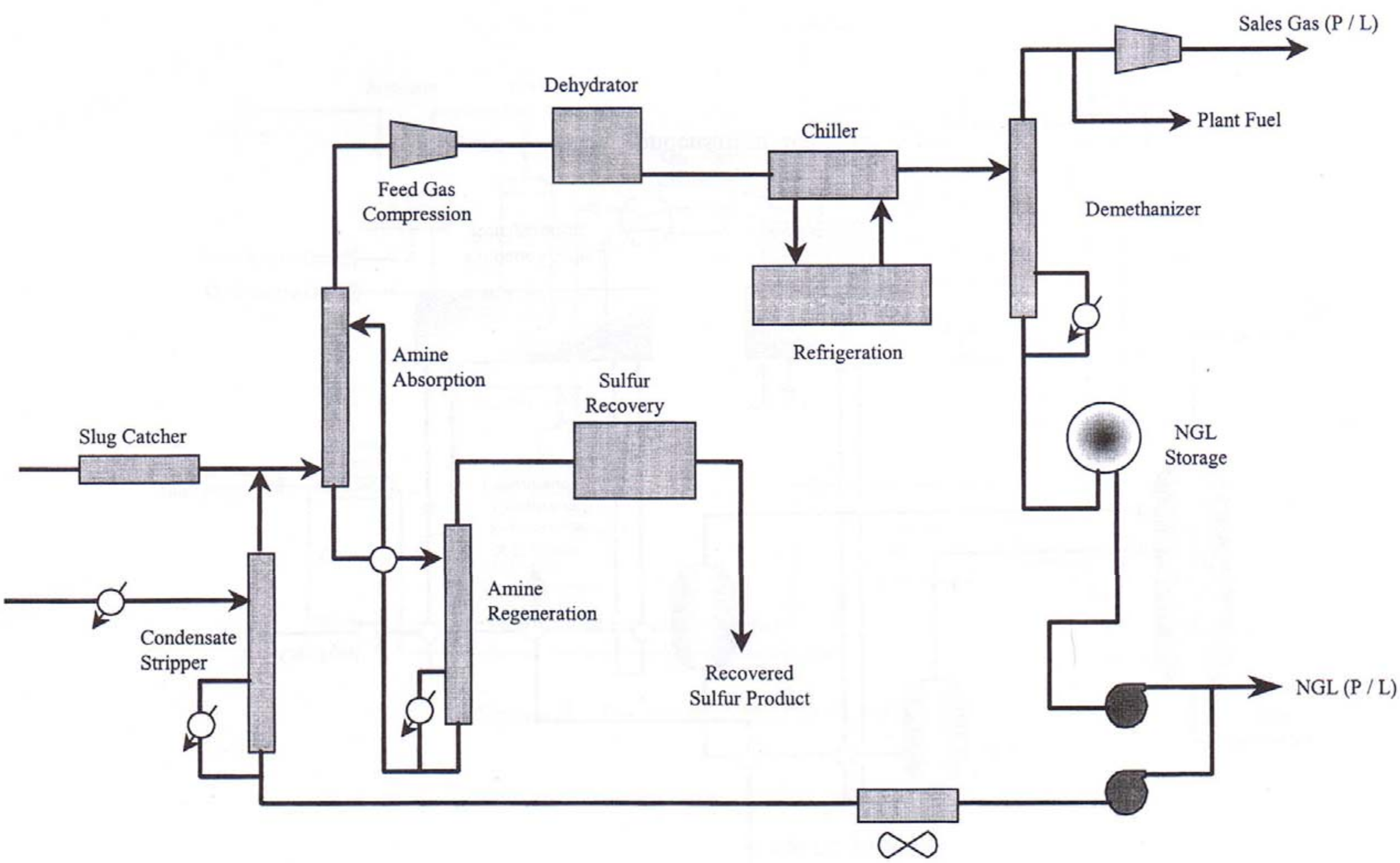


Figure 5 Atypical gas plant of NGL recovery.

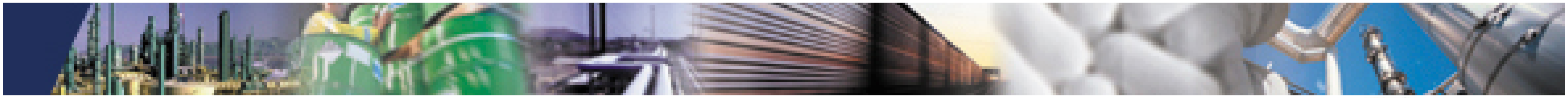
Fractionation of NGL

- In general, and in gas plants in particular, fractionating plants have common operating goals:
  1. The production of on-specification products
  2. The control of impurities in valuable products (either top or bottom)
  3. The control in fuel consumption
- As far as the tasks for system design of a fractionating facility, these goals are as follows:
  1. Fundamental knowledge on the process or processes selected to carry out the separation, in particular, distillation.
  2. Guidelines on the order of sequence of separation (i.e., synthesis of separation sequences).

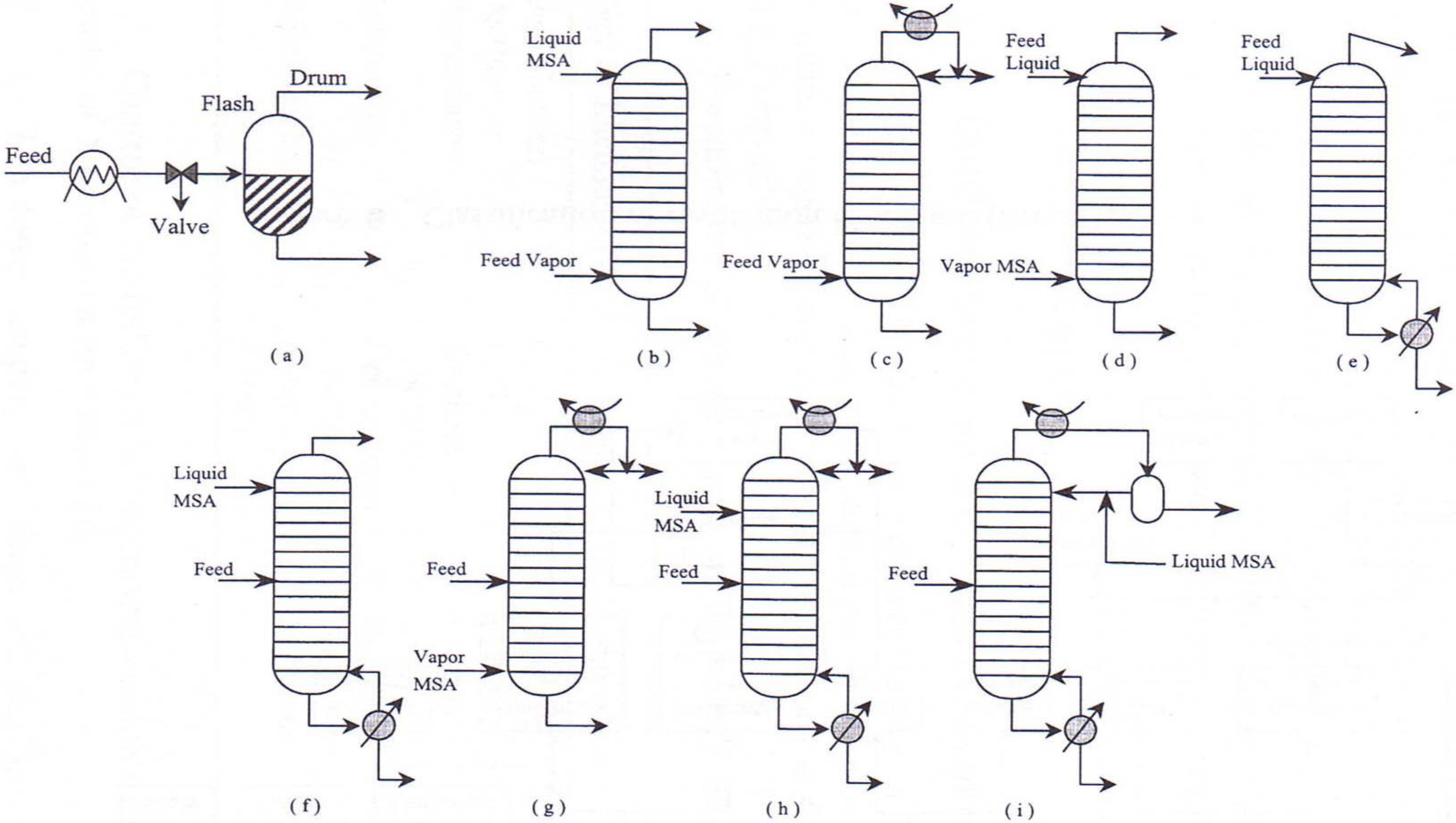
Fractionation of NGL

- Fractionators of different types are commonly used in gas plants:

Type of fractionator	Feed	Top product	Bottom product
Demethanizer	C1/C2	Methane	Ethane
Deethanizer	LPG	Ethane	Propane plus
Depropanizer	Deethanizer bottoms	Propane	Butanes plus
Debutanizer	Depropanizer bottoms	Butanes (iso+n)	Natural gasoline (pentanes plus)
Deisobutanizer	Debutanizer top	Isobutane	Normal butane



Fractionation of NGL



Separation operations related to distillation. (a) Flash vaporization or condensation; (b) Absorption; (c) Rectifier; (d) Stripping; (e) Reboiled stripping; (f) Reboiled absorption; (g) Refluxed stripping; (h) Extractive distillation; and (i) Azeotropic distillation. (From Ref. 3.)

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Fractionation of NGL

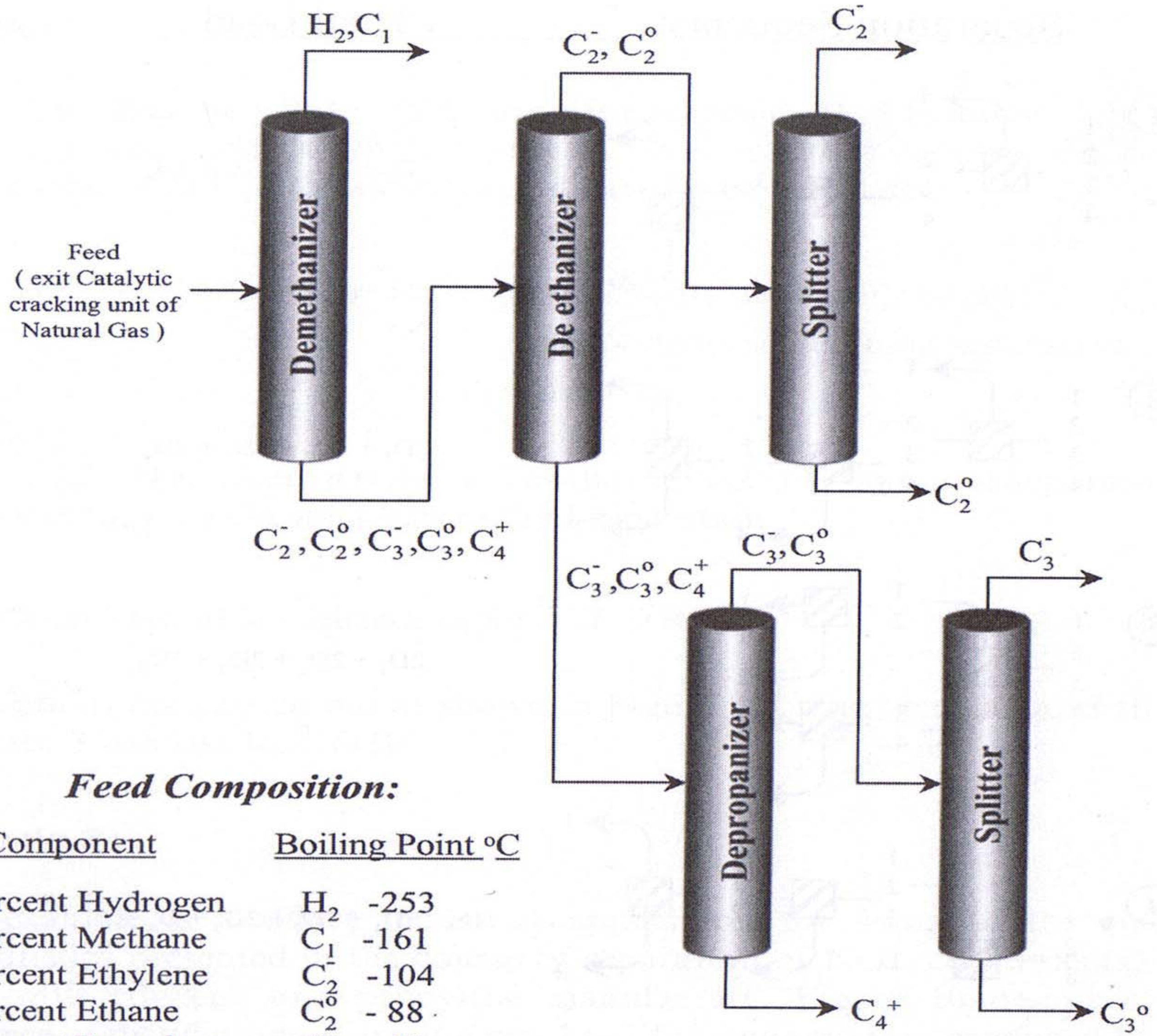
Control of the following key operating variables will ensure efficiant results of fractionation operations:

1. Top tower temperature, which sets the amount of the heavy hydrocarbons in the top product. This is controlled by the reflux ratio. Increasing the reflux rate will decrease this amount. We should observe that reflux liquid is produced as a result of overhead condensation of vapors. For columns using total condensers, such as depropanizers and debutanizers, all vapors are condensed to produce reflux and liquid product. On the other hand, for columns employing partial condensers, such as deethanizers, product is produced as vapor.
2. Bottom reboiler temperature, which sets the amount of light hydrocarbons in the bottom product. Adjusting the heat input to the reboiler controls this.

Fractionation of NGL

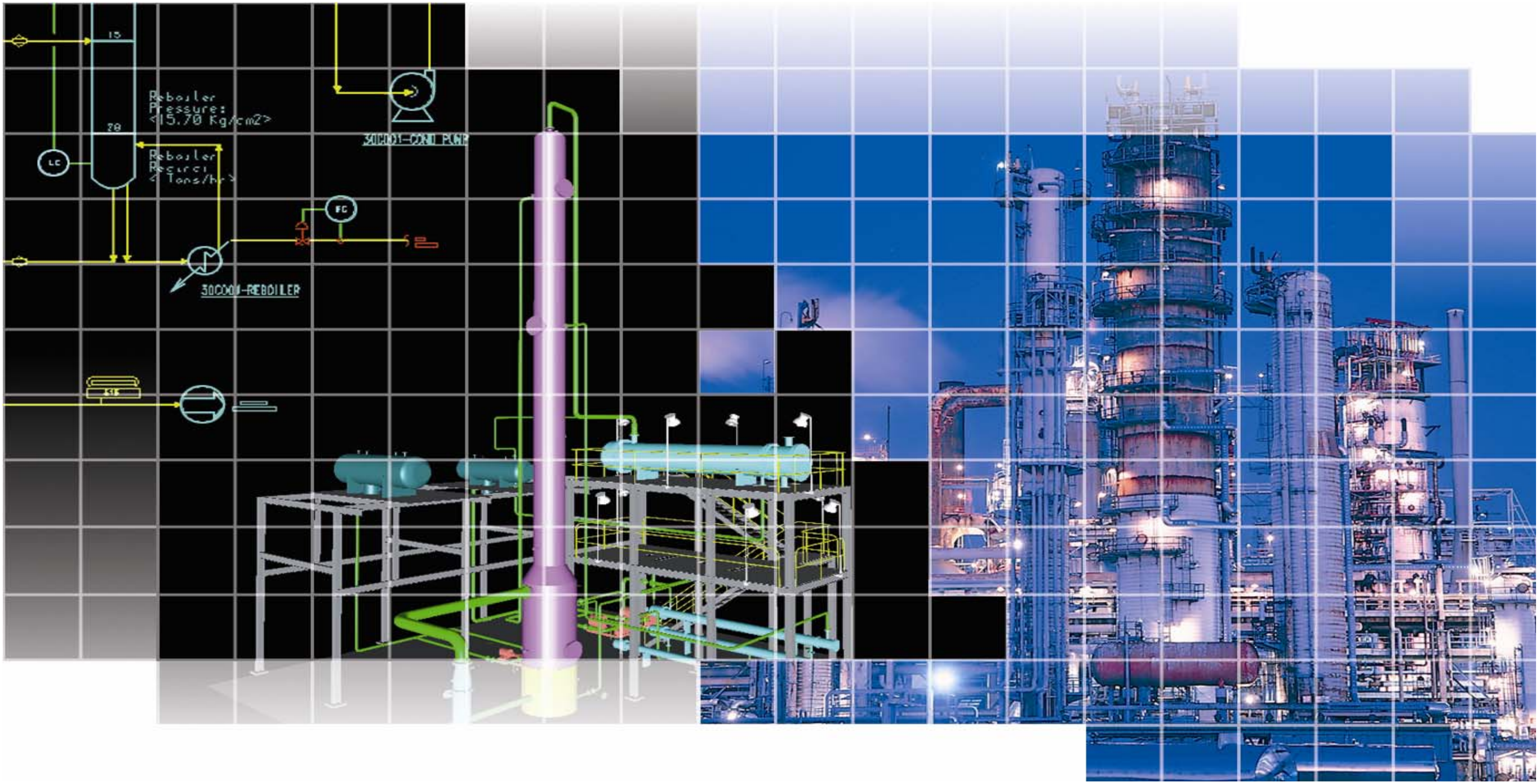
3. Tower operating pressure, which is fixed by the type of condensing medium (i.e., its temperature). Product quality is not affected, to a great extent, by changing the operating pressure.

Fractionation of NGL



Feed Composition:

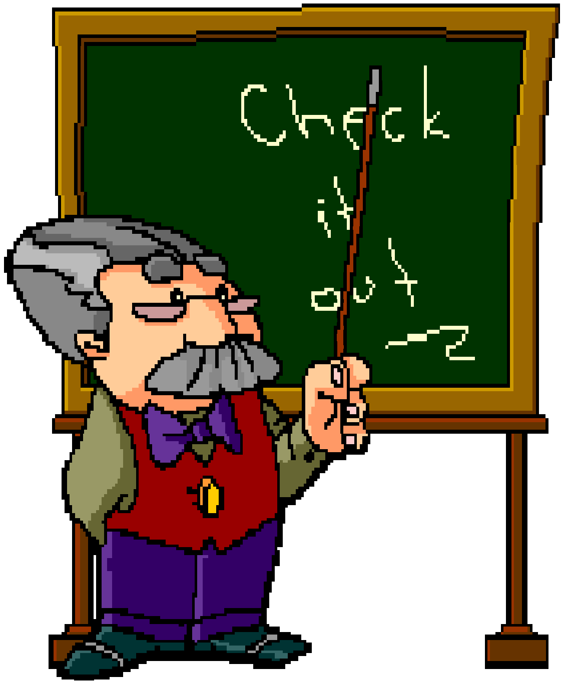
Component	Boiling Point °C
18 percent Hydrogen	H_2 -253
15 percent Methane	C_1 -161
24 percent Ethylene	C_2^- -104
15 percent Ethane	C_2^o - 88
14 percent Propylene	C_3^- - 48
6 percent Propane	C_3^o - 42
8 percent Heavies	C_4^+ - 1



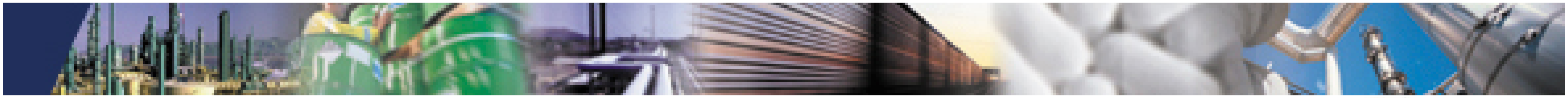
Chapter 13

Petroleum Refining Operations

Outline



- Introduction
- Refining Operations
- Refinery Process Chart



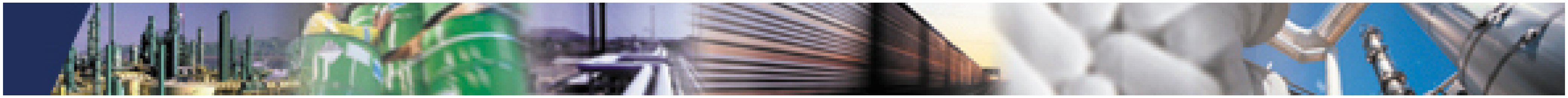
Introduction

- Petroleum refining begins with the distillation, or fractionation, of crude oils into separate hydrocarbon groups.
- The resultant products are directly related to the characteristics of the crude processed.
- Most distillation products are further converted into more usable products by changing the size and structure of the hydrocarbon molecules through cracking, reforming, and other conversion processes as discussed in this chapter.
- These converted products are then subjected to various treatment and separation processes such ac extraction, hydrotreating, and sweetening to removed undesirable constituents and improve product quality.
- Integrated refineries incorporate fractionation, conversion, treatment, and blending operations and may also include petrochemical processing as shown in Figure 1.

Refining Operations

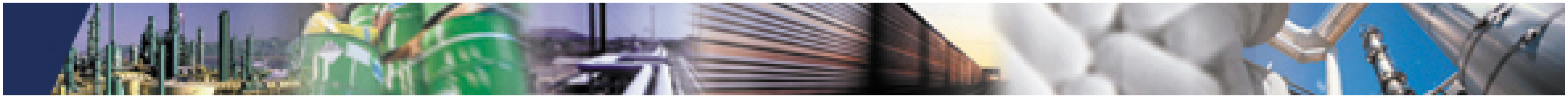
Petroleum refining processes and operations can be separated into five basic areas:

1. **Fractionation** (distillation) is the separation of crude oil in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of differing boiling-point ranges called “fractions” or “cuts”.
2. **Conversion** processes change the size and/or structure of hydrocarbon molecules. These processes include:
   - Decomposition (dividing) by thermal and catalytic cracking;
   - Unification (combining) through alkylation and polymerization; and
   - Alteration (rearranging) with isomerization and catalytic reforming



Refining Operations

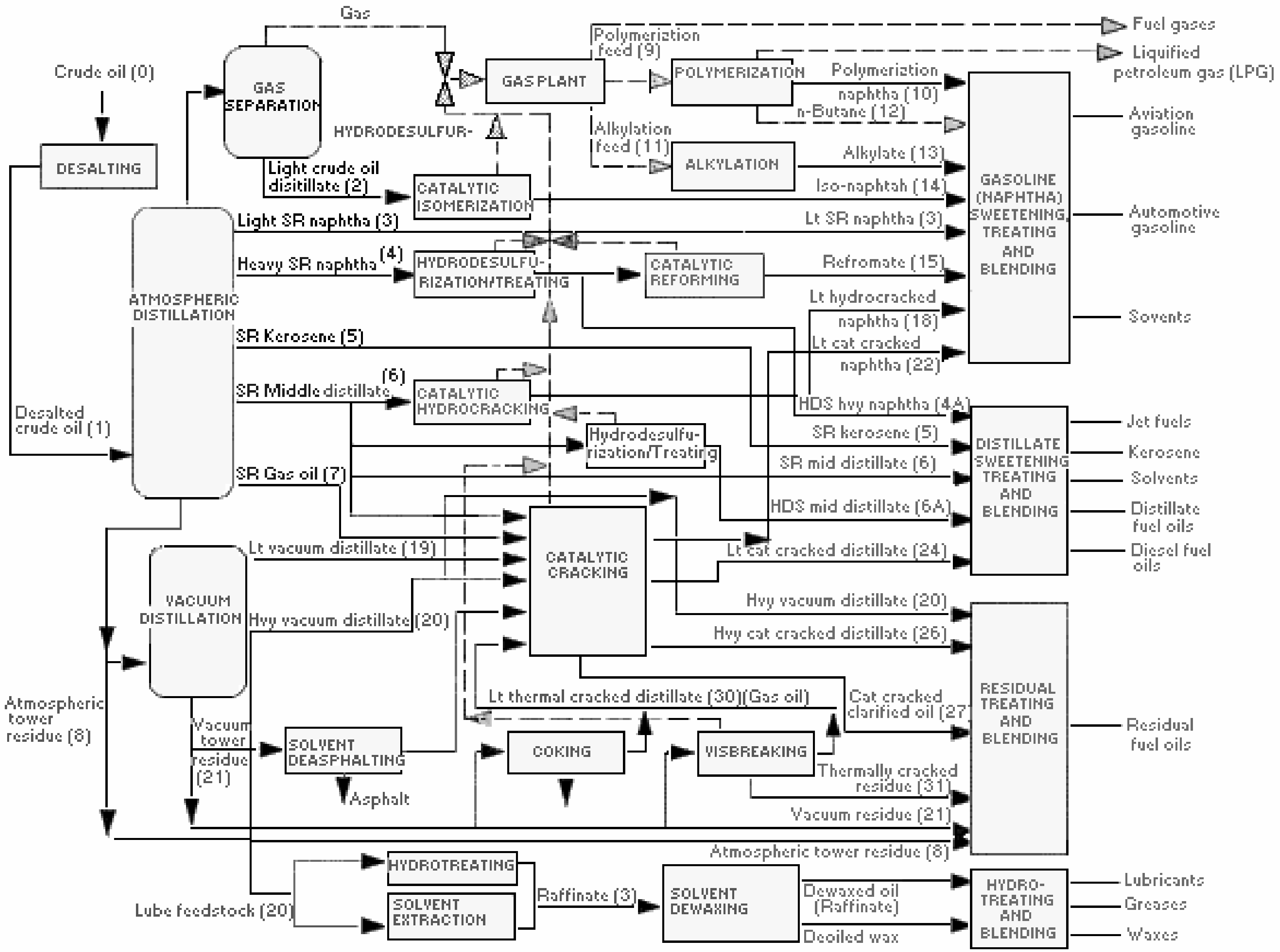
3. **Treatment** processes are intended to prepare hydrocarbon streams for additional processing and to prepare finished products. Treatment may include the removal or separation of aromatics and naphthenes as well as impurities and undesirable contaminants. Treatment may involve chemical or physical separation such as dissolving, absorption, or precipitation using a variety and combination of processes including desalting, drying, hydrodesulfurizing, solvent refining, sweetening, solvent extraction, and solvent dewaxing.
4. **Formulating and Blending** is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.

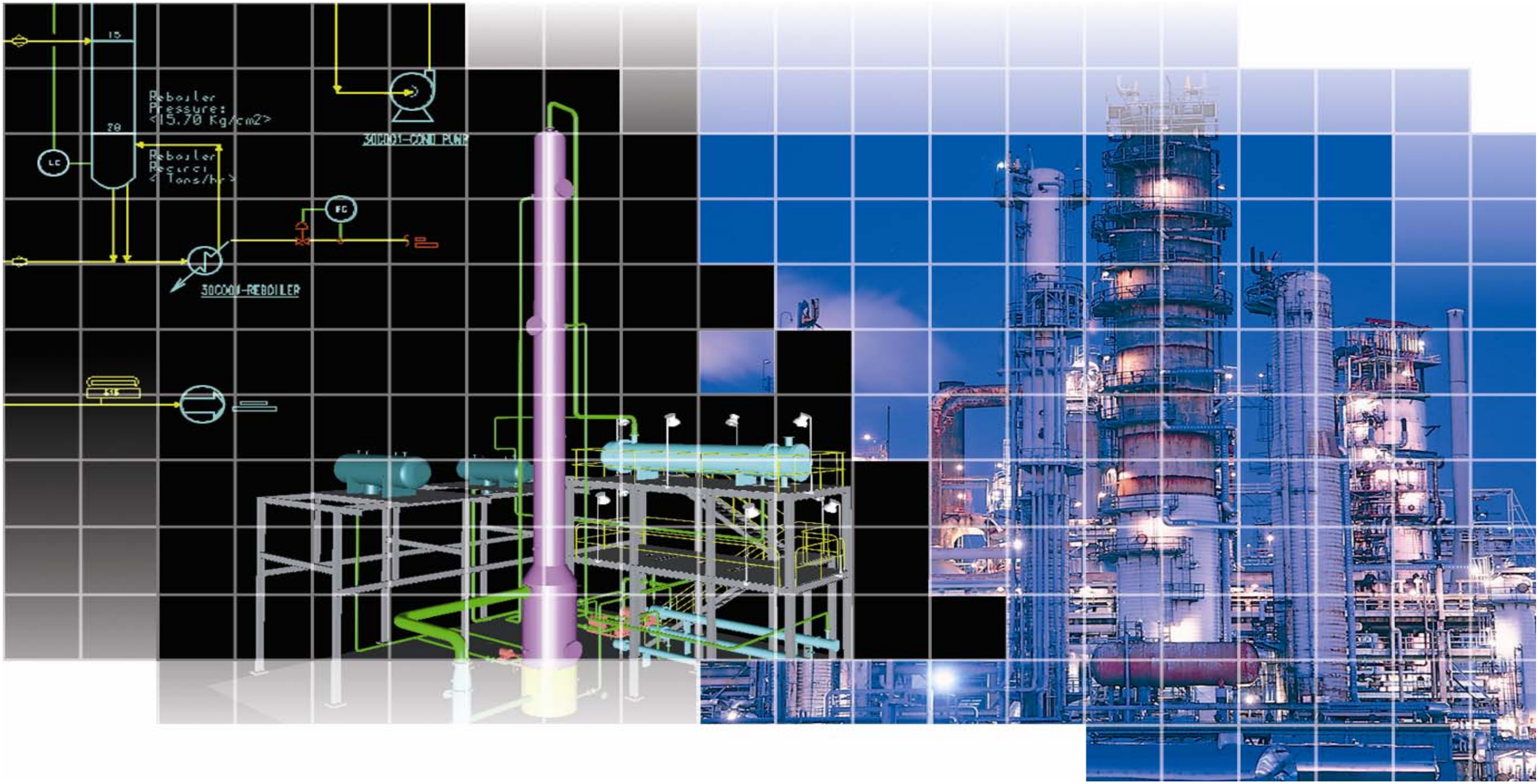


Refining Operations

5. **Other Refining Operations** include: light-ends recovery; sour-water stripping; solid waste and wastewater treatment; process-water treatment and cooling; storage and handling; product movement; hydrogen production; acid and tail-gas treatment; and sulfur recovery.

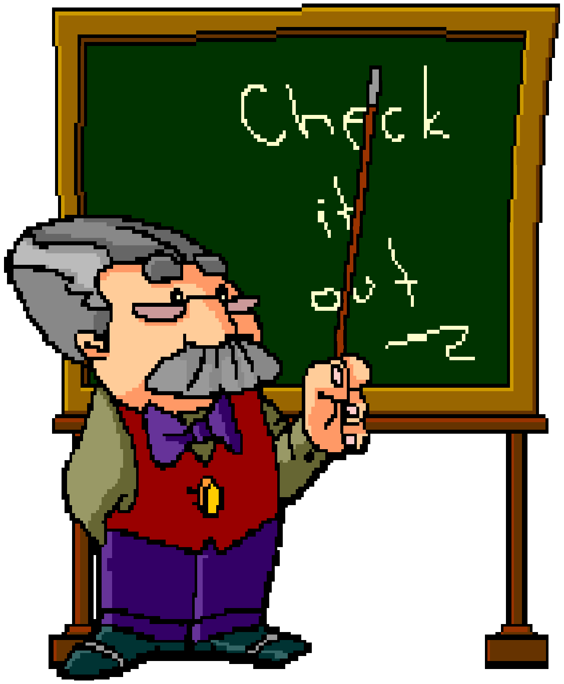
Refinery Process Chart



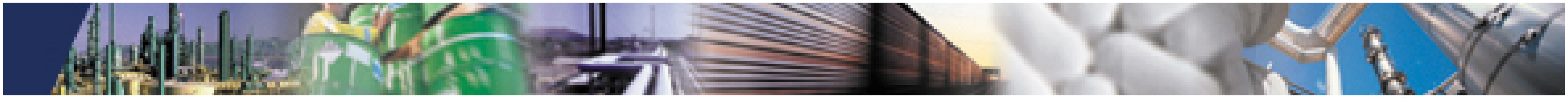


Chapter 14
Fractionation Processes

Outline

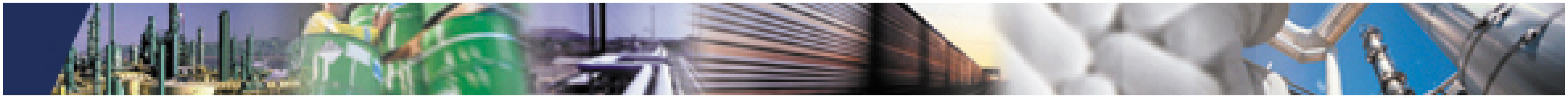


- Atmospheric Distillation
- Vacuum Distillation



Introduction

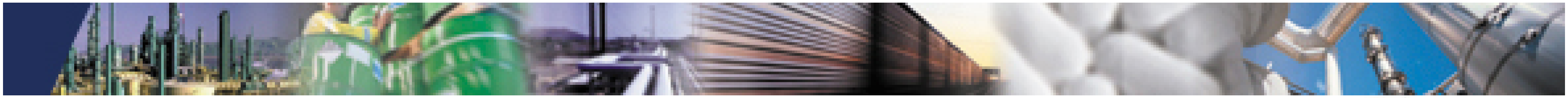
- The first step in the refining process is the separation of crude oil into various fractions or straight-run cuts by distillation in atmospheric and vacuum towers.
- The main fractions or “cuts” obtained have specific boiling-point ranges and can be classified in order of descreasing volatility into gases, light distillates, middle distillates, gas oils, and residuum.



Atmospheric Distillation Tower

Process Control & Safety

- At the refinery, the desalted crude feedstock is preheated using recovered process heat.
- The feedstock then flows to a direct-fired crude charge heater where it is fed into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 650 to 700 ^{o}F (heating crude oil above these temperatures may cause undesirable thermal cracking).
- All but the heaviest fractions flash into vapor.
- As the hot vapor rises in the tower, its temperature is reduced.
- Heavy fuel oil or asphalt residue is taken from the bottom.
- As successively higher points on the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off.

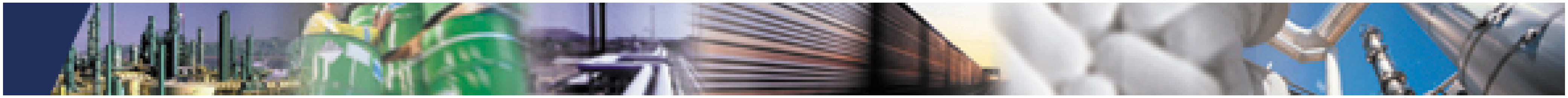


Atmospheric Distillation Tower

- The fractionating tower, a steel cylinder about 120 feet high, contains horizontal steel trays for separating and collecting the liquids.
- At each tray, vapors from below enter perforations and bubble caps.
- They permit the vapors to bubble through the liquid on the tray, causing some condensation at the temperature of that tray.
- An overflow pipe drains the condensed liquids from each tray back to the tray below, where the higher temperature causes re-evaporation.
- The evaporation, condensing, and scrubbing operation is repeated many times until the desired degree of product purity is reached.
- Then side streams from certain trays are taken off to obtain the desired fractions.

Atmospheric Distillation Tower

- Products ranging from uncondensed fixed gases at the top to heavy fuel oils at the bottom can be taken continuously from a fractionating tower.
- Steam is often used in towers to lower the vapor pressure and create a partial vacuum.
- The distillation process separates the major constituents of crude oil into so-called straight-run products.
- Sometimes crude oil is "topped" by distilling off only the lighter fractions, leaving a heavy residue that is often distilled further under high vacuum.

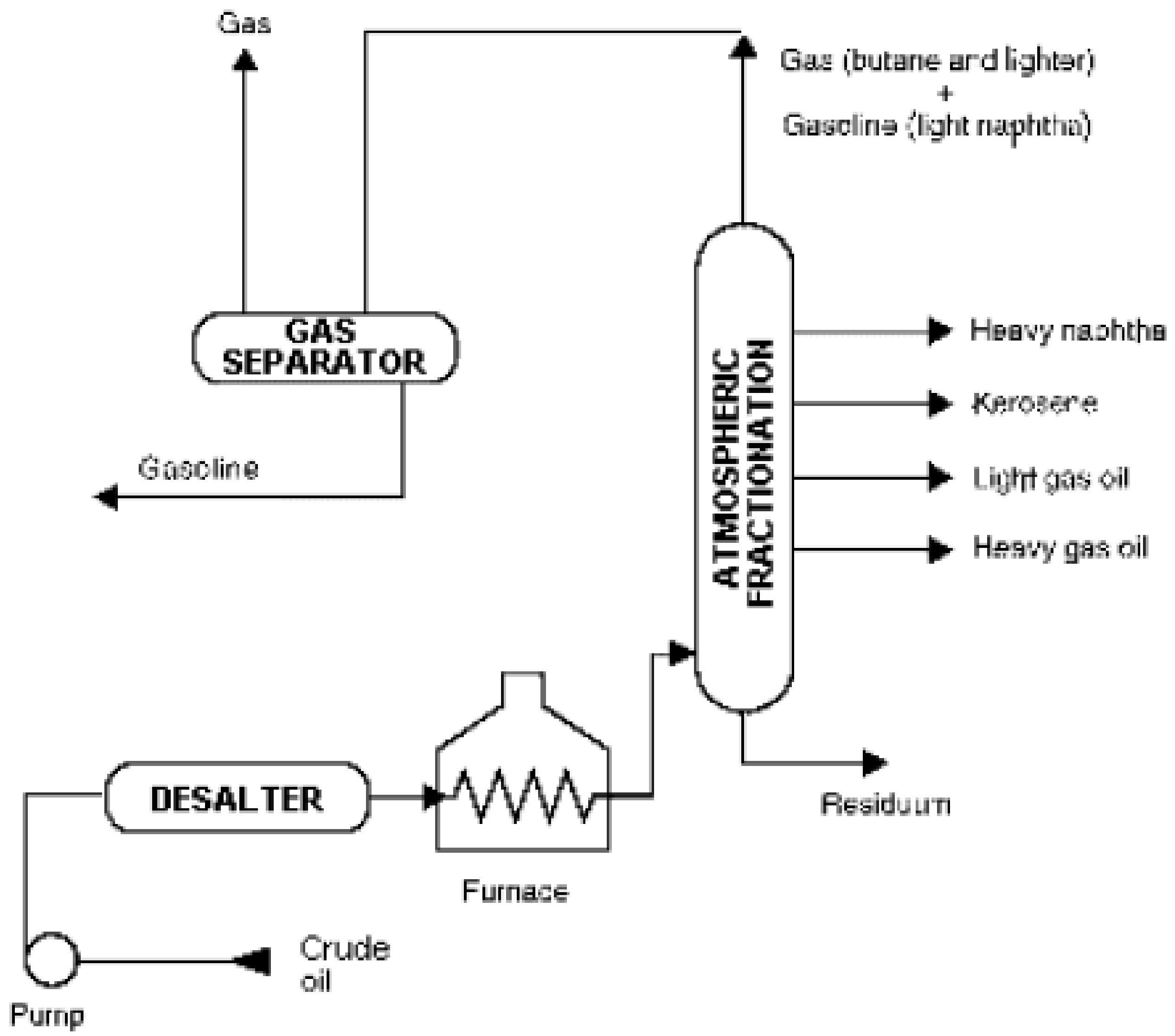


Atmospheric Distillation Tower

Table 1: Atmospheric Distillation Process

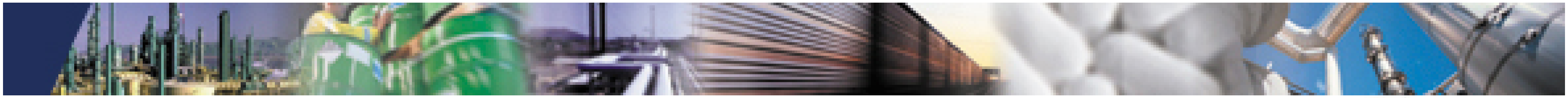
Feedstock	From	Process	Typical products . . . . . . To
Crude	Desalting	Separation	Gases…………………Gas Separator
			Naphthas……………..Reforming or treating
			Kerosene or distillates…Treating
			Gas oil…………………Catalytic cracking
			Residual………………..Vacuum tower or visbreaker

Atmospheric Distillation Tower



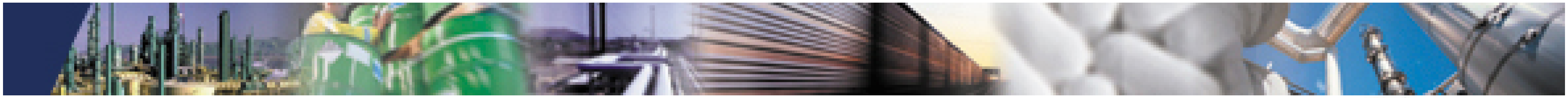
Vacuum Distillation Tower

- In order to further distill the residuum or topped crude from the atmospheric tower at higher temperatures, reduced pressure is required to prevent thermal cracking.
- The process takes place in one or more vacuum distillation towers.
- The principles of vacuum distillation resemble those of fractional distillation and, except that larger-diameter columns are used to maintain comparable vapor velocities at the reduced pressures, the equipment is also similar.
- The internal designs of some vacuum towers are different from atmospheric towers in that random packing and demister pads are used instead of trays.
- A typical first-phase vacuum tower may produce gas oils, lubricating-oil base stocks, and heavy residual for propane deasphalting.



Vacuum Distillation Tower

- A second-phase tower operating at lower vacuum may distill surplus residuum from the atmospheric tower, which is not used for lube-stock processing, and surplus residuum from the first vacuum tower not used for deasphalting.
- Vacuum towers are typically used to separate catalytic cracking feedstock from surplus residuum.

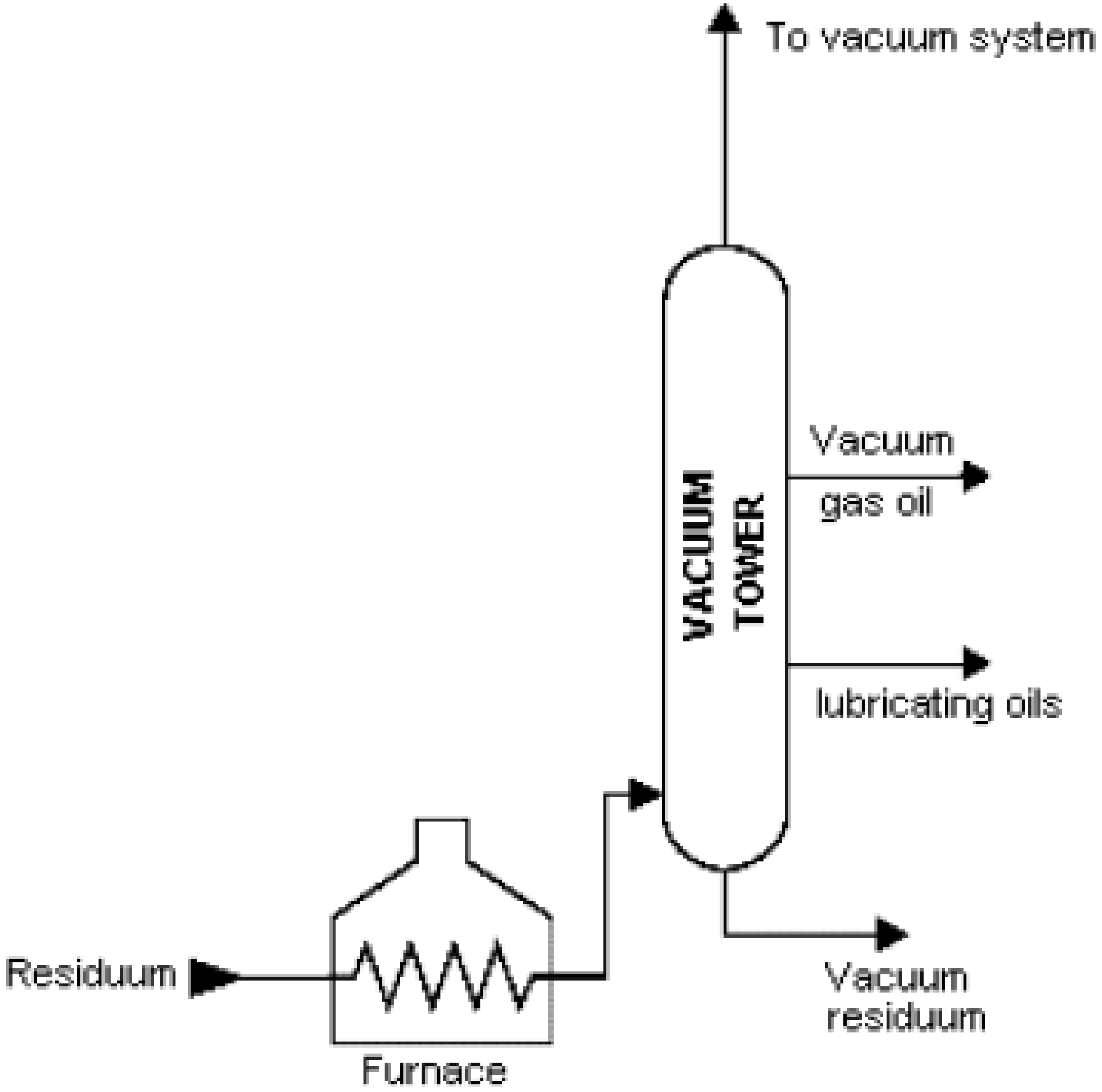


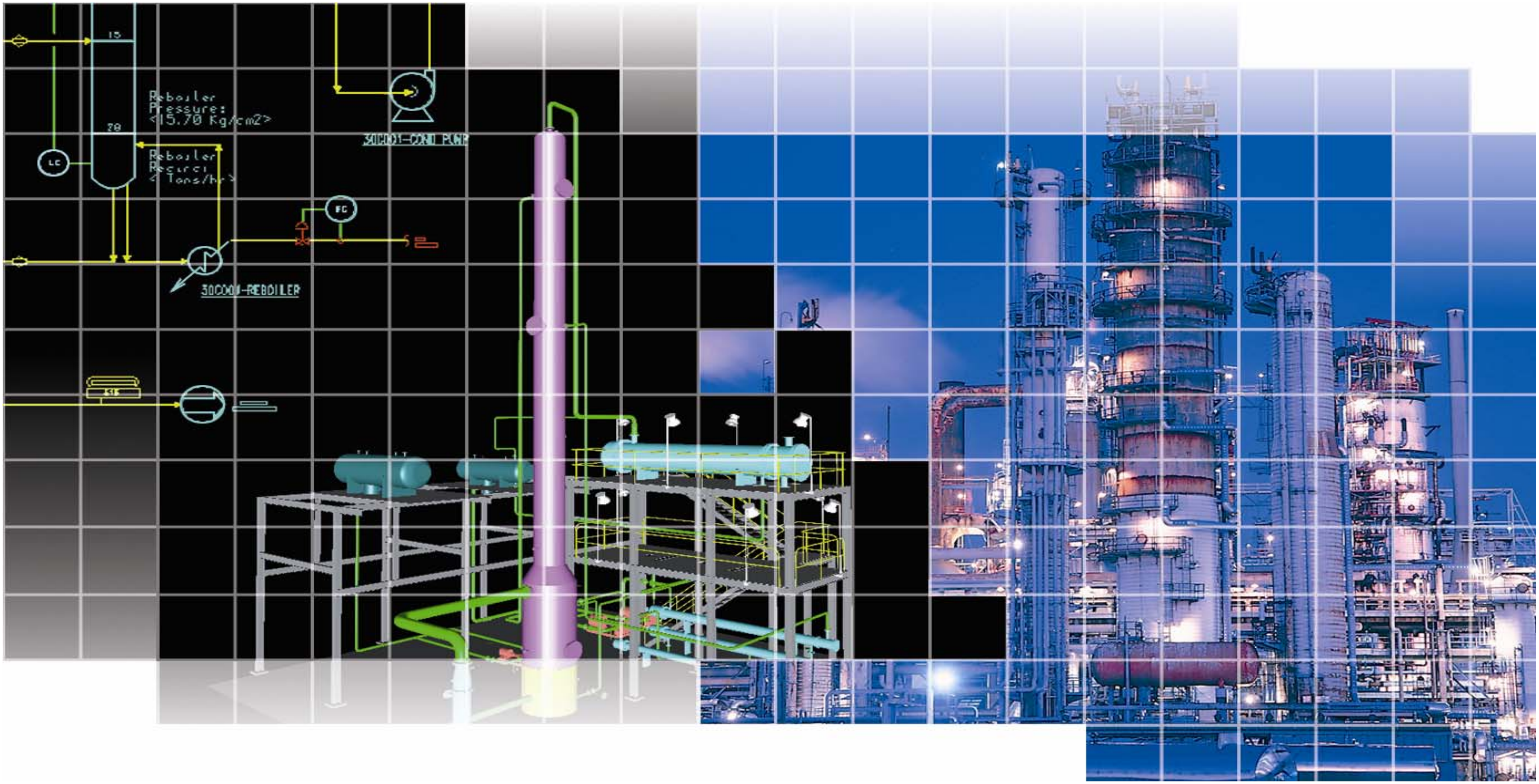
Vacuum Distillation Tower

Table 2: Vacuum Distillation Process

Feedstock	**From**	**Process**	**Typical products . . To**
Residuals	Atmospheric tower	Separation	Gas oils………..Catalytic cracker
			Lubricants……...Hydrotreating or solvent
			Residual………..Deasphalter, visbreaker, or coker

Vacuum Distillation Tower

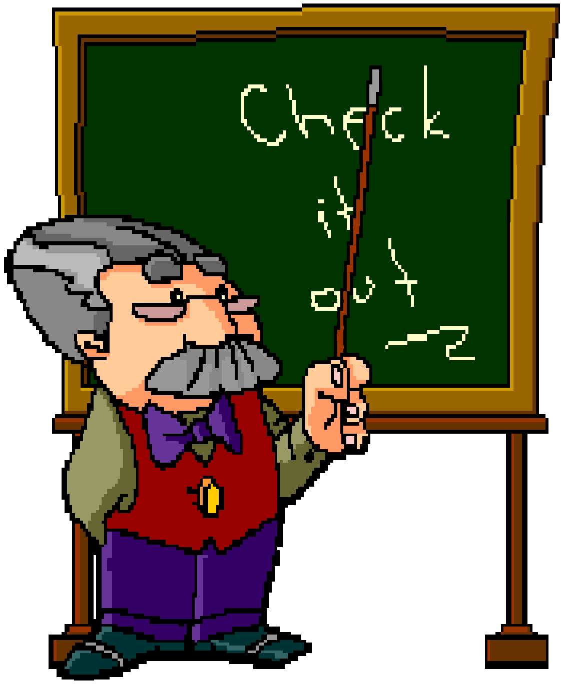




Chapter 15

Conversion Processes - Decomposition

Outline



- Thermal Cracking
  - Visbreaking, Steam Cracking, Coking
- Catalytic Cracking
  - FCC, MBCC, TCC
- Hydrocracking
- Hydrogen Production

Thermal Cracking

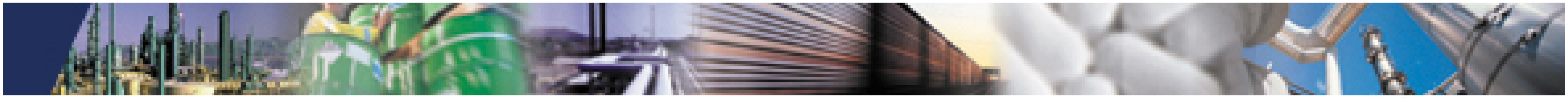
- Because the simple distillation of crude oil produces amounts and types of products that are not consistent with those required by the marketplace, subsequent refinery processes change the product mix by altering the molecular structure of the hydrocarbons.
- One of the ways of accomplishing this change is through "cracking," a process that breaks or cracks the heavier, higher boiling-point petroleum fractions into more valuable products such as gasoline, fuel oil, and gas oils.
- The two basic types of cracking are thermal cracking, using heat and pressure, and catalytic cracking.

Thermal Cracking

- The first thermal cracking process was developed around 1913.
- Distillate fuels and heavy oils were heated under pressure in large drums until they cracked into smaller molecules with better antiknock characteristics.
- However, this method produced large amounts of solid, unwanted coke.
- This early process has evolved into the following applications of thermal cracking: visbreaking, steam cracking, and coking.

Visbreaking

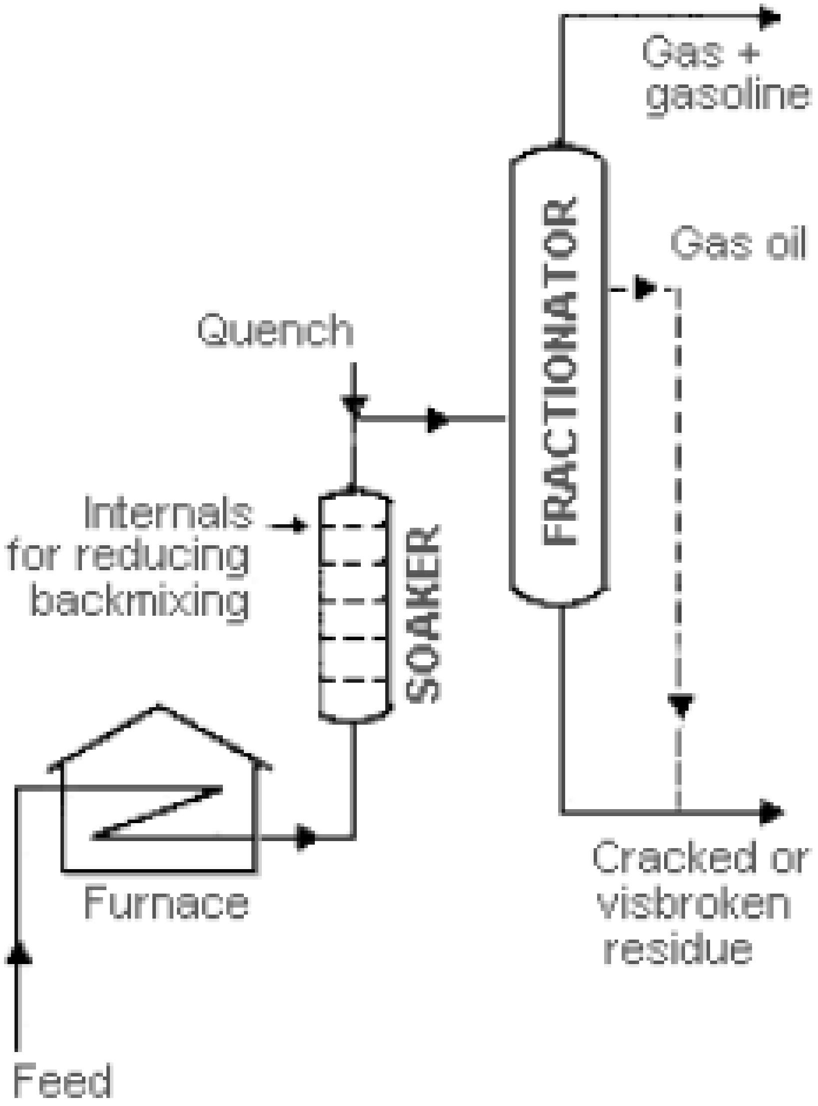
- Visbreaking, a mild form of thermal cracking, significantly lowers the viscosity of heavy crude-oil residue without affecting the boiling point range.
- Residual from the atmospheric distillation tower is heated (800°-950° F) at atmospheric pressure and mildly cracked in a heater.
- It is then quenched with cool gas oil to control overcracking, and flashed in a distillation tower.
- Middle distillates may also be produced, depending on product demand.
- The thermally cracked residue tar, which accumulates in the bottom of the fractionation tower, is vacuum flashed in a stripper and the distillate recycled.



Visbreaking

Feedstock	From	Process	Typical products . . . . . To
Residual	Atmospheric tower & Vacuum tower	Decompose	Gasoline or distillate…..Hydrotreating Vapor…………………..Hydrotreater Residue………………..Stripper or recycle Gases…………………Gas plant

Visbreaking

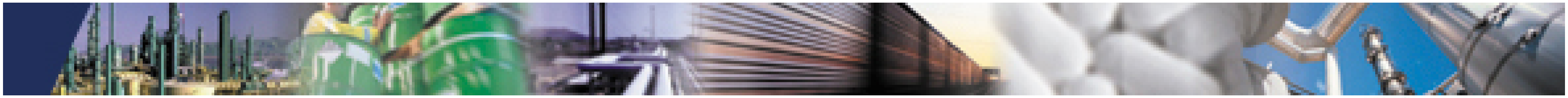


Steam Cracking

- Steam cracking is a petrochemical process sometimes used in refineries to produce olefinic raw materials (e.g., ethylene) from various feedstock for petrochemicals manufacture.
- The feedstock range from ethane to vacuum gas oil, with heavier feeds giving higher yields of by-products such as naphtha.
- The most common feeds are ethane, butane, and naphtha.
- Steam cracking is carried out at temperatures of 1,500°-1,600° F, and at pressures slightly above atmospheric.
- Naphtha produced from steam cracking contains benzene, which is extracted prior to hydrotreating.
- Residual from steam cracking is sometimes blended into heavy fuels.

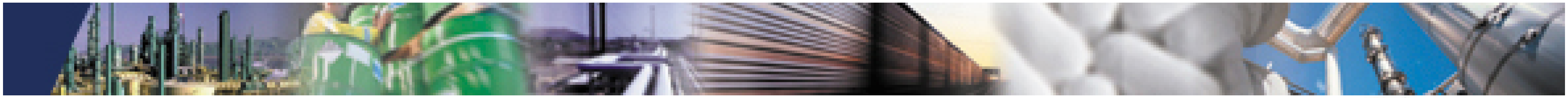
Coking

- Coking is a severe method of thermal cracking used to upgrade heavy residuals into lighter products or distillates.
- Coking produces straight-run gasoline (coker naphtha) and various middle-distillate fractions used as catalytic cracking feedstock.
- The process so completely reduces hydrogen that the residue is a form of carbon called "coke."
- The two most common processes are delayed coking and continuous (contact or fluid) coking.
- Three typical types of coke are obtained (sponge coke, honeycomb coke, and needle coke) depending upon the reaction mechanism, time, temperature, and the crude feedstock.



Coking

Feedstock	From	Process	Typical products . . . To
Residual……..	Atmospheric & vacuum catalytic cracker	Decomposition	Naphtha, gasoline….Distillation column,blending
Clarified oil…	Catalytic cracker		Coke………………..Shipping, recycle Gas oil……………..Catalytic cracking
Tars…………	Various units		
Wastewater (sour)………..	Treatment		
Gases………..	Gas plant		



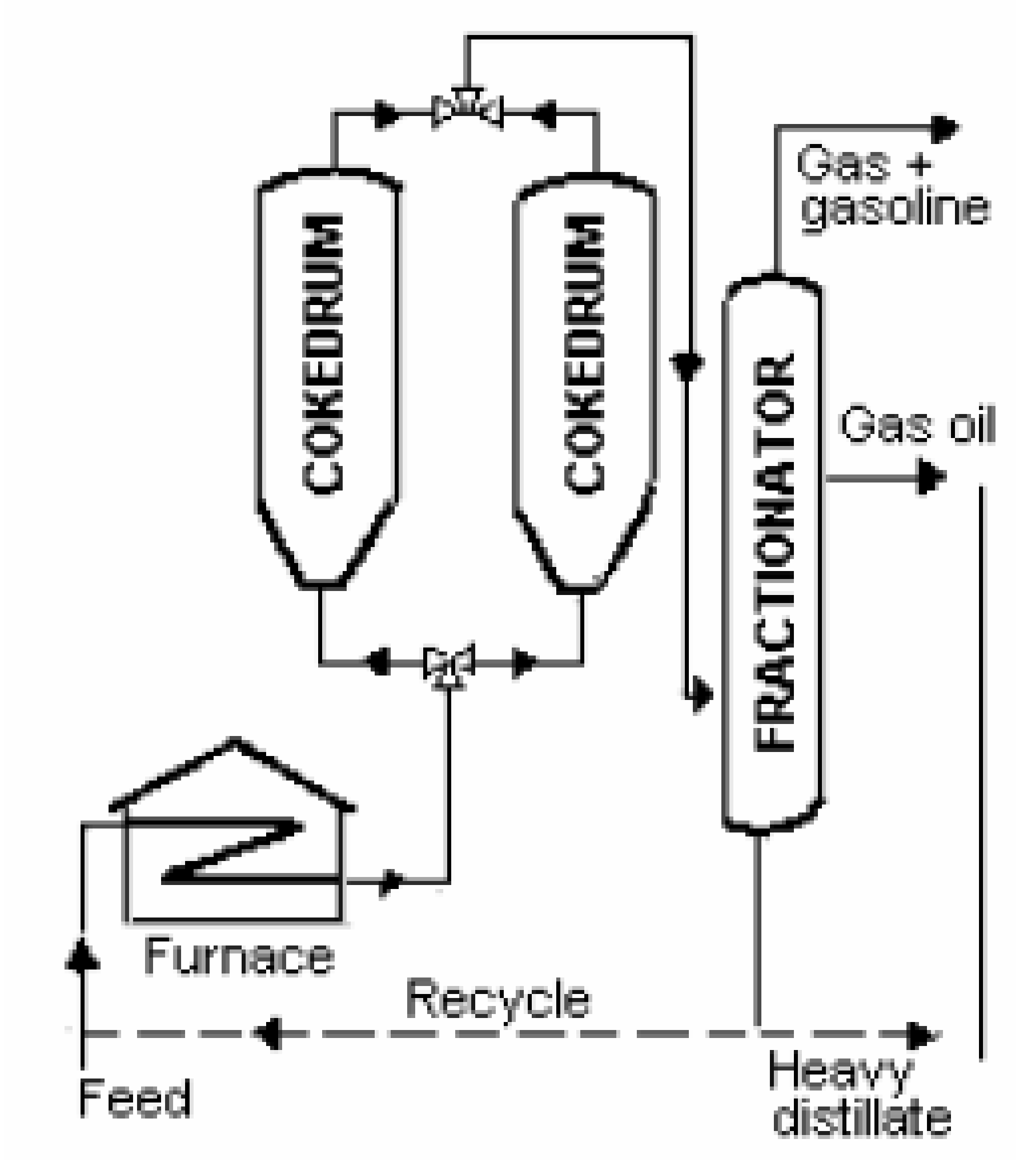
Delayed Coking

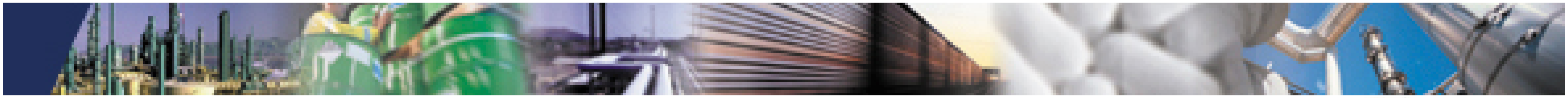
- In delayed coking the heated charge (typically residuum from atmospheric distillation towers) is transferred to large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion.
- Initially the heavy feedstock is fed to a furnace which heats the residuum to high temperatures (900°-950° F) at low pressures (25-30 psi) and is designed and controlled to prevent premature coking in the heater tubes.
- The mixture is passed from the heater to one or more coker drums where the hot material is held approximately 24 hours (delayed) at pressures of 25-75 psi, until it cracks into lighter products.

Delayed Coking

- Vapors from the drums are returned to a fractionator where gas, naphtha, and gas oils are separated out.
- The heavier hydrocarbons produced in the fractionator are recycled through the furnace.
- After the coke reaches a predetermined level in one drum, the flow is diverted to another drum to maintain continuous operation.
- The full drum is steamed to strip out uncracked hydrocarbons, cooled by water injection, and decoked by mechanical or hydraulic methods.
- The coke is mechanically removed by an auger rising from the bottom of the drum.
- Hydraulic decoking consists of fracturing the coke bed with high-pressure water ejected from a rotating cutter.

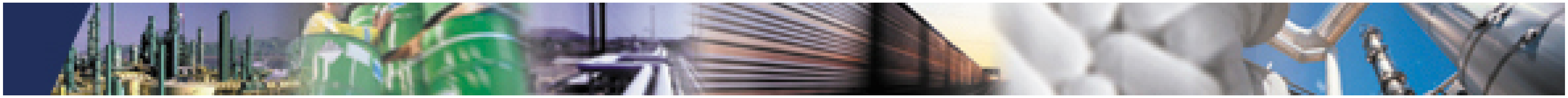
Delayed Coking





Continuous Coking

- Continuous (contact or fluid) coking is a moving-bed process that operates at temperatures higher than delayed coking.
- In continuous coking, thermal cracking occurs by using heat transferred from hot, recycled coke particles to feedstock in a radial mixer, called a reactor, at a pressure of 50 psi.
- Gases and vapors are taken from the reactor, quenched to stop any further reaction, and fractionated.
- The reacted coke enters a surge drum and is lifted to a feeder and classifier where the larger coke particles are removed as product.
- The remaining coke is dropped into the preheater for recycling with feedstock. Coking occurs both in the reactor and in the surge drum.
- The process is automatic in that there is a continuous flow of coke and feedstock.

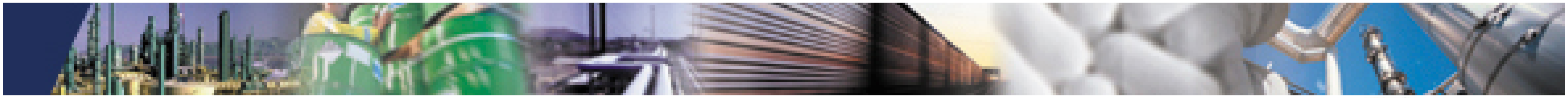


Catalytic Cracking

- Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals.
- This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, LPG, heating oil, and petrochemical feedstock.
- Catalytic cracking is similar to thermal cracking except that catalysts facilitate the conversion of the heavier molecules into lighter products.
- Use of a catalyst (a material that assists a chemical reaction but does not take part in it) in the cracking reaction increases the yield of improved-quality products under much less severe operating conditions than in thermal cracking.

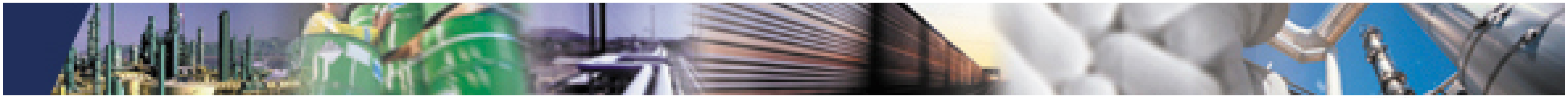
Catalytic Cracking

- Typical temperatures are from 850°-950° F at much lower pressures of 10-20 psi.
- The catalysts used in refinery cracking units are typically solid materials (zeolite, aluminum hydrosilicate, treated bentonite clay, fuller's earth, bauxite, and silica-alumina) that come in the form of powders, beads, pellets or shaped materials called extrudites.
- There are three basic functions in the catalytic cracking process:
  - Reaction: Feedstock reacts with catalyst and cracks into different hydrocarbons;
  - Regeneration: Catalyst is reactivated by burning off coke; and
  - Fractionation: Cracked hydrocarbon stream is separated into various products.



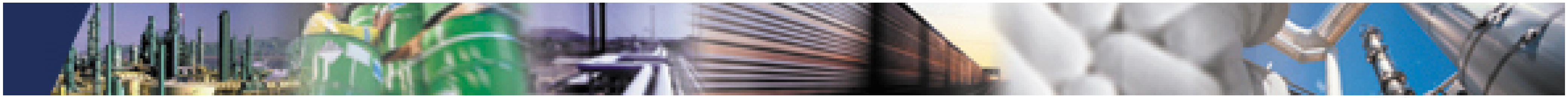
Catalytic Cracking

- The three types of catalytic cracking processes:
  - Fluid Catalytic Cracking (FCC),
  - Moving-Bed Catalytic Cracking, and
  - Thermofor Catalytic Cracking (TCC).
- The catalytic cracking process is very flexible, and operating parameters can be adjusted to meet changing product demand.
- In addition to cracking, catalytic activities include dehydrogenation, hydrogenation, and isomerization.



Catalytic Cracking

Feedstock	From	Process	Typical products . . . . To
Gas oils	Towers, coker visbreaker	Decomposition, alteration	Gasoline…………….Treater or blend Gases………………..Gas plant
Deasphalted oils	Deasphalter		Middle distillates……Hydrotreat, blend, or recycle Petrochem feedstock…Petrochem or other Residue………………Residual fuel blend

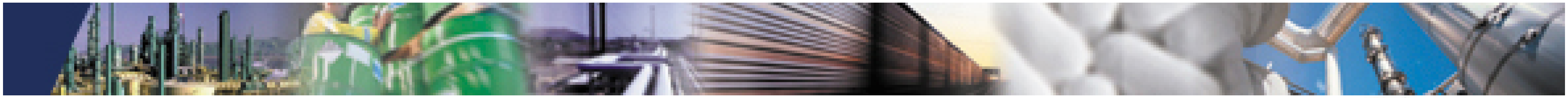


Fluid Catalytic Cracking

- The most common process is FCC, in which the oil is cracked in the presence of a finely divided catalyst which is maintained in an aerated or fluidized state by the oil vapors.
- The fluid cracker consists of a catalyst section and a fractionating section that operate together as an integrated processing unit.
- The catalyst section contains the reactor and regenerator, which, with the standpipe and riser, forms the catalyst circulation unit.
- The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media.
- A typical FCC process involves mixing a preheated hydrocarbon charge with hot, regenerated catalyst as it enters the riser leading to the reactor.

Fluid Catalytic Cracking

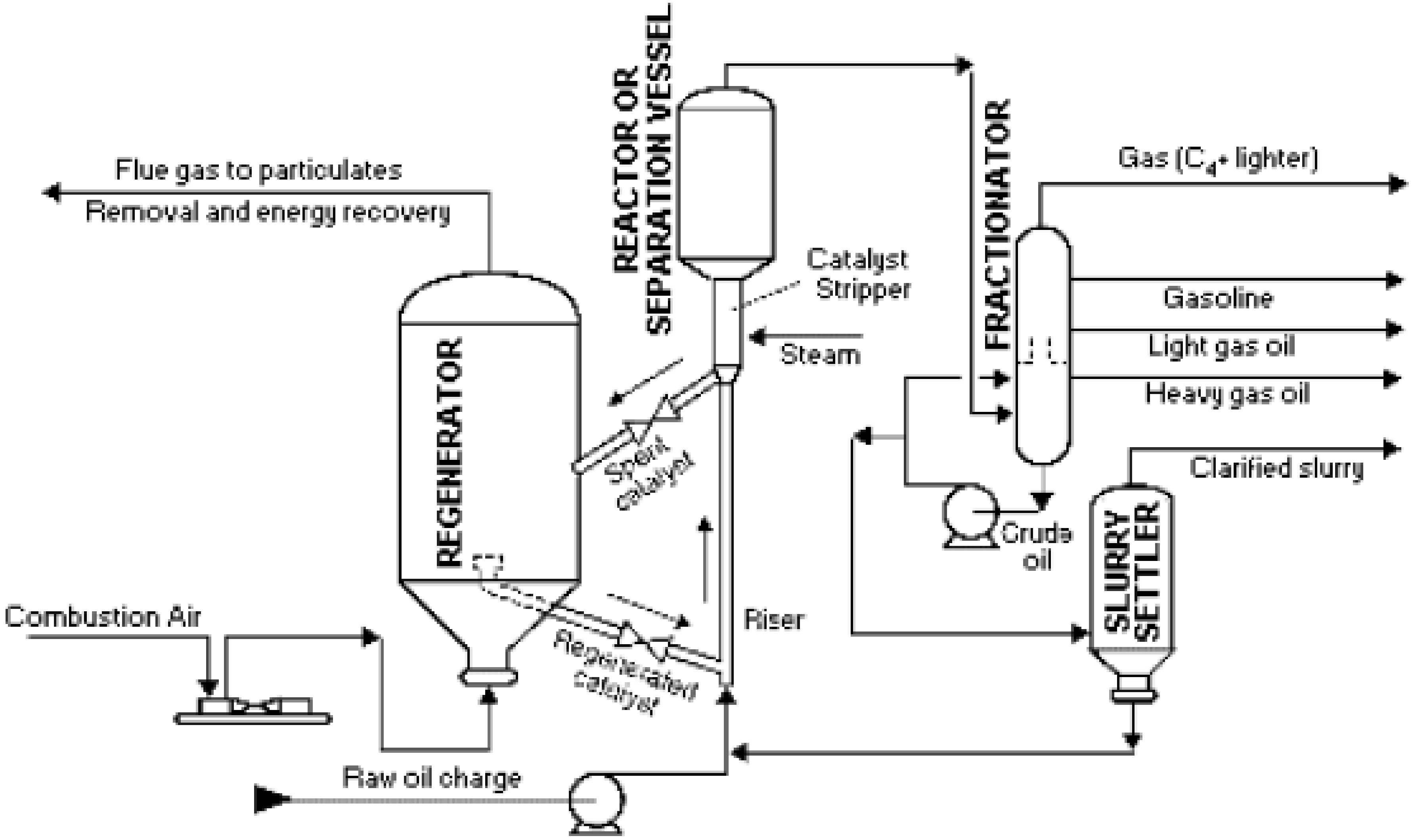
- The charge is combined with a recycle stream within the riser, vaporized, and raised to reactor temperature (900°-1,000° F) by the hot catalyst.
- As the mixture travels up the riser, the charge is cracked at 10-30 psi. In the more modern FCC units, all cracking takes place in the riser.
- The "reactor" no longer functions as a reactor; it merely serves as a holding vessel for the cyclones.
- This cracking continues until the oil vapors are separated from the catalyst in the reactor cyclones.
- The resultant product stream (cracked product) is then charged to a fractionating column where it is separated into fractions, and some of the heavy oil is recycled to the riser.



Fluid Catalytic Cracking

- Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process.
- Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed.
- Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.

Fluid Catalytic Cracking

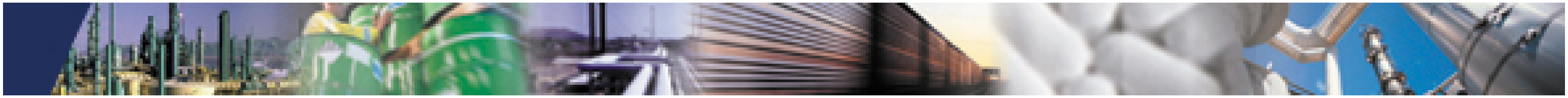


Moving-Bed Catalytic Cracking

- The moving-bed catalytic cracking process is similar to the FCC process.
- The catalyst is in the form of pellets that are moved continuously to the top of the unit by conveyor or pneumatic lift tubes to a storage hopper, then flow downward by gravity through the reactor, and finally to a regenerator.
- The regenerator and hopper are isolated from the reactor by steam seals.
- The cracked product is separated into recycle gas, oil, clarified oil, distillate, naphtha, and wet gas.

Thermofor Catalytic Cracking

- In a typical thermofor catalytic cracking unit, the preheated feedstock flows by gravity through the catalytic reactor bed.
- The vapors are separated from the catalyst and sent to a fractionating tower.
- The spent catalyst is regenerated, cooled, and recycled.
- The flue gas from regeneration is sent to a carbon-monoxide boiler for heat recovery.

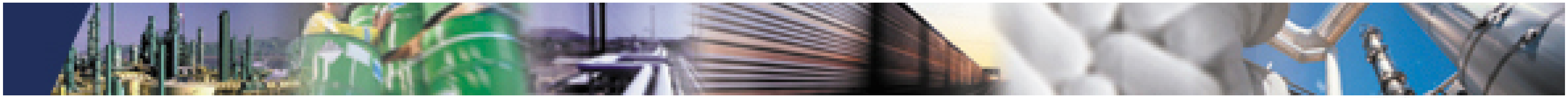


Hydrocracking

- Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feedstocks are cracked in the presence of hydrogen to produce more desirable products.
- The process employs high pressure, high temperature, a catalyst, and hydrogen.
- Hydrocracking is used for feedstocks that are difficult to process by either catalytic cracking or reforming, since these feedstocks are characterized usually by a high polycyclic aromatic content and/or high concentrations of the two principal catalyst poisons, sulfur and nitrogen compounds.
- The hydrocracking process largely depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking.

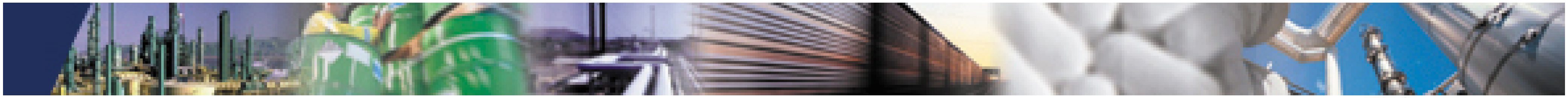
Hydrocracking

- Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (1,000-2,000 psi) and fairly high temperatures (750°-1,500° F), in the presence of hydrogen and special catalysts.
- When the feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds.
- Another important role of hydrogen in the hydrocracking process is to reduce tar formation and prevent buildup of coke on the catalyst.
- Hydrogenation also serves to convert sulfur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia.
- Hydrocracking produces relatively large amounts of isobutane for alkylation feedstock.



Hydrocracking

- In the first stage, preheated feedstock is mixed with recycled hydrogen and sent to the first-stage reactor, where catalysts convert sulfur and nitrogen compounds to hydrogen sulfide and ammonia.
- Limited hydrocracking also occurs.
- After the hydrocarbon leaves the first stage, it is cooled and liquefied and run through a hydrocarbon separator.
- The hydrogen is recycled to the feedstock. The liquid is charged to a fractionator.
- Depending on the products desired (gasoline components, jet fuel, and gas oil), the fractionator is run to cut out some portion of the first stage reactor out-turn.
- Kerosene-range material can be taken as a separate side-draw product or included in the fractionator bottoms with the gas oil.



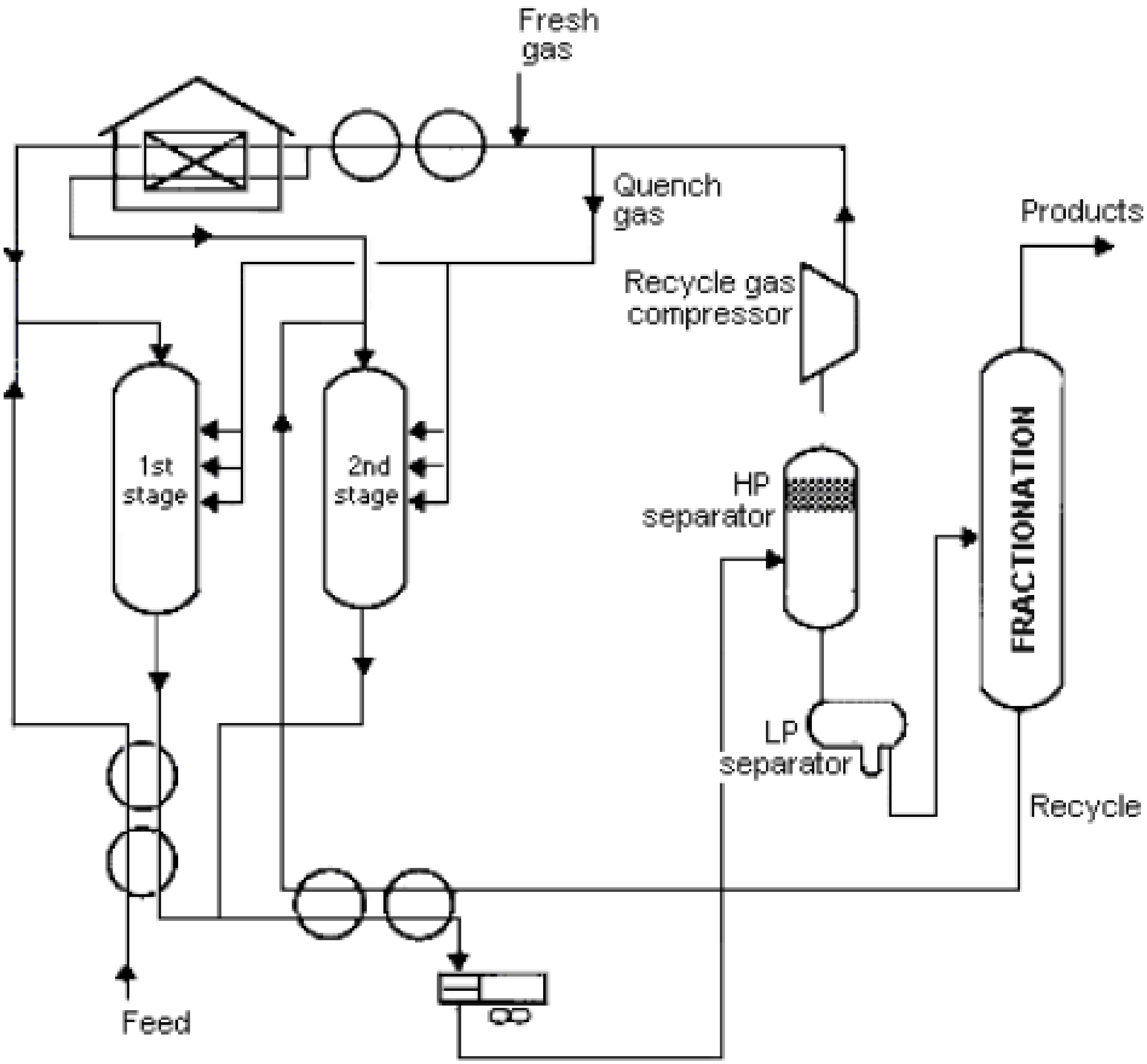
Hydrocracking

- The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage.
- Since this material has already been subjected to some hydrogenation, cracking, and reforming in the first stage, the operations of the second stage are more severe (higher temperatures and pressures).
- Like the outturn of the first stage, the second stage product is separated from the hydrogen and charged to the fractionator.

Hydrocracking

Feedstock	From	Process	Typical products . . . . To
High pour point	Catalytic cracker, atmospheric & vacuum tower	Decomposition, hydrogenation	Kerosene, jet fuel…….Blending
Gas oil	Vacuum tower, coker		Gasoline, distillates…..Blending
Hydrogen	Reformer		Recycle, reformer gas...Gas plant

Hydrocracking

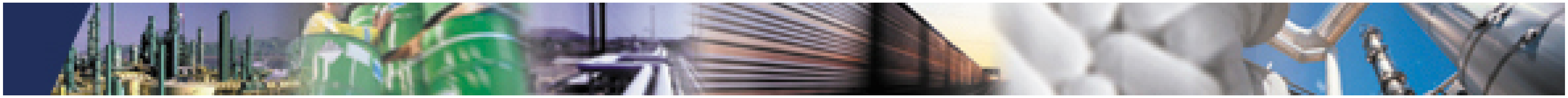


Hydrogen Production

- High-purity hydrogen (95%-99%) is required for hydrodesulfurization, hydrogenation, hydrocracking, and petrochemical processes.
- Hydrogen, produced as a by-product of refinery processes (principally hydrogen recovery from catalytic reformer product gases), often is not enough to meet the total refinery requirements, necessitating the manufacturing of additional hydrogen or obtaining supply from external sources.
- In steam-methane reforming, desulfurized gases are mixed with superheated steam (1,100°-1,600°F) and reformed in tubes containing a nickel base catalyst.
- The reformed gas, which consists of steam, hydrogen, carbon monoxide, and carbon dioxide, is cooled and passed through converters containing an iron catalyst where the carbon monoxide reacts with steam to form carbon dioxide and more hydrogen.

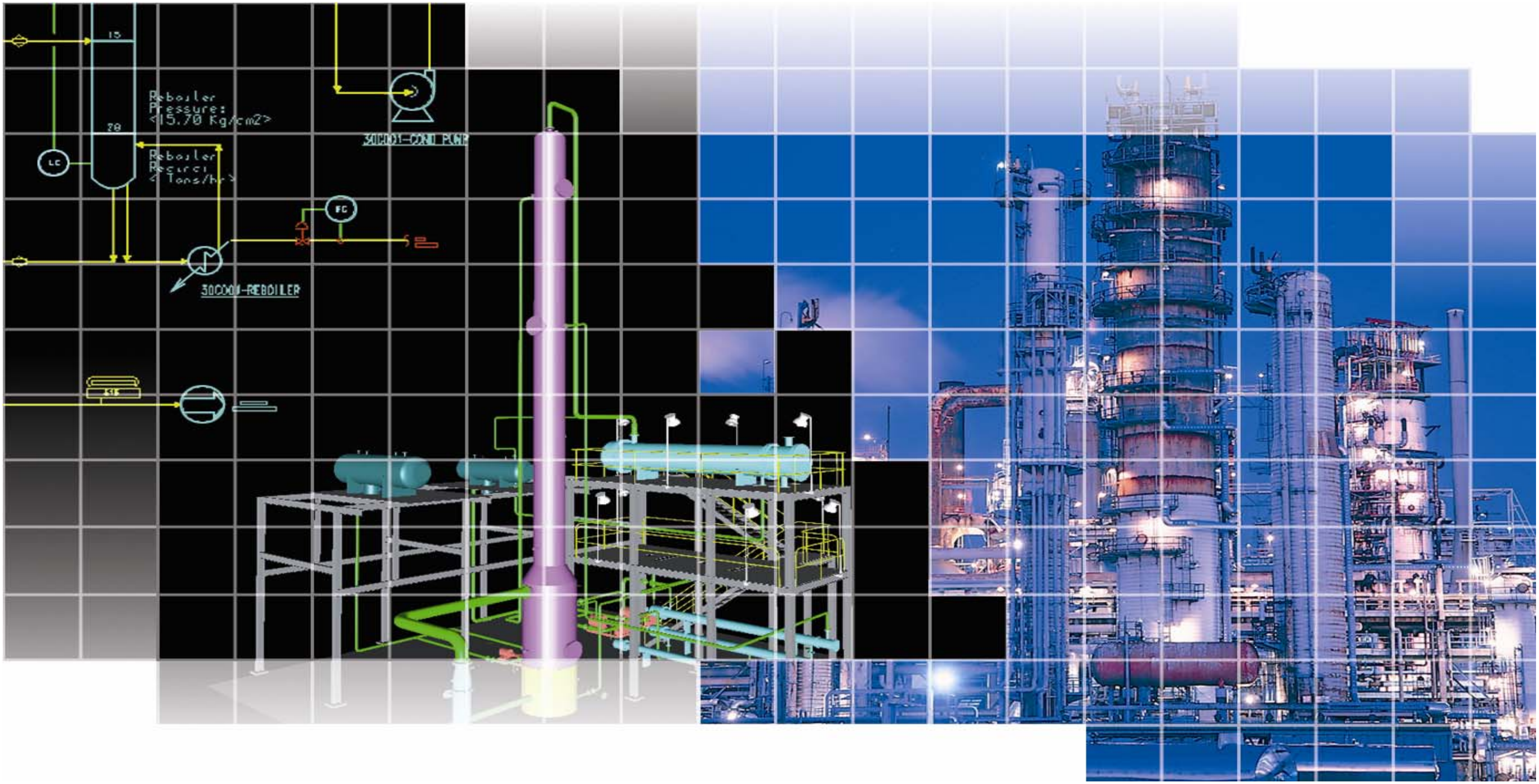
Hydrogen Production

- The carbon dioxide is removed by amine washing.
- Any remaining carbon monoxide in the product stream is converted to methane.
- Steam-naphtha reforming is a continuous process for the production of hydrogen from liquid hydrocarbons and is, in fact, similar to steam-methane reforming.
- A variety of naphthas in the gasoline boiling range may be employed, including fuel containing up to 35% aromatics.
- Following pretreatment to remove sulfur compounds, the feedstock is mixed with steam and taken to the reforming furnace (1,250°-1,500°F) where hydrogen is produced.

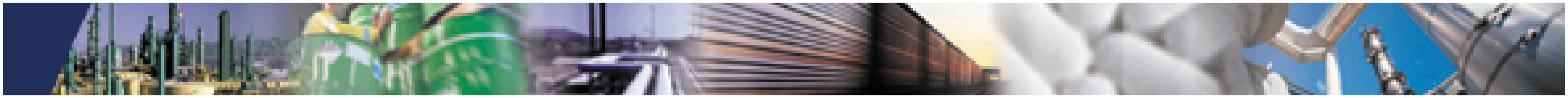


Hydrogen Production

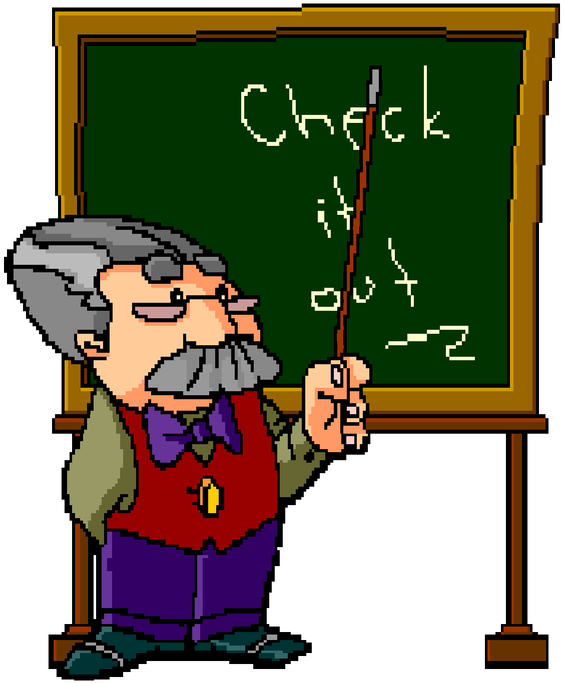
Feedstock	**From**	**Process**	**Typical products . . . To**
Desufurized refinery gas	Various treatment units	Decomposition	Hydrogen……………Processing Carbon dioxide………Atmosphere Carbon monoxide……Methane



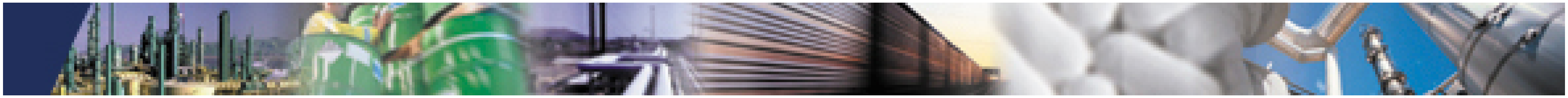
Chapter 16
Conversion Processes - Unification



Outline

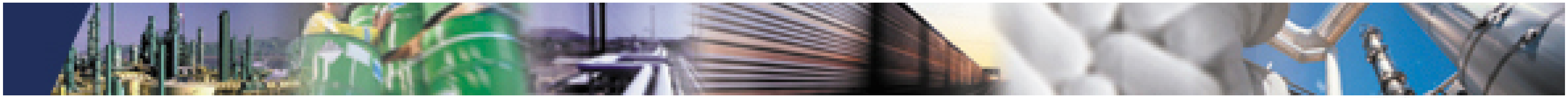


- Alkylation
- Polymerization
- Grease Compounding



Alkylation

- Alkylation combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with isobutene in the presence of a catalyst, either sulfuric acid or hydrofluoric acid.
- The product is called alkylate and is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons.
- Alkylate is a premium blending stock because it has exceptional antiknock properties and is clean burning.
- The octane number of the alkylate depends mainly upon the kind of olefins used and upon operating conditions.



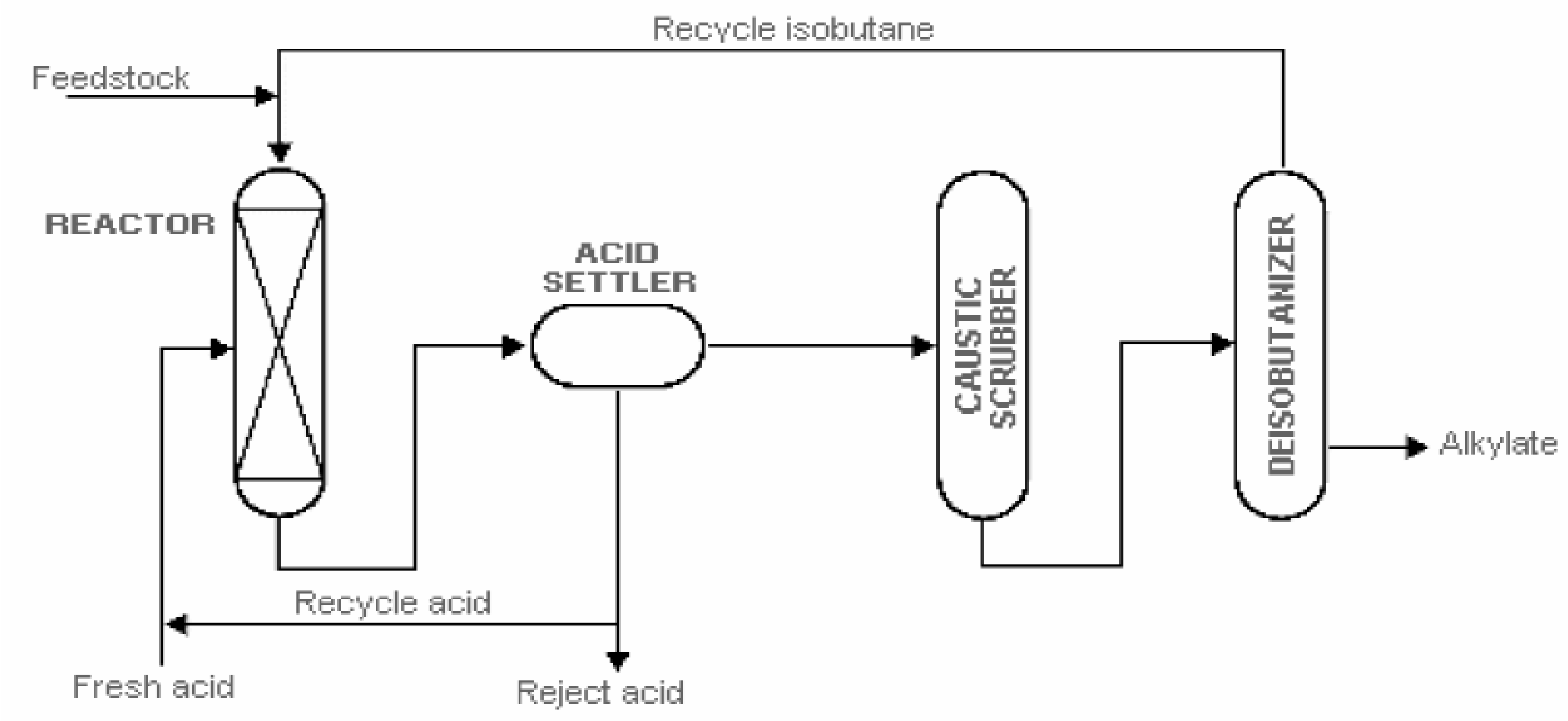
Alkylation

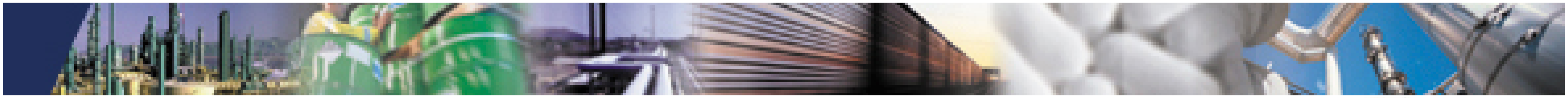
Feedstock	From	Process	Typical products . . . . To
Petroleum gas	Distillation or cracking	Unification	High octane gasoline…….Blending
Olefins	Cat. or hydro cracking		n-Butane & propane…….Stripper or blender
Isobutane	Isomerization		

Sulfuric Acid Alkylation

- In cascade type sulfuric acid (H_2SO_4) alkylation units, the feedstock (propylene, butylene, amylene, and fresh isobutane) enters the reactor and contacts the concentrated sulfuric acid catalyst (in concentrations of 85% to 95% for good operation and to minimize corrosion).
- The reactor is divided into zones, with olefins fed through distributors to each zone, and the sulfuric acid and isobutanes flowing over baffles from zone to zone.
- The reactor effluent is separated into hydrocarbon and acid phases in a settler, and the acid is returned to the reactor.
- The hydrocarbon phase is hot-water washed with caustic for pH control before being successively depropanized, deisobutanized, and debutanized.
- The alkylate obtained from the deisobutanizer can then go directly to motor-fuel blending or be rerun to produce aviation-grade blending stock.
- The isobutane is recycled to the feed.

Sulfuric Acid Alkylation



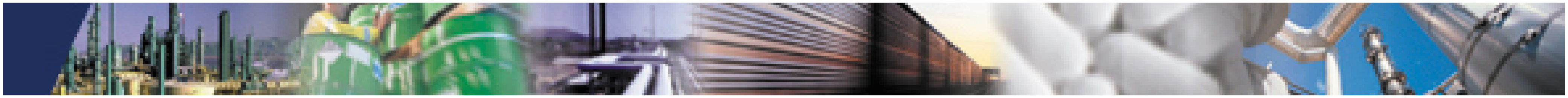


Hydrofluoric Alkylation

- Phillips and UOP are the two common types of hydrofluoric acid alkylation processes in use.
- In the Phillips process, olefin and isobutane feedstock are dried and fed to a combination reactor/settler system.
- Upon leaving the reaction zone, the reactor effluent flows to a settler (separating vessel) where the acid separates from the hydrocarbons.
- The acid layer at the bottom of the separating vessel is recycled.
- The top layer of hydrocarbons (hydrocarbon phase), consisting of propane, normal butane, alkylate, and excess (recycle) isobutane, is charged to the main fractionator, the bottom product of which is motor alkylate.
- The main fractionator overhead, consisting mainly of propane, isobutane, and HF, goes to a depropanizer.

Hydrofluoric Alkylation

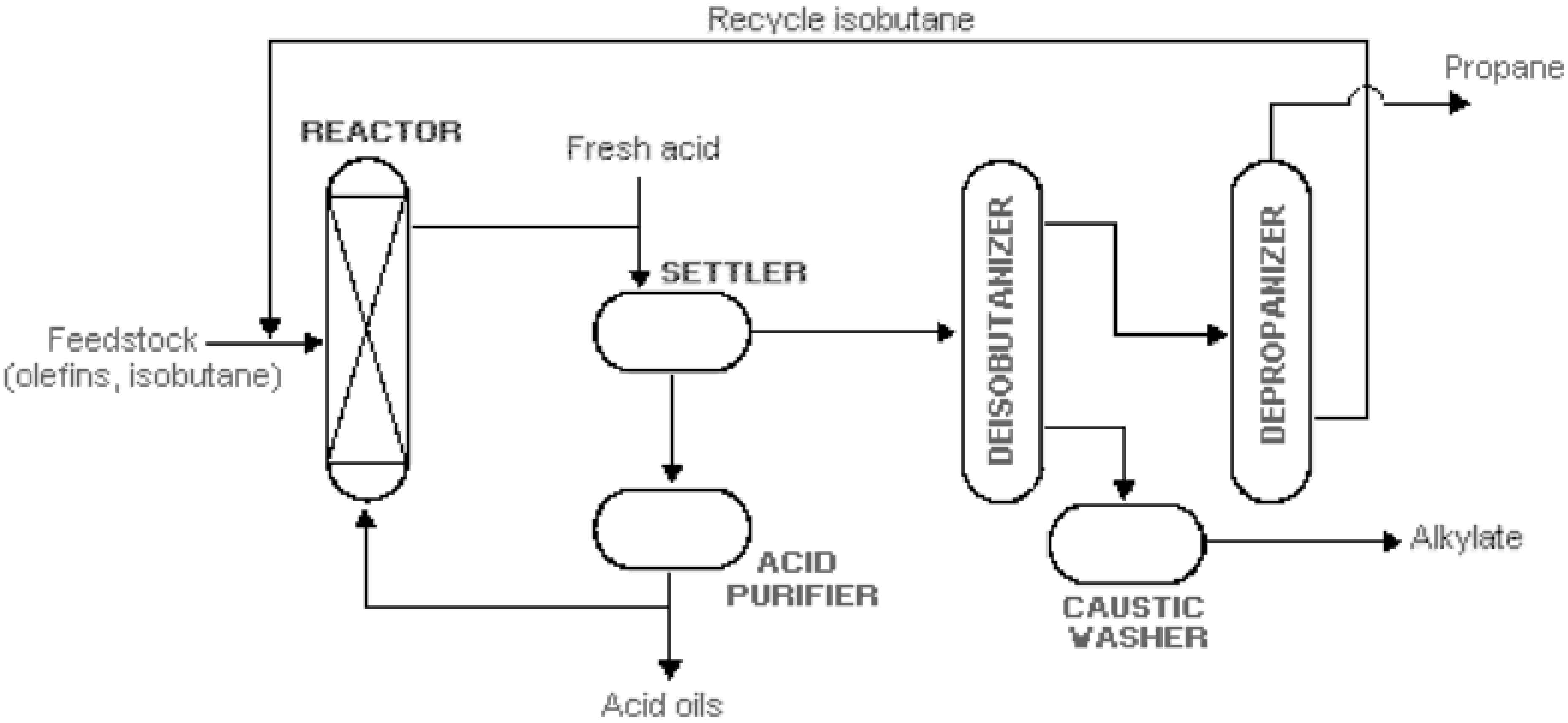
- Propane with trace amount of HF goes to an HF stripper for HF removal and is then catalytically defluorinated, treated, and sent to storage.
- Isobutane is withdrawn from the main fractionator and recycled to the reactor/settler, and alkylate from the bottom of the main fractionator is sent to product blending.
- The UOP process uses two reactors with separate settlers.
- Half of the dried feedstock is charged to the first reactor, along with recycle and makeup isobutane.
- The reactor effluent then goes to its settler, where the acid is recycled and the hydrocarbon charged to the second reactor.

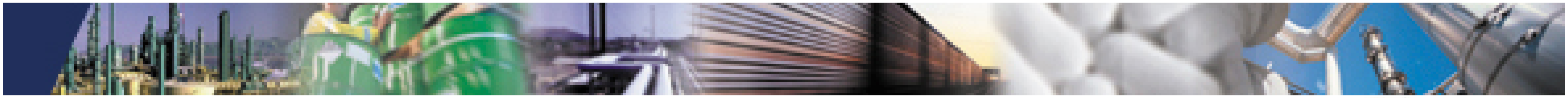


Hydrofluoric Alkylation

- The other half of the feedstock also goes to the second reactor, with the settler acid being recycled and the hydrocarbons charged to the main fractionator.
- Subsequent processing is similar to the Phillips process.
- Overhead from the main fractionator goes to a depropanizer.
- Isobutane is recycled to the reaction zone and alkylate is sent to product blending.

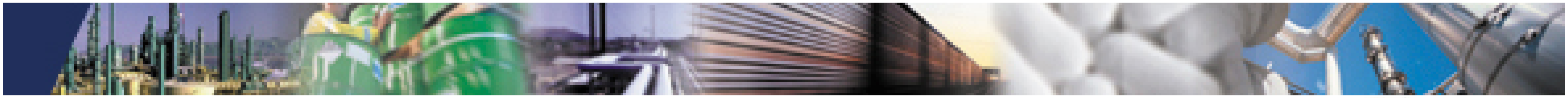
Hydrofluoric Alkylation





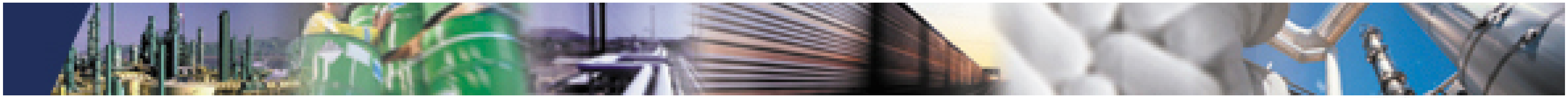
Polymerization

- Polymerization in the petroleum industry is the process of converting light olefin gases including ethylene, propylene, and butylene into hydrocarbons of higher molecular weight and higher octane number that can be used as gasoline blending stocks.
- Polymerization combines two or more identical olefin molecules to form a single molecule with the same elements in the same proportions as the original molecules.
- Polymerization may be accomplished thermally or in the presence of a catalyst at lower temperatures.
- The olefin feedstock is pretreated to remove sulfur and other undesirable compounds.



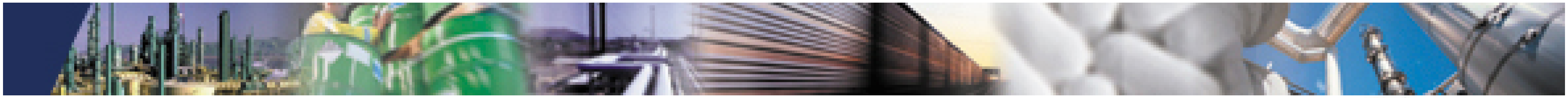
Polymerization

- In the catalytic process the feedstock is either passed over a solid phosphoric acid catalyst or comes in contact with liquid phosphoric acid, where an exothermic polymeric reaction occurs.
- This reaction requires cooling water and the injection of cold feedstock into the reactor to control temperatures between 300° and 450° F at pressures from 200 psi to 1,200 psi.
- The reaction products leaving the reactor are sent to stabilization and/or fractionator systems to separate saturated and unreacted gases from the polymer gasoline product.
- In the petroleum industry, polymerization is used to indicate the production of gasoline components, hence the term "polymer" gasoline.



Polymerization

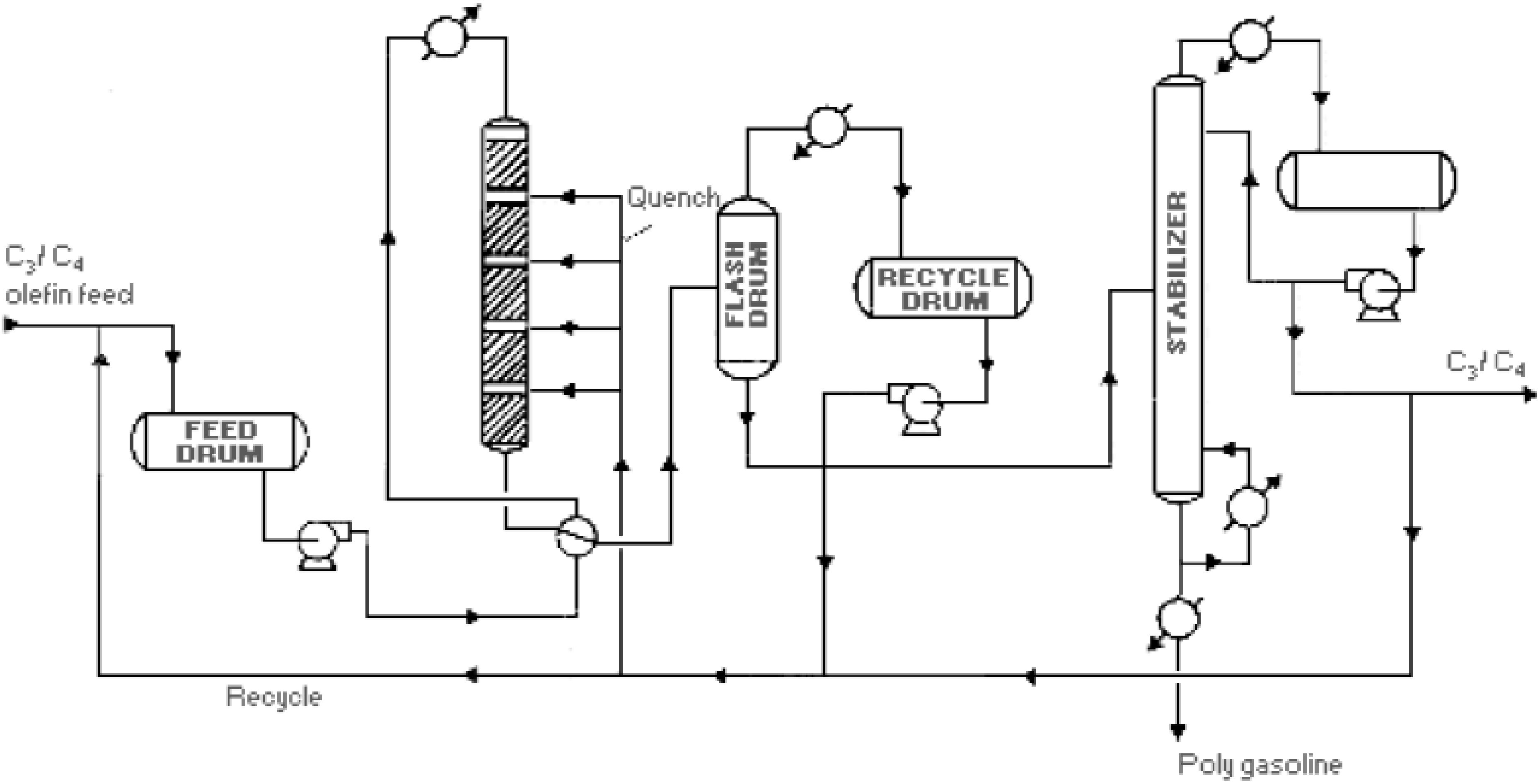
- Furthermore, it is not essential that only one type of monomer be involved.
- If unlike olefin molecules are combined, the process is referred to as "copolymerization."
- Polymerization in the true sense of the word is normally prevented, and all attempts are made to terminate the reaction at the dimer or trimer (three monomers joined together) stage.
- However, in the petrochemical section of a refinery, polymerization, which results in the production of, for instance, polyethylene, is allowed to proceed until materials of the required high molecular weight have been produced.



Polymerization

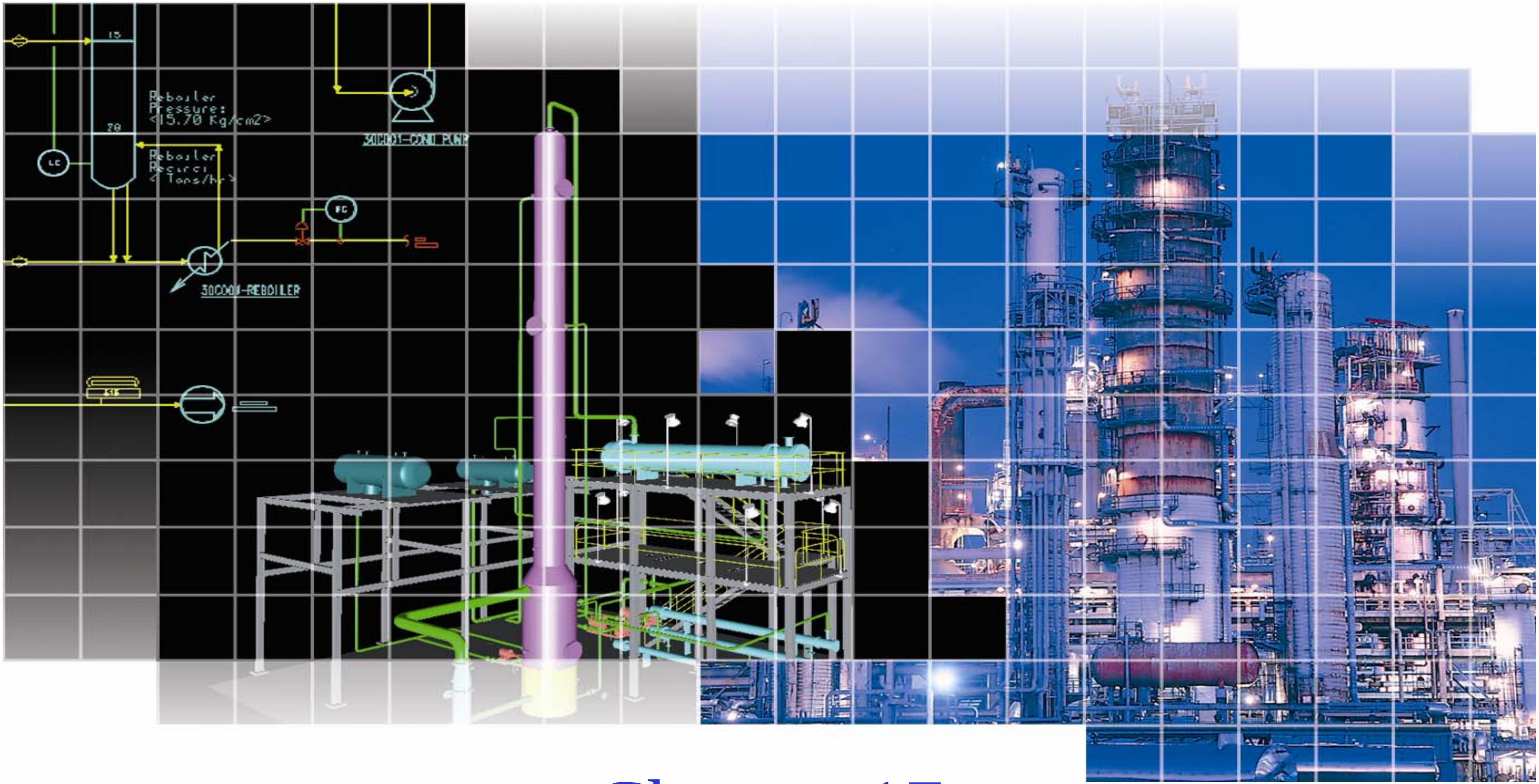
Feedstock	From	Process	Typical products . . . . . . To
Olefins	Cracking processes	Unification	High octane naphtha…..Gasoline blending Petrochem. Feedstock…Petrochemical Liquefied petro. Gas…...Storage

Polymerization



Grease Compounding

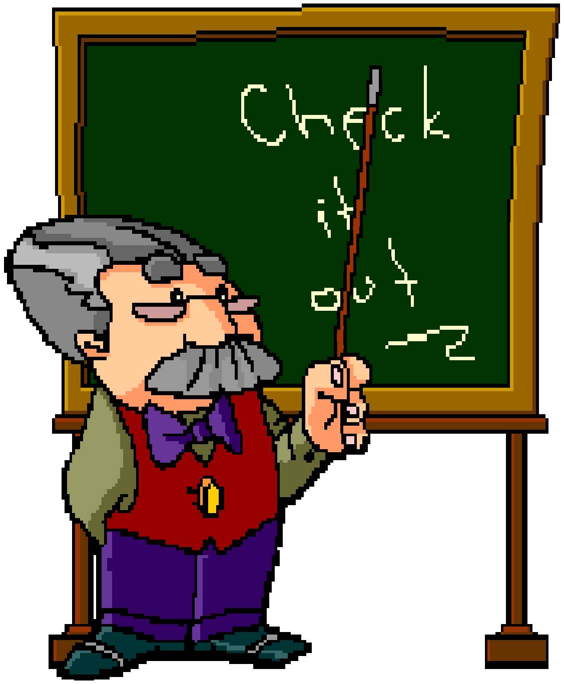
- Grease is made by blending metallic soaps (salts of long-chained fatty acids) and additives into a lubricating oil medium at temperatures of 400°-600° F.
- Grease may be either batch-produced or continuously compounded.
- The characteristics of the grease depend to a great extent on the metallic element (calcium, sodium, aluminum, lithium, etc.) in the soap and the additives used.



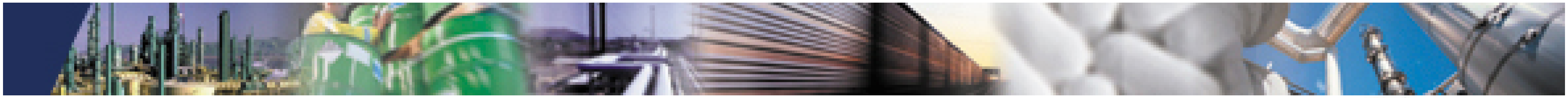
Chapter 17

Conversion Processes – Alteration or Rearrangement

Outline



- Catalytic Reforming
- Isomerization

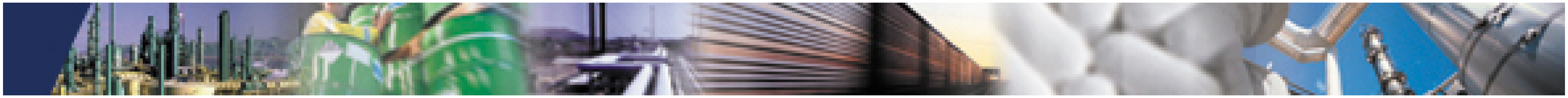


Catalytic Reforming

- Catalytic reforming is an important process used to convert low-octane naphthas into high-octane gasoline blending components called reformates.
- Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, and isomerization taking place simultaneously.
- Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations of toluene, benzene, xylene, and other aromatics useful in gasoline blending and petrochemical processing.
- Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes.

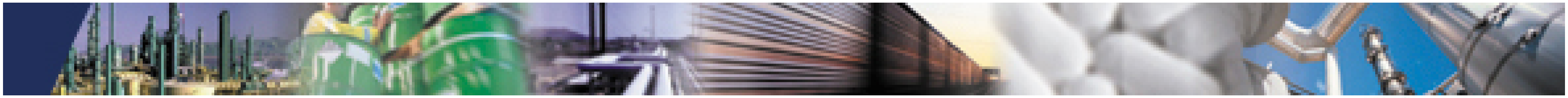
Catalytic Reforming

- A catalytic reformer comprises a reactor section and a product-recovery section.
- More or less standard is a feed preparation section in which, by combination of hydrotreatment and distillation, the feedstock is prepared to specification.
- Most processes use platinum as the active catalyst.
- Sometimes platinum is combined with a second catalyst (bimetallic catalyst) such as rhenium or another noble metal.
- There are many different commercial catalytic reforming processes including platforming, powerforming, ultraforming, and Thermofor catalytic reforming.



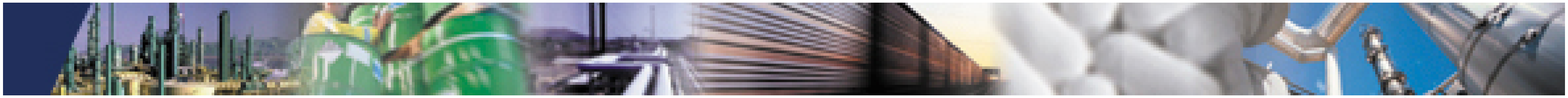
Catalytic Reforming

- In the platforming process, the first step is preparation of the naphtha feed to remove impurities from the naphtha and reduce catalyst degradation.
- The naphtha feedstock is then mixed with hydrogen, vaporized, and passed through a series of alternating furnace and fixed-bed reactors containing a platinum catalyst.
- The effluent from the last reactor is cooled and sent to a separator to permit removal of the hydrogen-rich gas stream from the top of the separator for recycling.
- The liquid product from the bottom of the separator is sent to a fractionator called a stabilizer (butanizer).
- It makes a bottom product called reformate; butanes and lighter go overhead and are sent to the saturated gas plant.



Catalytic Reforming

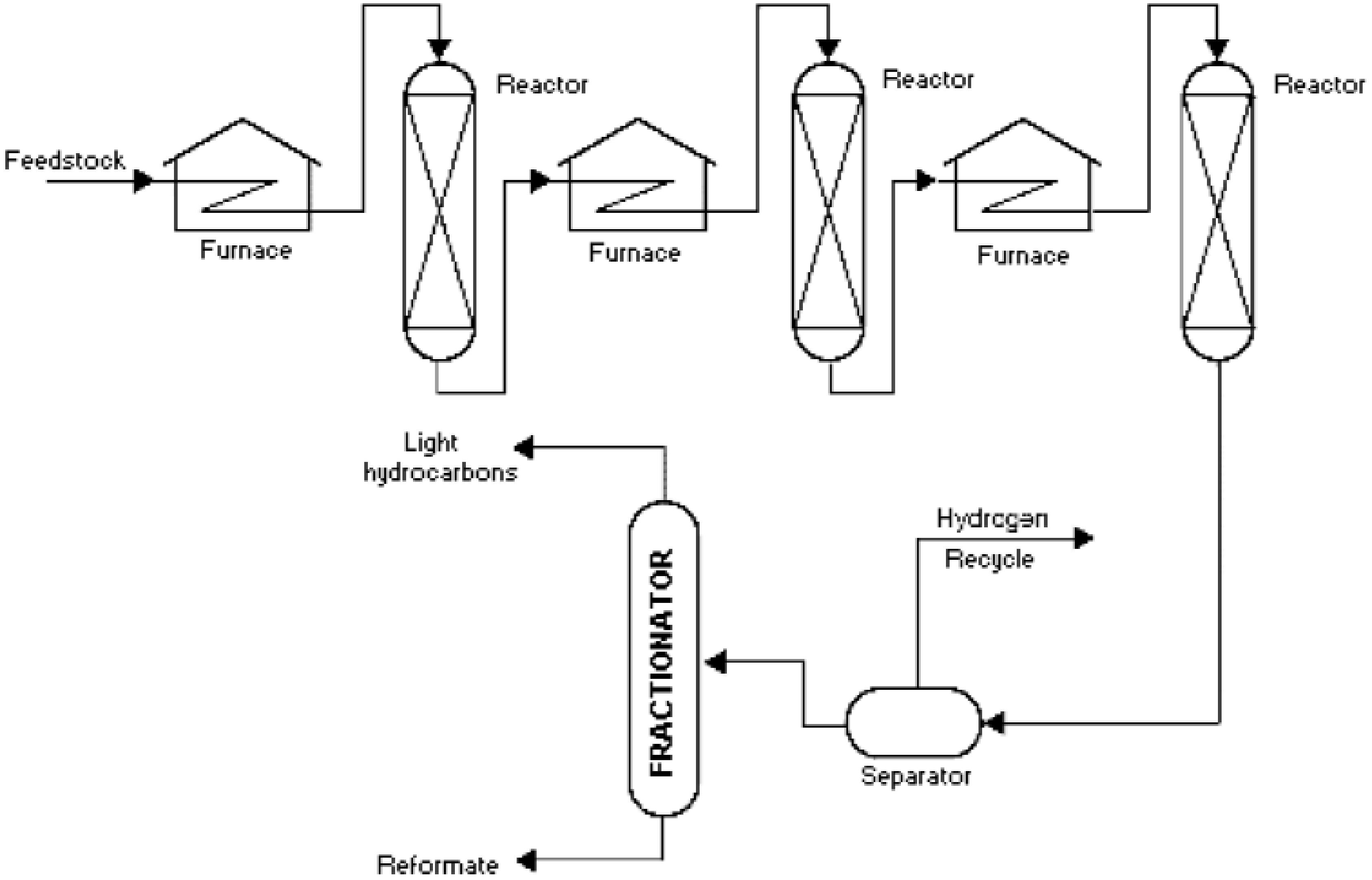
- Some catalytic reformers operate at low pressure (50-200 psi), and others operate at high pressures (up to 1,000 psi).
- Some catalytic reforming systems continuously regenerate the catalyst in other systems.
- One reactor at a time is taken off-stream for catalyst regeneration, and some facilities regenerate all of the reactors during turnarounds.



Catalytic Reforming

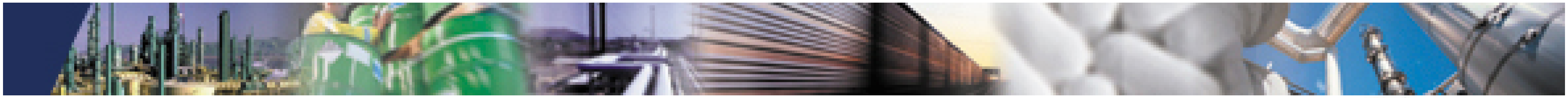
Feedstock	From	Process	Typical products . . . . To
Desulfurized naphtha	Coker	Rearrange, dehydrogenate	High octane gasoline…Blending
			Aromatics…………….Petrochemical
Naphthene-rich fractions	hydrocracker, hydrodesulfur		Hydrogen……………..Recycle, hydrotreat, etc.
Straight-run naphtha	Atmospheric fractionator		Gas……………………Gas plant

Catalytic Reforming



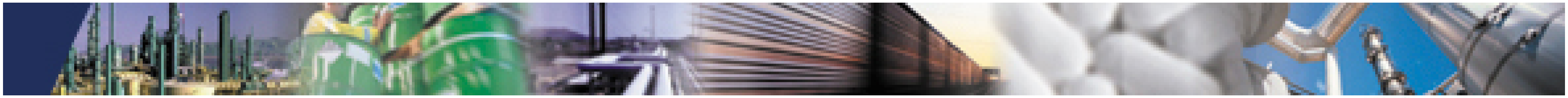
Isomerization

- Isomerization converts n-butane, n-pentane and n-hexane into their respective isoparaffins of substantially higher octane number.
- The straight-chain paraffins are converted to their branched-chain counterparts whose component atoms are the same but are arranged in a different geometric structure.
- Isomerization is important for the conversion of n-butane into isobutane, to provide additional feedstock for alkylation units, and the conversion of normal pentanes and hexanes into higher branched isomers for gasoline blending.
- Isomerization is similar to catalytic reforming in that the hydrocarbon molecules are rearranged, but unlike catalytic reforming, isomerization just converts normal paraffins to isoparaffins.



Isomerization

- There are two distinct isomerization processes, butane (C_4) and pentane/hexane (C_5/C_6).
- Butane isomerization produces feedstock for alkylation.
- Aluminum chloride catalyst plus hydrogen chloride are universally used for the low-temperature processes.
- Platinum or another metal catalyst is used for the higher-temperature processes.
- In a typical low-temperature process, the feed to the isomerization plant is n-butane or mixed butanes mixed with hydrogen (to inhibit olefin formation) and passed to the reactor at 230-340°F and 200-300 psi.
- Hydrogen is flashed off in a high-pressure separator and the hydrogen chloride removed in a stripper column.

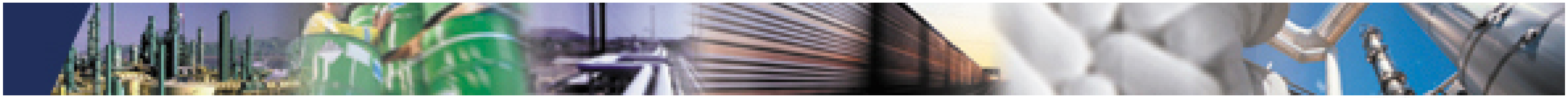


Isomerization

- The resultant butane mixture is sent to a fractionator (deisobutanizer) to separate n-butane from the isobutane product.
- Pentane/hexane isomerization increases the octane number of the light gasoline components n-pentane and n-hexane, which are found in abundance in straight-run gasoline.
- In a typical C_5/C_6 isomerization process, dried and desulfurized feedstock is mixed with a small amount of organic chloride and recycled hydrogen, and then heated to reactor temperature.
- It is then passed over supported-metal catalyst in the first reactor where benzene and olefins are hydrogenated.

Isomerization

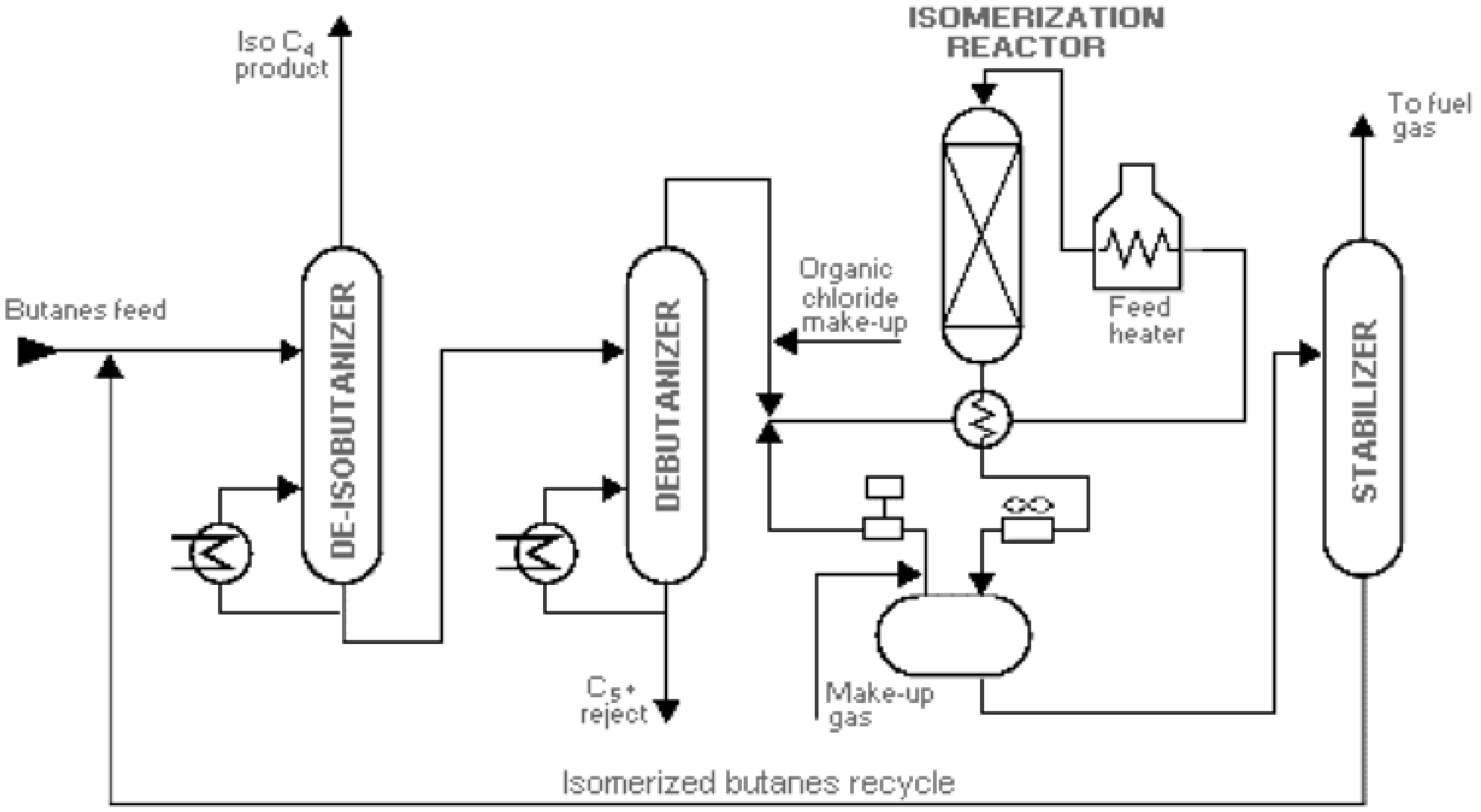
- The feed next goes to the isomerization reactor where the paraffins are catalytically isomerized to isoparaffins.
- The reactor effluent is then cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle hydrogen-gas stream.
- The isomerate is washed (caustic and water), acid stripped, and stabilized before going to storage.



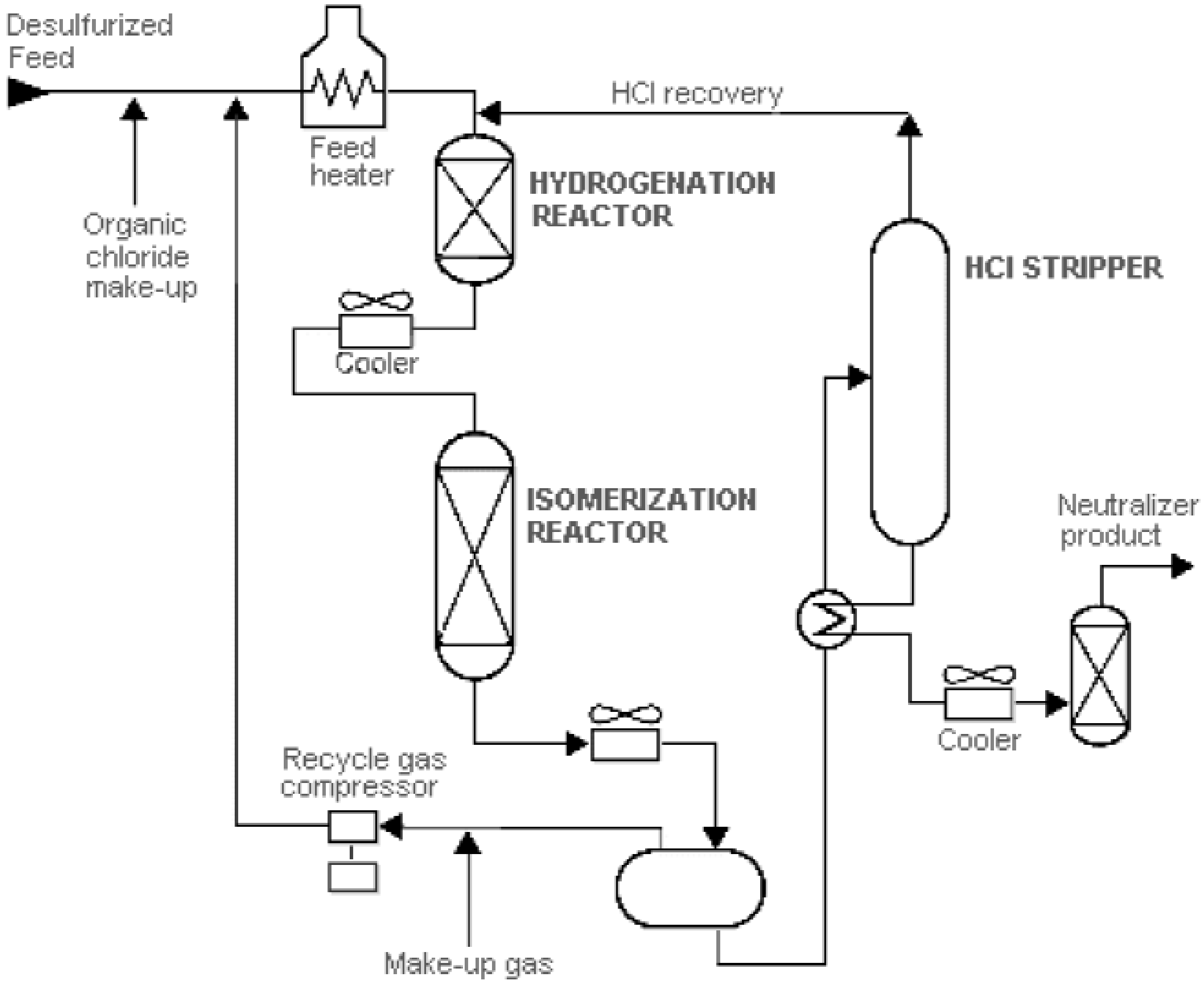
Isomerization

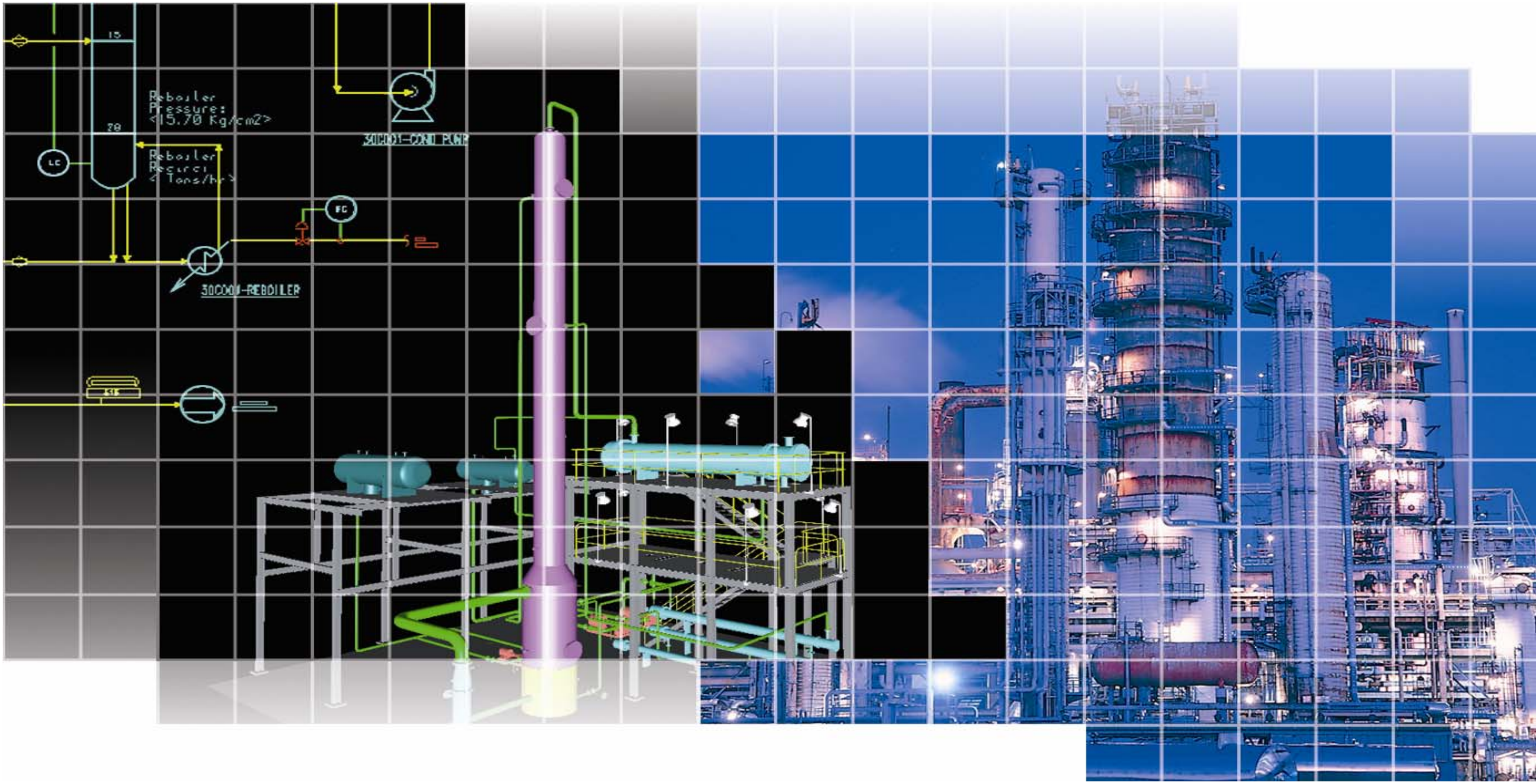
Feedstock	From	Process	Typical products . . . To
n-Butane	Various Processes	Rearrangement	Isobutane . . . . Alkylation
n-Pentane			Isopentane . . . . . . Blending
n-Hexane			Isohexane . . . . Blending
			Gas . . . . Gas Plant

C_4 Isomerization



C_5/C_6 Isomerization

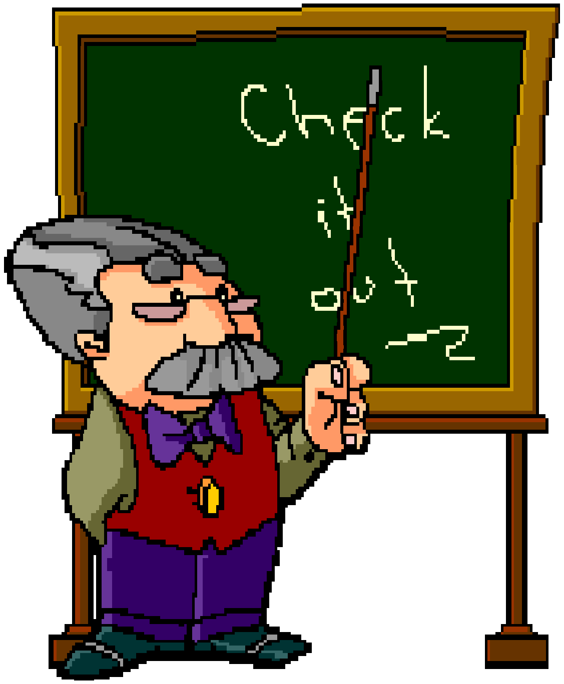




Chapter 18

Treatment Processes

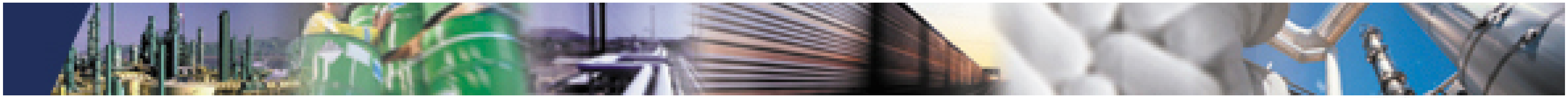
Outline



- Amine Treating
- Drying and Sweetening
- Hydrodesulfurization
- Hydrotreating
- Solvent Deasphalting
- Solvent Dewaxing
- Solvent Extraction

Amine Treating

- Amine plants remove acid contaminants from sour gas and hydrocarbon streams.
- In amine plants, gas and liquid hydrocarbon streams containing carbon dioxide and/or hydrogen sulfide are charged to a gas absorption tower or liquid contactor where the acid contaminants are absorbed by counterflowing amine solutions (i.e., MEA, DEA, MDEA).
- The stripped gas or liquid is removed overhead, and the amine is sent to a regenerator.
- In the regenerator, the acidic components are stripped by heat and reboiling action and disposed of, and the amine is recycled



Drying and Sweetening

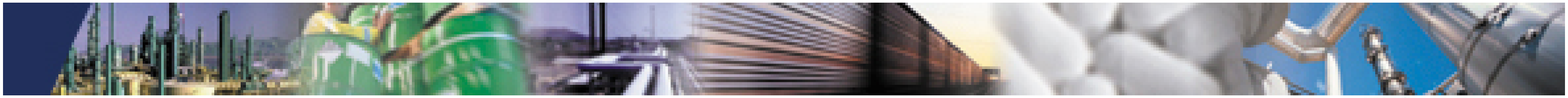
- Feedstocks from various refinery units are sent to gas treating plants where butanes and butenes are removed for use as alkylation feedstock, heavier components are sent to gasoline blending, propane is recovered for LPG, and propylene is removed for use in petrochemicals.
- Some mercaptans are removed by water-soluble chemicals that react with the mercaptans.
- Caustic liquid (sodium hydroxide), amine compounds (diethanolamine) or fixed-bed catalyst sweetening also may be used.
- Drying is accomplished by the use of water absorption or adsorption agents to remove water from the products.
- Some processes simultaneously dry and sweeten by adsorption on molecular sieves.

Catalytic Hydrodesulfurization

- Hydrotreating for sulfur removal is called hydrodesulfurization.
- In a typical catalytic hydrodesulfurization unit, the feedstock is deaerated and mixed with hydrogen, preheated in a fired heater (600°-800° F) and then charged under pressure (up to 1,000 psi) through a fixed-bed catalytic reactor.
- In the reactor, the sulfur and nitrogen compounds in the feedstock are converted into H_2S and NH_3.
- The reaction products leave the reactor and after cooling to a low temperature enter a liquid/gas separator.
- The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock, and the low-pressure gas stream rich in H_2S is sent to a gas treating unit where H_2S is removed.

Catalytic Hydrodesulfurization

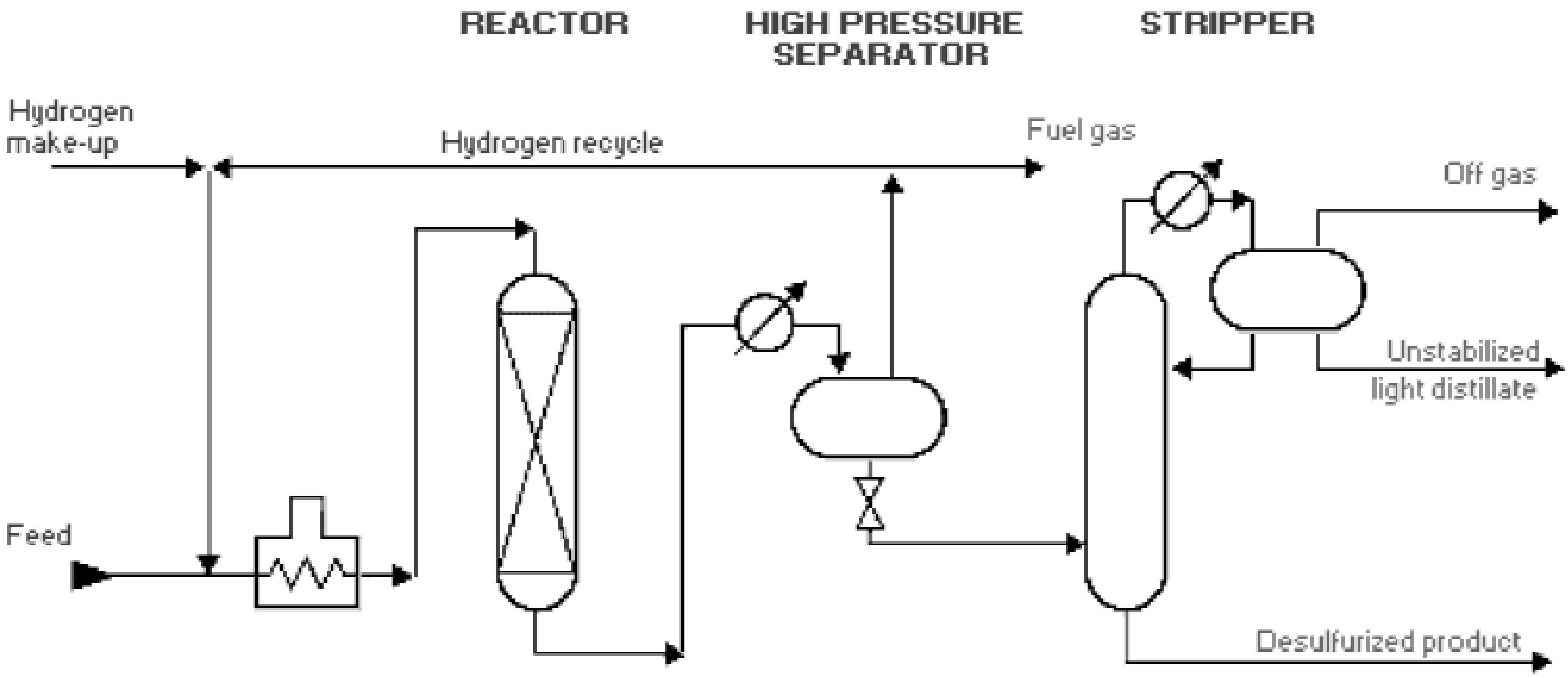
- The clean gas is then suitable as fuel for the refinery furnaces.
- The liquid stream is the product from hydrotreating and is normally sent to a stripping column for removal of H_2S and other undesirable components.
- In cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water.
- Hydrodesulfurized products are blended or used as catalytic reforming feedstock.

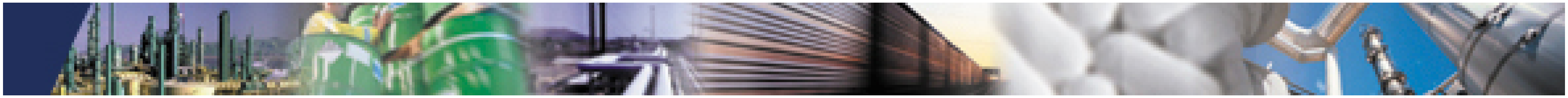


Catalytic Hydrodesulfurization

Feedstock	From	Process	Typical products . . To
Naphthas, distillates sour gas oil, residuals	Atmospheric & vacuum tower, catalytic & thermal cracker	Treating, hydrogenation	Naphtha . . . . Blending Hydrogen . . . . Recycle Distillates . . . . Blending H_2S, ammonia . . Sulfure plant, treater Gas . . . . Gas plant

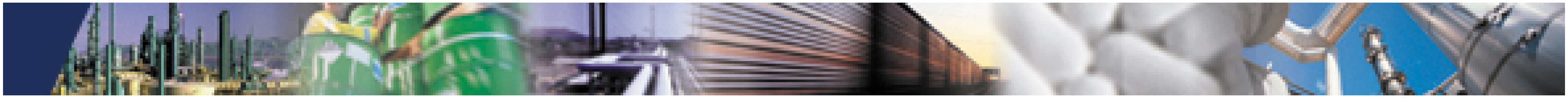
Catalytic Hydrodesulfurization





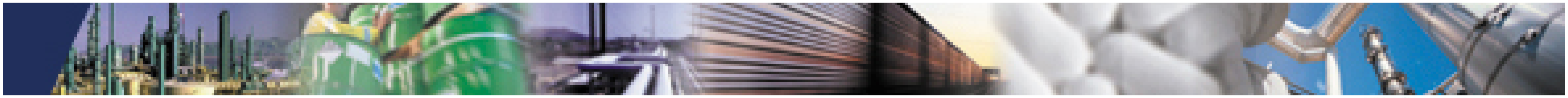
Catalytic Hydrotreating

- Catalytic hydrotreating is a hydrogenation process used to remove about 90% of contaminants such as nitrogen, sulfur, oxygen, and metals from liquid petroleum fractions.
- These contaminants, if not removed from the petroleum fractions as they travel through the refinery processing units, can have detrimental effects on the equipment, the catalysts, and the quality of the finished product.
- Typically, hydrotreating is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock.



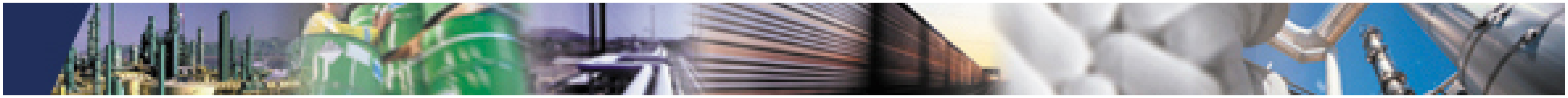
Catalytic Hydrotreating

- Hydrotreating is also used prior to catalytic cracking to reduce sulfur and improve product yields, and to upgrade middle-distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils.
- In addition, hydrotreating converts olefins and aromatics to saturated compounds.



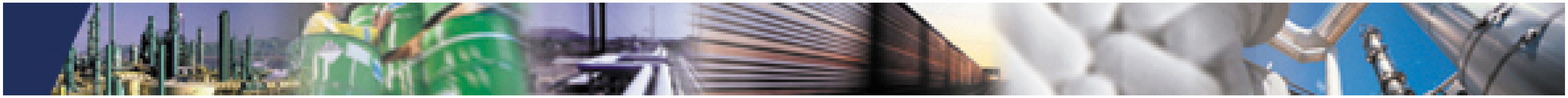
Solvent Deasphalting

- In this extraction process, which uses propane (or hexane) as a solvent, heavy oil fractions are separated to produce heavy lubricating oil, catalytic cracking feedstock, and asphalt.
- Feedstock and liquid propane are pumped to an extraction tower at precisely controlled mixtures, temperatures (150°-250° F), and pressures of 350-600 psi.
- Separation occurs in a rotating disc contactor, based on differences in solubility.
- The products are then evaporated and steam stripped to recover the propane, which is recycled.
- Deasphalting also removes some sulfur and nitrogen compounds, metals, carbon residues, and paraffins from the feedstock.



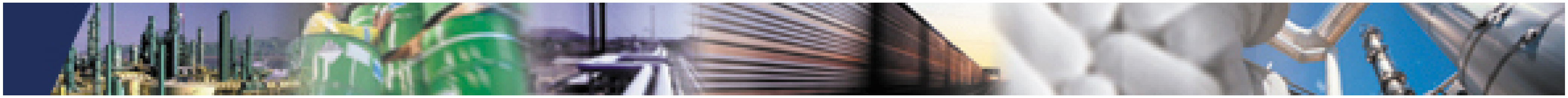
Solvent Deasphalting

Feedstock	From	Process	Typical products . . To
Residual, reduced crude	Atmospheric tower & Vacuum tower	Treatment	Heavy lube oil . . . Treating or lube blending Asphalt . . . . Storage of shipping Deasphalted oil . . Hydrotreat & catalytic cracker Propane . . . . Recycle



Solvent Dewaxing

- Solvent dewaxing is used to remove wax from either distillate or residual basestocks at any stage in the refining process.
- There are several processes in use for solvent dewaxing, but all have the same general steps, which are:
  - (1) mixing the feedstock with a solvent,
  - (2) precipitating the wax from the mixture by chilling, and
  - (3) recovering the solvent from the wax and dewaxed oil for recycling by distillation and steam stripping.
- Usually two solvents are used: toluene, which dissolves the oil and maintains fluidity at low temperatures, and methyl ethyl ketone (MEK), which dissolves little wax at low temperatures and acts as a wax precipitating agent.

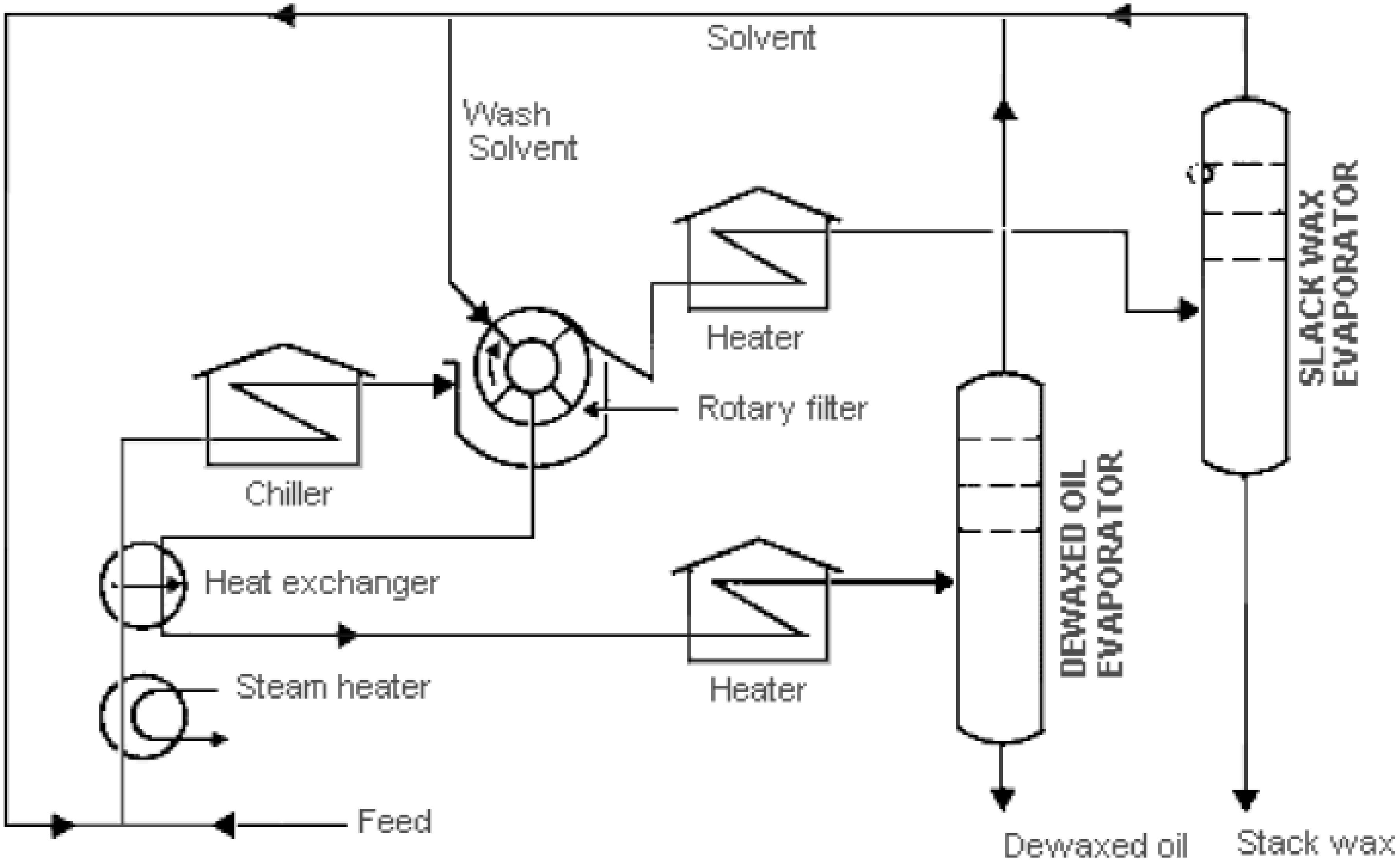


Solvent Dewaxing

- Other solvents that are sometimes used include benzene, methyl isobutyl ketone, propane, petroleum naphtha, ethylene dichloride, methylene chloride, and sulfur dioxide.
- In addition, there is a catalytic process used as an alternate to solvent dewaxing.

Feedstock	**From**	**Process**	**Typical products . .**	**To**
Lube basestock	Vacuum tower	Treating	Dewaxed lubes	Hydrotreating
			Wax	Hydrotreating
			Spent agents	Treatment or recycle

Solvent Dewaxing



Solvent Extraction

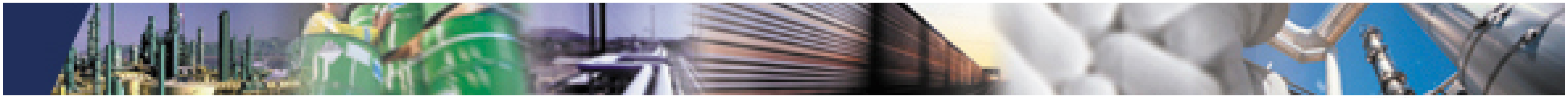
- The purpose of solvent extraction is to prevent corrosion, protect catalyst in subsequent processes, and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricant and grease stocks.
- The solvent extraction process separates aromatics, naphthenes, and impurities from the product stream by dissolving or precipitation.
- The feedstock is first dried and then treated using a continuous countercurrent solvent treatment operation.
- In one type of process, the feedstock is washed with a liquid in which the substances to be removed are more soluble than in the desired resultant product.
- In another process, selected solvents are added to cause impurities to precipitate out of the product.

Solvent Extraction

- In the adsorption process, highly porous solid materials collect liquid molecules on their surfaces.
- The solvent is separated from the product stream by heating, evaporation, or fractionation, and residual trace amounts are subsequently removed from the raffinate by steam stripping or vacuum flashing.
- Electric precipitation may be used for separation of inorganic compounds.
- The solvent is then regenerated to be used again in the process.
- The most widely used extraction solvents are phenol, furfural, and cresylic acid.

Solvent Extraction

- Other solvents less frequently used are liquid sulfur dioxide, nitrobenzene, and 2,2'-dichloroethyl ether.
- The selection of specific processes and chemical agents depends on the nature of the feedstock being treated, the contaminants present, and the finished product requirements.



Solvent Extraction

Feedstock	From	Process	Typical products . . . To
Naphthas, distillates, kerosene	Atm. tower	Treating/ blending	High octane gasoline . . Storage Refined fuels . . . . Treating and blending Spent agents . . . . Treatment and blending

Solvent Extraction