16 Gas Cleaning

16.1 INTRODUCTION

Natural gas, as it is used by consumers, is much different from the natural gas that is brought from underground formations to the wellhead. Although the processing of natural gas is in many respects less complicated than the processing and refining of crude oil, it is equally as necessary before its use by end users. Gas is often referred to as natural gas because it is a naturally occurring hydrocarbon mixture (which does contain some nonhydrocarbon constituents, which might be labeled as impurities but often find use in other areas of technology). For the most part, natural gas consists mainly of methane, which is the simplest hydrocarbon; nevertheless, processing (purification, refining) is required before transportation to the consumer.

Gas processing (also called gas cleaning or gas refining) consists of separating all of the various hydrocarbons and fluids from the pure natural gas (Figure 16.1; Kidnay and Parrish, 2006; Mokhatab et al., 2006; Speight, 2007, 2014a). While often assumed to be hydrocarbons in nature, there are also components of the gaseous products that must be removed prior to the release of the gases to the atmosphere or prior to the use of the gas in another part of the refinery, that is, as a fuel gas or as a process feedstock.

Gas processing involves the use of several different types of processes to remove contaminants from gas streams, but there is always overlap between the various processing concepts. In addition, the terminology used for gas processing can often be confusing and/or misleading because of the overlap (Curry, 1981; Maddox, 1982). Gas processing is necessary to ensure that the natural gas prepared for transportation (usually by pipeline) and for sales must be as clean and pure as the specifications dictate. Thus, natural gas, as it is used by consumers, is much different from the natural gas that is brought from underground formations up to the wellhead. Moreover, although natural gas produced at the wellhead is composed primarily of methane, it is by no means as pure.

Raw natural gas comes from three types of wells: oil wells (associated gas), gas wells (non-associated gas), and condensate wells (condensate gas, also called nonassociated gas). Associated gas can exist separate from oil in the formation (free gas) or dissolved in the crude oil (dissolved gas). Whatever the source of the natural gas, once separated from crude oil (if present), it commonly exists in mixtures with other hydrocarbons; principally ethane, propane, butane, and pentane isomers (natural gas liquids) as well as a mixture of higher-molecular-weight (higher-boiling) hydrocarbons that are often referred to as natural gasoline. In addition, raw natural gas contains water vapor, hydrogen sulfide (H2S), carbon dioxide, helium, nitrogen, and other compounds. Natural gas liquids are sold separately and have a variety of different uses such as providing feedstocks for oil refineries or petrochemical plants.

Acidic constituents such as carbon dioxide and hydrogen sulfide as well as mercaptan derivatives (also called thiols, RSH) can contribute to corrosion of refining equipment, harm catalysts, pollute the atmosphere, and prevent the use of hydrocarbon components in petrochemical manufacture (Mokhatab et al., 2006; Speight, 2014b). When the amount of hydrogen sulfide is high, it may be removed from a gas stream and converted to sulfur or sulfuric acid; a recent option for hydrogen sulfide removal is the use of chemical scavengers (Kenreck, 2014). Some natural gases contain sufficient carbon dioxide to warrant recovery as dry ice (Bartoo, 1985).

The processes that have been developed to accomplish gas purification vary from a simple single-stage once-through washing-type operation to complex multistep recycling systems (Mokhatab et al., 2006; Speight, 2007, 2014a). In many cases, the process complexities arise because of the need for the recovery of the materials used to remove the contaminants or even recovery of the
contaminants in the original, or altered, form (Katz, 1959; Kohl and Riesenfeld, 1985; Newman, 1985; Mokhatab et al., 2006). In addition, the precise area of application of a given process is difficult to define and several factors must be considered before process selection: (1) the types of contaminants in the gas, (2) the concentrations of contaminants in the gas, (3) the degree of contaminant removal desired, (4) the selectivity of acid gas removal required, (5) the temperature of the gas to be processed, (6) the pressure of the gas to be processed, (7) the volume of the gas to be processed, (8) the composition of the gas to be processed, (9) the ratio of carbon dioxide to hydrogen sulfide ratio in the gas feedstock, and (10) the desirability of sulfur recovery due to process economics or environmental issues.

There are four general processes used for emission control (often referred to in another, more specific context as flue gas desulfurization): (1) adsorption, (2) absorption, (3) catalytic oxidation, and (4) thermal oxidation (Soud and Takeshita, 1994; Mokhatab et al., 2006; Speight, 2007, 2014a).

Adsorption is a physical–chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. It must be emphasized that absorption differs from adsorption in that absorption is not a physical–chemical surface phenomenon but a process in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). The process depends only on physical solubility and may include chemical reactions in the liquid phase (chemisorption). Common absorbing media used are water, aqueous amine solutions, caustic, sodium carbonate, and nonvolatile hydrocarbon oils, depending on the type of gas to be absorbed. Usually, the gas–liquid contactor designs that are employed are plate columns or packed beds (Table 16.1).

On the other hand, adsorption is usually a gas–solid interaction in which an adsorbent such as activated carbon (the adsorbent or adsorbing medium) can be regenerated upon desorption (Mokhatab et al., 2006; Speight, 2007, 2014a). The quantity of material adsorbed is proportional to the surface area of the solid and, consequently, adsorbents are usually granular solids with a large surface area per unit mass. Subsequently, the captured (adsorbed) gas can be desorbed with hot air.
or steam either for recovery or for thermal destruction. Adsorber units are widely used to increase a low gas concentration prior to incineration unless the gas concentration is very high in the inlet air stream and the process is also used to reduce problem odors (or obnoxious odors) from gases. There are several limitations to the use of adsorption systems, but it is generally the case that the major limitation is the requirement for the minimization of particulate matter and/or condensation of liquids (e.g., water vapor) that could mask the adsorption surface and drastically reduce its efficiency (Table 16.2).

Absorption is achieved by dissolution (a physical phenomenon) or by reaction (a chemical phenomenon) (Barbouteau and Dalaud, 1972; Ward, 1972; Mokhatab et al., 2006; Speight, 2007, 2014a). In addition to economic issues or constraints, the solvents used for gas processing should have (1) high capacity for acid gas, (2) low tendency to dissolve hydrogen, (3) low tendency to dissolve low-molecular-weight hydrocarbons, (4) low vapor pressure at operating temperatures to minimize solvent losses, (5) low viscosity, (6) low thermal stability, (7) no reactivity toward gas components, (8) low tendency for fouling, (9) low tendency for corrosion, and (10) low economic cost (Mokhatab et al., 2006; Speight, 2007, 2014a,b).

Chemical adsorption processes adsorb sulfur dioxide onto a carbon surface where it is oxidized (by oxygen in the flue gas) and absorbs moisture to give sulfuric acid impregnated into and on the adsorbent. Liquid absorption processes (which usually employ temperatures below 50°C (120°F) are classified either as physical solvent processes or chemical solvent processes. The former processes employ an organic solvent, and absorption is enhanced by low temperatures or high pressure, or both. Regeneration of the solvent is often accomplished readily (Staton et al., 1985). In chemical solvent processes, absorption of the acid gases is achieved mainly by the use of alkaline solutions such as amine derivatives or carbonate derivatives (Kohl and Riesenfeld, 1985; Mokhatab et al., 2006; Abdel-Aal et al., 2016). Regeneration (desorption) can be brought about by the use of reduced pressures and/or high temperatures, whereby the acid gases are stripped from the solvent.

### TABLE 16.1
Factors to Be Considered in the Use of Packed Column and Plate Column Absorption Systems
1. Relatively low pressure drop
2. Capabilities of achieving relatively high mass transfer efficiencies
3. Capacity to increase the height and/or type of packing or number of plates capable of improving mass transfer without purchasing a new piece of equipment
4. Ability to collect particulate materials as well as gases
5. Possibility to require water (or liquid) disposal

### TABLE 16.2
Factors to Be Considered in the Use of Adsorption Systems
1. Possibility of product recovery
2. Excellent control and response to process changes
3. No chemical disposal problem when pollutant (product) recovered and returned to process
4. Capability to remove gaseous or vapor contaminants from process streams to extremely low levels
5. Product recovery that may require distillation or extraction
6. Adsorbent that may deteriorate as the number of cycles increase
7. Adsorbent regeneration
8. Prefiltering of gas stream possibly required to remove particulate materials capable of plugging the adsorbent bed
Amine washing of gas emissions involves chemical reaction of the amine with any acid gases with the liberation of an appreciable amount of heat, and it is necessary to compensate for the absorption of heat. Amine derivatives such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) have been used in commercial applications (Table 16.3; Katz, 1959; Jou et al., 1985; Kohl and Riesenfeld, 1985; Maddox et al., 1985; Polasek and Bullin, 1985; Pitsinigos and Lygeros, 1989; Mokhatab et al., 2006; Speight, 2007, 2014a; Abdel-Aal et al., 2016).

The chemistry of the amine process (also called the olamine process) can be represented by simple equations for low partial pressures of the acid gases:

\[ 2RNH_2 + H_2S \rightarrow (RNH_3)_2S \]
\[ 2RHN_2 + CO_2 + H_2O \rightarrow (RNH_3)_2CO_3 \]

At high acid gas partial pressure, the reactions will lead to the formation of other products:

\[ (RNH_3)_2S + H_2S \rightarrow 2RHNH_2S \]
\[ (RNH_3)_2CO_3 + H_2O \rightarrow 2RNH_2HCO_3 \]

The reaction is extremely rapid and the absorption of hydrogen sulfide is limited only by mass transfer—this is not the case for carbon dioxide—and the reaction is also more complex that these equations would indicate and can lead to a series on unwanted side reactions and by-products (Mokhatab et al., 2006; Speight, 2007). Regeneration of the amine (olamine) solution leads to near complete desorption of carbon dioxide and hydrogen sulfide. A comparison between monoethanolamine, diethanolamine, and diisopropanolamine shows that monoethanolamine is the cheapest of the three olamines but exhibits the highest heat of reaction and corrosion. On the other hand, diisopropanolamine is the most expensive of the three olamines but exhibits the lowest heat of reaction with a lower propensity for corrosion.

Carbone washing is a mild alkali process (typically, the alkali is potassium carbonate, \( K_2CO_3 \)) for gas processing for the removal of acid gases (such as carbon dioxide and hydrogen sulfide) from gas streams and uses the principle that the rate of absorption of carbon dioxide by potassium carbonate increases with temperature (Mokhatab et al., 2006; Speight, 2007, 2014a).

### Table 16.3

<table>
<thead>
<tr>
<th>Olamine</th>
<th>Formula</th>
<th>Derived Name</th>
<th>Molecular Weight</th>
<th>Specific Gravity</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Flash Point (°C)</th>
<th>Relative Capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanolamine</td>
<td>HOC(_2)H(_2)NH(_2)</td>
<td>MEA</td>
<td>61.08</td>
<td>1.01</td>
<td>10</td>
<td>170</td>
<td>85</td>
<td>100</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>(HOC(_2)H(_3))(_2)NH</td>
<td>DEA</td>
<td>105.14</td>
<td>1.097</td>
<td>27</td>
<td>217</td>
<td>169</td>
<td>58</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>(HOC(_2)H(_3))(_3)NH</td>
<td>TEA</td>
<td>148.19</td>
<td>1.124</td>
<td>18</td>
<td>335, d</td>
<td>185</td>
<td>41</td>
</tr>
<tr>
<td>Diglycolamine (hydroxyethanolamine)</td>
<td>H(OOC(_2)H(_3))(_2)NH</td>
<td>DGA</td>
<td>105.14</td>
<td>1.057</td>
<td>−11</td>
<td>223</td>
<td>127</td>
<td>58</td>
</tr>
<tr>
<td>Diisopropanolamine</td>
<td>(HOC(_3)H(_6))(_2)NH</td>
<td>DIPA</td>
<td>133.19</td>
<td>0.99</td>
<td>42</td>
<td>248</td>
<td>127</td>
<td>46</td>
</tr>
<tr>
<td>Methyl diethanolamine</td>
<td>(HOC(_2)H(_4))(_2)NCH(_3)</td>
<td>MDEA</td>
<td>119.17</td>
<td>1.03</td>
<td>−21</td>
<td>247</td>
<td>127</td>
<td>51</td>
</tr>
</tbody>
</table>

*d: with decomposition.*
It has been demonstrated that the process works best near the temperature of reversibility of the reactions:

\[
K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3
\]

\[
K_2CO_3 + H_2S \rightarrow KHS + KHCO_3
\]

The Fluor process uses propylene carbonate to remove carbon dioxide, hydrogen sulfide, carbonyl sulfide, water, and higher-boiling hydrocarbons (C\textsubscript{2+}) from natural gas (Abdel-Aal et al., 2016).

Water washing, in terms of the outcome, is almost analogous to (but often less effective than) washing with potassium carbonate (Kohl and Riesenfeld, 1985), and it is also possible to carry out the desorption step by pressure reduction. The absorption is purely physical and there is also a relatively high absorption of hydrocarbons, which are liberated at the same time as the acid gases.

In chemical conversion processes, contaminants in gas emissions are converted to compounds that are not objectionable or that can be removed from the stream with greater ease than the original constituents. For example, a number of processes have been developed, which remove hydrogen sulfide and sulfur dioxide from gas streams by absorption in an alkaline solution.

Catalytic oxidation is a chemical conversion process that is used predominantly for the destruction of volatile organic compounds and carbon monoxide. These systems operate in a temperature regime on the order of 205°C–595°C (400°F–1100°F) in the presence of a catalyst—in the absence of the catalyst, the system would require a higher operating temperature. The catalysts used are typically a combination of noble metals deposited on a ceramic base in a variety of configurations (e.g., honeycomb shaped) to enhance good surface contact. Catalytic systems are usually classified on the basis of bed types such as fixed bed (or packed bed) and fluid bed (fluidized bed). These systems generally have very high destruction efficiencies for most volatile organic compounds, resulting in the formation of carbon dioxide, water, and varying amounts of hydrogen chloride (from halogenated hydrocarbons). The presence in emissions of chemicals such as heavy metals, phosphorus, sulfur, chlorine, and most halogens in the incoming air stream act as poison to the system and can foul up the catalyst. Thermal oxidation systems, without the use of catalysts, also involve chemical conversion (more correctly, chemical destruction) and operate at temperatures in excess of 815°C (1500°F), or 220°C–610°C (395°F–1100°F) higher than catalytic systems.

Historically, particulate matter control (dust control) has been one of the primary concerns of industries, since the emission of particulate matter is readily observed through the deposition of fly ash and soot as well as in impairment of visibility (Mody and Jakhete, 1988). Different degrees of control can be achieved by the use of various types of equipment, but selection of the process equipment depends upon proper characterization of the particulate matter emitted by a specific process, that is, the appropriate piece of equipment must be selected, sized, installed, and performance tested. The general classes of control devices for particulate matter are categorized as (1) cyclone collectors, (2) fabric filters, and (3) wet scrubbers.

Cyclone collectors are the most common of the inertial collector class and are effective in removing coarser fractions of particulate matter and operate by contacting the particles in the gas stream with a liquid. In principle, the particles are incorporated in a liquid bath or in liquid particles, which are much larger and therefore more easily collected. In the process, the particle-laden gas stream enters an upper cylindrical section tangentially and proceeds downward through a conical section. Particles migrate by centrifugal force generated by providing a path for the carrier gas to be subjected to a vortex-like spin. The particles are forced to the wall and are removed through a seal at the apex of the inverted cone. A reverse-direction vortex moves upward through the cyclone and discharges through a top center opening. Cyclones are often used as primary collectors because of their relatively low efficiency (50%–90% is usual). The equipment can be arranged either in parallel or in series to both increase efficiency and decrease pressure drop but there are disadvantages that must be recognized (Table 16.4).
Fabric filters are typically designed with nondisposable filter bags. As the gaseous (dust-containing) emissions flow through the filter media (typically cotton, polypropylene, fiberglass, or Teflon), particulate matter is collected on the bag surface as a dust cake. Fabric filters operate with collection efficiencies up to 99.9% although other advantages are evident, but there are several issues that arise during the use of such equipment (Table 16.5).

Wet scrubbers are devices in which a countercurrent spray liquid is used to remove particles from an air stream. Device configurations include plate scrubbers, packed bed scrubbers, orifice scrubbers, venturi scrubbers, and spray towers, individually or in various combinations. Wet scrubbers can achieve high collection efficiencies at the expense of prohibitive pressure drops (Table 16.6). The foam scrubber is a modification of a wet scrubber in which the particle-laden gas is passed through a foam generator, where the gas and particles are enclosed by small bubbles of foam.

**TABLE 16.4**
Factors to Be Considered in the Use of Cyclone Collectors
1. Relatively low operating pressure drops (for the degree of particulate removal obtained) in the range of approximately 2–6 inch water column
2. Dry collection and disposal
3. Relatively low overall particulate collection efficiencies, especially on particulates below 10 mm
4. Usually inability to process semisolid (tacky) materials

**TABLE 16.5**
Factors to Be Considered in the Use of Fabric Filter Systems
1. High collection efficiency on both coarse and fine (submicrometer) particulates
2. Collected material recovered dry for subsequent processing of disposal
3. Corrosion and rusting of components, usually not major issues
4. Relatively simple operation
5. Temperatures much in excess of 288°C (550°F) that require special refractory materials
6. Potential for dust explosion hazard
7. Fabric life possibly shortened at elevated temperatures and in the presence of acid or alkaline particulate or gas constituents
8. Hygroscopic materials, condensation of moisture, or tarry adhesive components possibly causing crusty caking or plugging of the fabric or requiring special additives

**TABLE 16.6**
Factors to Be Considered in the Use of Wet Scrubbers
1. No secondary dust sources
2. Ability to collect gases as well as particulates (especially “sticky” ones)
3. Ability to handle high-temperature, high-humidity gas streams
4. Ability to achieve high collection efficiencies on fine particulates (however at the expense of pressure drop)
5. Possibility to necessitate water disposal
6. Corrosion problems more severe than with dry systems
7. Potential for solid buildup at the wet–dry interface
Other methods include the use of high-energy input *venturi scrubbers* or electrostatic scrubbers where particles or water droplets are charged, and flux force/condensation scrubbers where a hot humid gas is contacted with cooled liquid or where steam is injected into saturated gas. In the latter scrubber, the movement of water vapor toward the cold water surface carries the particles with it (*diffusiophoresis*), while the condensation of water vapor on the particles causes the particle size to increase, thus facilitating the collection of fine particles.

Electrostatic precipitators (Table 16.7) operate on the principle of imparting an electric charge to particles in the incoming air stream, which are then collected on an oppositely charged plate across a high-voltage field. Particles of high resistivity create the most difficulty in collection. Conditioning agents such as sulfur trioxide (SO₃) have been used to lower resistivity. Important parameters include design of electrodes, spacing of collection plates, minimization of air channeling, and collection-electrode rapping techniques (used to dislodge particles). Techniques under study include the use of high-voltage pulse energy to enhance particle charging, electron-beam ionization, and wide plate spacing. Electrical precipitators are capable of efficiencies >99% under optimum conditions, but performance is still difficult to predict in new situations.

### 16.2 GAS STREAMS

Gas streams produced during petroleum and natural gas refining are not always hydrocarbon in nature and may contain contaminants, such as carbon oxides (COₓ, where \( x = 1 \) and/or 2), sulfur oxides (SOₓ, where \( x = 2 \) and/or 3), as well as ammonia (NH₃), mercaptan derivatives (RSH), carbonyl sulfide (COS), and mercaptan derivatives (RSH). The presence of these impurities may eliminate some of the sweetening processes from use since some of these processes remove considerable amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes not designed to remove (or incapable of removing) large amounts of acid gases whereas they are capable of removing the acid gas impurities to very low levels when the acid gases are present only in low-to-medium concentration in the gas (Katz, 1959; Mokhatab et al., 2006; Speight, 2007, 2014a).

#### 16.2.1 GAS STREAMS FROM CRUDE OIL

There are two broad categories of gas that is produced from crude oil. The first category is the associated gas, which originated from crude oil formations and also from condensate wells (*condensate gas*, also called *nonassociated gas*). Associated gas can exist separate from oil in the formation (*free gas*) or dissolved in the crude oil (*dissolved gas*). The second category of the gas is produced during crude oil refining, and the terms *refinery gas* and *process gas* are also often used to include all of the gaseous products and by-products that emanate from a variety of refinery processes.

---

**TABLE 16.7**

Factors to Be Considered in the Use of Electrostatic Precipitators

1. High particulate (coarse and fine) collection efficiencies
2. Dry collection and disposal
3. Operation under high pressure (to 150 lb/in.²) or vacuum conditions
4. Operation at high temperatures (up to 704°C, 1300°F) when necessary
5. Relatively large gas flow rates capable of effective handling
6. Sensitivity to fluctuations in gas-stream conditions
7. Explosion hazard when treating combustible gases/particulates
8. Ozone produced during gas ionization
In order to process and transport associated dissolved natural gas, it must be separated from the oil in which it is dissolved and is most often performed using equipment installed at or near the wellhead. The actual process used to separate oil from natural gas, as well as the equipment that is used, can vary widely. Although dry pipeline quality natural gas is virtually identical across different geographic areas, raw natural gas from different regions will vary in composition (Table 16.8; Chapter 1), and therefore, separation requirements may emphasize or deemphasize the optional separation processes. In many instances, natural gas is dissolved in oil underground primarily due to the formation pressure. When this natural gas and oil is produced, it is possible that it will separate on its own but, in general, a separator is required. The conventional type of separator is consisting of a simple closed tank, where the force of gravity serves to separate the liquids like oil from the natural gas.

In certain instances, however, specialized equipment is necessary to separate oil and natural gas. An example of this type of equipment is the low-temperature separator. This is most often used for wells producing high-pressure gas along with light crude oil or condensate. These separators use pressure differentials to cool the wet natural gas and separate the oil and condensate. Wet gas enters the separator, being cooled slightly by a heat exchanger. The gas then travels through a high-pressure liquid knockout pot that serves to remove any liquids into a low-temperature separator. The gas then flows into this low-temperature separator through a choke mechanism, which expands the gas as it enters the separator. This rapid expansion of the gas allows for the lowering of the temperature in the separator. After removal of the liquids, the dry gas is sent back through the heat exchanger where it is warmed by the incoming wet gas. By varying the pressure of the gas in various sections of the separator, it is possible to vary the temperature, which causes the crude oil and some water to be condensed out of the wet gas stream.

On the other hand, petroleum refining produces gas streams that contain substantial amounts of acid gases such as hydrogen sulfide and carbon dioxide. These gas streams are produced during initial distillation of the crude oil and during the various conversion processes. Of particular interest is the hydrogen sulfide (H₂S) that arises from the hydrodesulfurization (Chapter 10) and hydrocracking (Chapter 11) of feedstocks that contain organically bound sulfur:

\[ [S]_{\text{feedstock}} + H_2 \rightarrow H_2S + \text{Hydrocarbons} \]

Petroleum refining involves, with the exception of heavy crude oil, primary distillation (Chapter 7) that results in separation into fractions differing in carbon number, volatility, specific gravity, and

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>% v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>&gt;85</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>3–8</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>1–5</td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>1–2</td>
</tr>
<tr>
<td>Pentane</td>
<td>C₅H₁₂⁻⁰</td>
<td>1–2</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>1–2</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S</td>
<td>1–2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>1–5</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

Note: Pentane⁻⁰, pentane, and higher-molecular-weight hydrocarbons, including benzene and toluene.
other characteristics. The most volatile fraction that contains most of the gases, which are generally dissolved in the crude, is referred to as **pipestill gas** or **pipestill light ends** and consists essentially of hydrocarbon gases ranging from methane to butane(s), or sometimes pentane(s).

The gas varies in composition and volume, depending on crude origin and on any additions to the crude made at the loading point. It is not uncommon to reinject light hydrocarbons such as propane and butane into the crude oil before dispatch by tanker or pipeline. This results in a higher vapor pressure of the crude, but it allows one to increase the quantity of light products obtained at the refinery. Since light ends in most petroleum markets command a premium, while in the oil field itself propane and butane may have to be reinjected or flared, the practice of **spiking** crude oil with liquefied petroleum gas is becoming fairly common.

In addition to the gases obtained by distillation of petroleum, more highly volatile products result from the subsequent processing of naphtha and middle distillate to produce gasoline. Hydrogen sulfide is produced in the desulfurization processes involving hydrogen treatment of naphtha, distillate, and residual fuel and from the coking or similar thermal treatments of vacuum gas oils and heavy feedstocks (Chapter 8). The most common processing step in the production of gasoline is the catalytic reforming of hydrocarbon fractions in the heptane (C7) to decane (C10) range.

Additional gases are produced in **thermal cracking processes**, such as the coking or visbreaking processes (Chapter 8) for the processing of heavy feedstocks. In the visbreaking process, fuel oil is passed through externally fired tubes and undergoes liquid phase cracking reactions, which result in the formation of lighter fuel oil components. Oil viscosity is thereby reduced, and some gases, mainly hydrogen, methane, and ethane, are formed. Substantial quantities of both gas and carbon are also formed in coking (both fluid coking and delayed coking) in addition to the middle distillate and naphtha. When coking a residual fuel oil or heavy gas oil, the feedstock is preheated and contacted with hot carbon (coke), which causes extensive cracking of the feedstock constituents of higher molecular weight to produce lower-molecular-weight products ranging from methane, via liquefied petroleum gas(es) and naphtha, to gas oil and heating oil. Products from coking processes tend to be unsaturated and olefin components predominate in the tail gases from coking processes.

Another group of refining operations that contributes to gas production is the **catalytic cracking processes** (Chapter 9). These consist of fluid-bed catalytic cracking, and there are many process variants in which heavy feedstocks are converted into cracked gas, liquefied petroleum gas, catalytic naphtha, fuel oil, and coke by contacting the heavy hydrocarbon with the hot catalyst. Both catalytic and thermal cracking processes, the latter being now largely used for the production of chemical raw materials, result in the formation of not only unsaturated hydrocarbons, particularly ethylene (CH2=CH2), but also propylene (propene, CH3CH=CH2), *iso*-butylene [iso-butene, (CH3)3C=CH2] and *n*-butenes (CH3CH2CH=CH2, and CH3CH=CHCH3) in addition to hydrogen (H2), methane (CH4) and smaller quantities of ethane (CH3CH3), propane (CH3CH2CH3), and butanes [CH3CH2CH2CH3, (CH3)2CH]. Diolefins such as butadiene (CH2=CHCH=CH2) are also present.

A further source of refinery gas is **hydrocracking**, a catalytic high-pressure pyrolysis process in the presence of fresh and recycled hydrogen (Chapter 11). The feedstock is again heavy gas oil or residual fuel oil, and the process is mainly directed at the production of additional middle distillates and gasoline. Since hydrogen is to be recycled, the gases produced in this process again have to be separated into lighter and heavier streams; any surplus recycle gas and the liquefied petroleum gas from the hydrocracking process are both saturated.

In a series of **reforming processes** (Chapter 13), commercialized under names such as **Platforming**, paraffin and naphthene (cyclic nonaromatic) hydrocarbons are converted in the presence of hydrogen and a catalyst and are converted into aromatics or isomerized to more highly branched hydrocarbons. Catalytic reforming processes thus not only result in the formation of a liquid product of higher octane number but also produce substantial quantities of gases. The latter are rich in hydrogen but also contain hydrocarbons from methane to butanes, with a preponderance of propane (CH3CH2CH3), *n*-butane (CH3CH2CH2CH3), and *iso*-butane [(CH3)2CH].
The composition of the process gas varies in accordance with reforming severity and reformer feedstock. All catalytic reforming processes require substantial recycling of a hydrogen stream. Therefore, it is normal to separate reformer gas into a propane \((\text{CH}_3\text{CH}_2\text{CH}_3)\) and/or a butane stream \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3, \text{plus (CH}_3)_3\text{CH})\), which becomes part of the refinery liquefied petroleum gas production, and a lighter gas fraction, part of which is recycled. In view of the excess of hydrogen in the gas, all products of catalytic reforming are saturated, and there are usually no olefin gases present in either gas stream.

Both hydrocracker gases and catalytic reformer gases are commonly used in catalytic desulfurization processes. In the latter, feedstocks ranging from light to vacuum gas oils are passed at pressures of 500–1000 psi with hydrogen over a hydrofining catalyst. This results mainly in the conversion of organic sulfur compounds to hydrogen sulfide,

\[
[S]_{\text{feedstock}} + H_2 \rightarrow H_2S + \text{Hydrocarbons}
\]

This process also produces some light hydrocarbons by hydrocracking. Thus, refinery gas streams, while ostensibly being hydrocarbon in nature, may contain large amounts of acid gases such as hydrogen sulfide and carbon dioxide. Most commercial plants employ hydrogenation to convert organic sulfur compounds into hydrogen sulfide. Hydrogenation is affected by means of recycled hydrogen-containing gases or external hydrogen over a nickel molybdate or cobalt molybdate catalyst.

The presence of impurities in gas streams may eliminate some of the sweetening processes, since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes not designed to remove (or incapable of removing) large amounts of acid gases whereas they are capable of removing the acid gas impurities to very low levels when the acid gases are present only in low-to-medium concentration in the gas.

The processes that have been developed to accomplish gas purification vary from a simple once-through wash operation to complex multistep recycling systems. In many cases, the process complexities arise because of the need for the recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form (Katz, 1959; Kohl and Riesenfeld, 1985; Newman, 1985). In addition to the corrosion of equipment of acid gases (Speight, 2014b), the escape into the atmosphere of sulfur-containing gases can eventually lead to the formation of the constituents of acid rain, that is, the oxides of sulfur (sulfur dioxide, \(\text{SO}_2\), and sulfur trioxide, \(\text{SO}_3\)). Similarly, the nitrogen-containing gases can also lead to nitrous and nitric acids (through the formation of the oxides \(\text{NO}_x\), where \(x = 1\) or 2), which are the other major contributors to acid rain. The release of carbon dioxide and hydrocarbons as constituents of refinery effluents can also influence the behavior and integrity of the ozone layer.

Finally, another acid gas, hydrogen chloride (HCl), although not usually considered to be a major emission, is produced from mineral matter and the brine that often accompany petroleum during production and is gaining increasing recognition as a contributor to acid rain. However, hydrogen chloride may exert severe local effects because it does not need to participate in any further chemical reaction to become an acid. Under atmospheric conditions that favor a buildup of stack emissions in the areas where hydrogen chloride is produced, the amount of hydrochloric acid in rain water could be quite high.

In summary, refinery process gas, in addition to hydrocarbons, may contain other contaminants, such as carbon oxides \((\text{CO}_x, \text{where } x = 1 \text{ and/or } 2)\), sulfur oxides \((\text{SO}_x, \text{where } x = 2 \text{ and/or } 3)\), as well as ammonia \((\text{NH}_3)\), mercaptan derivatives \((\text{RSH})\), and carbonyl sulfide \((\text{COS})\). From an environmental viewpoint, petroleum processing can result in a variety of gaseous emissions. It is a question of degree insofar as the composition of the gaseous emissions may vary from process to process but the constituents are, in the majority of cases, the same.
16.2.2 GAS STREAMS FROM NATURAL GAS

Natural gas is also capable of producing emissions that are detrimental to the environment. While the major constituent of natural gas is methane, there are components such as carbon dioxide (CO₂), hydrogen sulfide (H₂S), and mercaptan derivatives (thiols; RSH), as well as trace amounts of sundry other emissions such as carbonyl sulfide (COS). The fact that methane has a foreseen and valuable end use makes it a desirable product, but in several other situations it is considered a pollutant, having been identified a greenhouse gas.

A sulfur removal process (Table 16.9) must be very precise, since natural gas contains only a small quantity of sulfur-containing compounds that must be reduced several orders of magnitude. Most consumers of natural gas require less than 4 ppm in the gas—a characteristic feature of natural gas that contains hydrogen sulfide is the presence of carbon dioxide (generally in the range of 1%–4% v/v). In cases where the natural gas does not contain hydrogen sulfide, there may also be a relative lack of carbon dioxide.

In practice, scrubbers are usually installed at or near to the wellhead. The scrubbers serve primarily to remove sand and other large-particle impurities and the heaters ensure that the temperature of the gas does not drop too low. With natural gas that contains even low quantities of water, natural gas hydrates (CₙH₂ₙ₊₂·xH₂O) have a tendency to form when temperatures drop. These hydrates are solid or semisolid compounds, resembling ice-like crystals. If the hydrates accumulate, they can impede the passage of natural gas through valves and gathering systems (Zhang et al., 2007). To reduce the occurrence of hydrates, small natural gas-fired heating units are typically installed along the gathering pipe wherever it is likely that hydrates may form.

Natural gas hydrates are usually considered as possible nuisances in the development of oil and gas fields, caution in handling the hydrates cannot be overemphasized because of their tendency to explosively decompose. On the other hand, if handled correctly and with caution, hydrates can be used for the safe and economic storage of natural gas. In remote offshore areas, the use of hydrates for natural gas transportation is also presently considered as an economic alternative to the processes based either on liquefaction or on compression (Lachet and Béhar, 2000).

TABLE 16.9
Sulfur Removal/Recovery Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydrosulfide</td>
<td>Fuel gas containing hydrogen sulfide is contacted with sodium hydroxide in an absorption column. The resulting liquid is the product sodium hydrosulfide (NaHS).</td>
</tr>
<tr>
<td>Iron chelate</td>
<td>Fuel gas containing hydrogen sulfide is contacted with iron chelate catalyst dissolved in solution; hydrogen sulfide is converted to elemental sulfur, which is recovered.</td>
</tr>
<tr>
<td>Stretford</td>
<td>Stretford solution is used instead of iron chelate solution.</td>
</tr>
<tr>
<td>Ammonium thiosulfate</td>
<td>In this process, hydrogen sulfide is contacted with air to form sulfur dioxide, which is contacted with ammonia in a series of absorption column to produce ammonium thiosulfate for offsite sale.</td>
</tr>
<tr>
<td>Hyperion</td>
<td>Fuel gas is contacted over a solid catalyst to form elemental sulfur; the sulfur is collected and sold. The catalyst comprises iron and naphthoquinone sulfonic acid.</td>
</tr>
<tr>
<td>Sulfatreat</td>
<td>The Sulfatreat material is a black, granular solid powder; the hydrogen sulfide forms a chemical bond with the solid; when the bed reaches capacity, the Sulfatreat solids are removed and replaced with fresh material. The sulfur is not recovered.</td>
</tr>
<tr>
<td>Hysulf</td>
<td>Hydrogen sulfide is contacted with a liquid quinone in an organic solvent such as n-methyl-2-pyrolidone (NMP), forming sulfur; the sulfur is removed and the quinone reacted to its original state, producing hydrogen gas.</td>
</tr>
</tbody>
</table>
16.3 ENRICHMENT

The natural gas product fed into a gas transportation system must meet specific quality measures in order for the pipeline grid to operate properly. Consequently, natural gas produced at the wellhead, which in most cases contains contaminants and natural gas liquids, must be processed, that is, cleaned, before it can be safely delivered to the high-pressure, long-distance pipelines that transport the product to the consuming public. Natural gas that is not within certain specific gravities, pressures, Btu content range, or water content levels will cause operational problems, pipeline deterioration, or can even cause pipeline rupture. Thus, the purpose of enrichment is to produce natural gas for sale and enriched tank oil. The tank oil contains more light hydrocarbon liquids than natural petroleum, and the residue gas is drier (leaner, i.e., has lesser amounts of the higher-molecular-weight hydrocarbons). Therefore, the process concept is essentially the separation of hydrocarbon liquids from the methane to produce a lean, dry gas.

The natural gas received and transported must (especially in the United States and many other countries) meet the quality standards specified by the pipeline. These quality standards vary from pipeline to pipeline and are usually a function of (1) the design of the pipeline system, (2) the design of any downstream interconnecting pipelines, and (3) the requirements of the customer. In general, these standards specify that the natural gas should (1) be within a specific Btu content range, typically 1035 ± 50 Btu ft\(^3\); (2) be delivered at a specified hydrocarbon dew point temperature level to prevent any vaporized gas liquid in the mix from condensing at pipeline pressure; (3) contain no more than trace amounts of elements such as hydrogen sulfide, carbon dioxide, nitrogen, water vapor, and oxygen; and (4) be free of particulate solids and liquid water that could be detrimental to the pipeline or its ancillary operating equipment. Gas processing equipment, whether in the field or at processing/treatment plants, assures that these specifications can be met.

In most cases, processing facilities extract contaminants and higher-boiling hydrocarbons from the gas stream. However, in some cases, the gas processors blend higher-boiling hydrocarbons into the gas stream in order to bring it within acceptable Btu levels. For example, in some areas if the produced gas (including coalbed methane) does not meet specifications the Btu requirements of the pipeline operator, in which case a blend of higher-Btu-content natural gas or a propane–air mixture is injected to enrich the heat content (Btu value) prior to delivery to the pipeline. In other instances, such as at liquefied natural gas (LNG) import facilities where the heat content of the regasified gas may be too high for pipeline receipt, vaporized nitrogen may be injected into the natural gas stream to lower its Btu content.

Briefly, and because it is sometime combined with petroleum-based natural gas for processing purposes, coalbed methane (CBM) is the generic term given to methane gas held in coal and released or produced when the water pressure within the buried coal is reduced by pumping from either vertical or inclined to horizontal surface holes. Thermogenic coalbed methane is predominantly formed during the coalification process whereby organic matter is slowly transformed into coal by increasing temperature and pressure as the organic matter is buried deeper and deeper by additional deposits of organic and inorganic matter over long periods of geological time. On the other hand, late-stage biogenic coalbed methane is formed by relatively recent bacterial processes (involving naturally occurring bacteria associated with meteoric water recharge at outcrop or subcrop), which can dominate the generation of coalbed methane. The amount of methane stored in coal is closely related to the rank and depth of the coal: the higher the coal rank and the deeper the coal seam is presently buried (causing pressure on coal), the greater its capacity to produce and retain methane gas. Gas derived from coal is generally pure and requires little or no processing because it is solely methane and not mixed with heavier hydrocarbons, such as ethane, which is often present in conventional natural gas.

The number of steps and the type of techniques used in the process of creating pipeline-quality natural gas most often depends upon the source and makeup of the wellhead production stream. Among the several stages of gas processing are (1) gas oil separation, (2) water removal, (3) liquids removal, (4) nitrogen removal, (5) acid gas removal, and (6) fractionation.
In many instances, pressure relief at the wellhead will cause a natural separation of gas from oil (using a conventional closed tank, where gravity separates the gas hydrocarbons from the heavier oil). In some cases, however, a multistage gas–oil separation process is needed to separate the gas stream from the crude oil. These gas–oil separators are commonly closed cylindrical shells, horizontally mounted with inlets at one end, an outlet at the top for the removal of gas, and an outlet at the bottom for the removal of oil. Separation is accomplished by alternately heating and cooling (by compression) the flow stream through multiple steps. However, the number of steps and the type of techniques used in the process of creating pipeline-quality natural gas most often depend upon the source and makeup of the gas stream. In some cases, several of the steps may be integrated into one unit or operation, performed in a different order or at alternative locations (lease/plant), or not required at all.

16.4 WATER REMOVAL

Water is a common impurity in gas streams, and removal of water is necessary to prevent the condensation of the water and the formation of ice or the formation of gas hydrates (USGS, 2014). Water in the liquid phase causes corrosion or erosion problems in pipelines and equipment, particularly when carbon dioxide and hydrogen sulfide are present in the gas. The simplest method of water removal (refrigeration or cryogenic separation) is to cool the gas to a temperature at least equal to or (preferentially) below the dew point (Figure 16.2).

In addition to separating petroleum and some condensate from the wet gas stream, it is necessary to remove most of the associated water. Most of the liquid, free water associated with extracted natural gas is removed by simple separation methods at or near the wellhead. However, the removal of the water vapor that exists in solution in natural gas requires a more complex treatment. This treatment consists of dehydrating the natural gas, which usually involves one of two processes: either absorption or adsorption.

Absorption occurs when the water vapor is taken out by a dehydrating agent. Adsorption occurs when the water vapor is condensed and collected on the surface. In a majority of cases, cooling alone is insufficient and, for the most part, impractical for use in field operations. Other more convenient water removal options use (1) hygroscopic liquids (e.g., diethylene glycol or triethylene glycol) and (2) solid adsorbents or desiccants (e.g., alumina, silica gel, and molecular sieves). Ethylene glycol can be directly injected into the gas stream in refrigeration plants.

![Figure 16.2 Glycol refrigeration process. (From Geist, J.M., Oil Gas J., 83 56, 1985.)](image-url)
16.4.1 Absorption

An example of absorption dehydration is known as glycol dehydration—the principal agent in this process is diethylene glycol, which has a chemical affinity for water (Mokhatab et al., 2006; Speight, 2007; Abdel-Aal et al., 2016). Glycol dehydration involves using a solution of a glycol such as diethylene glycol (DEG) or triethylene glycol (TEG), which is brought into contact with the wet gas stream in a contactor. In practice, absorption systems recover 90%–99% by volume of methane that would otherwise be flared into the atmosphere.

In the process, a liquid desiccant dehydrator serves to absorb water vapor from the gas stream. The glycol solution absorbs water from the wet gas and, once absorbed, the glycol particles become heavier and sink to the bottom of the contactor where they are removed. The dry natural gas is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the natural gas, is recycled through a specialized boiler designed to vaporize only the water out of the solution. The boiling point differential between water (100°C, 212°F) and glycol (204°C, 400°F) makes it relatively easy to remove water from the glycol solution.

As well as absorbing water from the wet gas stream, the glycol solution occasionally carries with it small amounts of methane and other compounds found in the wet gas. In order to decrease the amount of methane and other compounds that would otherwise be lost, flash tank separator condensers are employed to remove these compounds before the glycol solution reaches the boiler. The flash tank separator (Chapter 6) consists of a device that reduces the pressure of the glycol solution stream, allowing the methane and other hydrocarbons to vaporize (flash). The glycol solution then travels to the boiler, which may also be fitted with air or water-cooled condensers, which serve to capture any remaining organic compounds that may remain in the glycol solution. The regeneration (stripping) of the glycol is limited by temperature: diethylene glycol and triethylene glycol decompose at or even before their respective boiling points. Such techniques as stripping of hot triethylene glycol with dry gas (e.g., heavy hydrocarbon vapors, the Drizo process) or vacuum distillation are recommended.

Another absorption process, the Rectisol process, is a physical acid gas removal process using an organic solvent (typically methanol) at subzero temperatures, and characteristic of physical acid gas removal processes, it can purify synthesis gas down to 0.1 ppm total sulfur, including hydrogen sulfide (H₂S) and carbonyl sulfide (COS), and carbon dioxide (CO₂) in the ppm range (Mokhatab et al., 2006; Liu et al., 2010; Abdel-Aal et al., 2016). The process uses methanol as a wash solvent and the wash unit operates at temperatures below 0°C (32°F). To lower the temperature of the feed as temperatures, it is cooled against the cold-product streams, before entering the absorber tower. At the absorber tower, carbon dioxide and hydrogen sulfide (with carbonyl sulfide) are removed. By the use of an intermediate flash, coabsorbed products such as hydrogen and carbon monoxide are recovered, thus increasing the product recovery rate. To reduce the required energy demand for the carbon dioxide compressor, the carbon dioxide product is recovered in two different pressure steps (medium pressure and lower pressure). The carbon dioxide product is essentially sulfur-free (H₂S-free, COS-free) and water-free. The carbon dioxide products can be used for enhanced oil recovery (EOR) and/or sequestration or as pure carbon dioxide for other processes.

16.4.2 Solid Adsorbents

Adsorption is a physical–chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. It must be emphasized that adsorption differs from absorption in that absorption is not a physical–chemical surface phenomenon but a process in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). Dehydration using a solid adsorbent or solid desiccant is the primary form of dehydrating natural gas using adsorption and usually consists of two or more adsorption towers, which are filled with a solid desiccant (Mokhatab et al., 2006; Speight, 2007; Abdel-Aal et al., 2016). Typical desiccants include activated alumina or
a granular silica gel material. Wet natural gas is passed through these towers, from top to bottom. As the wet gas passes around the particles of desiccant material, water is retained on the surface of these desiccant particles. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit the bottom of the tower. There are several solid desiccants that possess the physical characteristic to adsorb water from natural gas. These desiccants are generally used in dehydration systems consisting of two or more towers and associated regeneration equipment.

Molecular sieves—a class of aluminosilicates that produce the lowest water dew points and can be used to simultaneously sweeten and dry gases and liquids (Mokhatab et al., 2006; Speight, 2007; Maple, and Williams 2008; Abdel-Aal et al., 2016)—are commonly used in dehydrators ahead of plants designed to recover ethane and other natural gas liquids. These plants operate at very cold temperatures and require very dry feed gas to prevent the formation of hydrates. Dehydration to −100°C (−148°F) dew point is possible with molecular sieves. Water dew points less than −100°C (−148°F) can be accomplished with special design and definitive operating parameters (Mokhatab et al., 2006).

Molecular sieves are commonly used to selectively adsorb water and sulfur compounds from light hydrocarbon streams such as liquefied petroleum gas (LPG), propane, butane, pentane, light olefins, and alkylation feed. Sulfur compounds that can be removed are hydrogen sulfide, mercaptan derivatives, sulfide derivatives, and disulfide derivatives. In the process, the sulfur-containing feedstock is passed through a bed of sieves at ambient temperature. The operating pressure must be high enough to keep the feed in the liquid phase. The operation is cyclic in that the adsorption step is stopped at a predetermined time before sulfur breakthrough occurs. Sulfur and water are removed from the sieves by purging with fuel gas at 205°C–315°C (400°F–600°F).

Solid-adsorbent dehydrators are typically more effective than liquid absorption dehydrators (e.g., glycol dehydrators) and are usually installed as a type of straddle system along natural gas pipelines. These types of dehydration systems are best suited for large volumes of gas under very high pressure and are thus usually located on a pipeline downstream of a compressor station. Two or more towers are required due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water. To regenerate and recycle the desiccant, a high-temperature heater is used to heat gas to a very high temperature and passage of the heated gas stream through a saturated desiccant bed vaporizes the water in the desiccant tower, leaving it dry and allowing for further natural gas dehydration.

Although two-bed adsorbent treaters have become more common (while one bed is removing water from the gas, the other undergoes alternate heating and cooling), on occasion, a three-bed system is used: one bed adsorbs, one is being heated, and one is being cooled. An additional advantage of the three-bed system is the facile conversion of a two-bed system so that the third bed can be maintained or replaced, thereby ensuring the continuity of the operations and reducing the risk of a costly plant shutdown.

Silica gel (SiO₂) and alumina (Al₂O₃) have good capacities for water adsorption (up to 8% by weight). Bauxite (crude alumina, Al₂O₃) adsorbs up to 6% by weight water, and molecular sieves adsorb up to 15% by weight water. Silica is usually selected for the dehydration of sour gas because of its high tolerance to hydrogen sulfide and to protect molecular sieve beds from plugging by sulfur. Alumina guard beds, which serve as protectors by the act of attrition and may be referred to as an attrition reactor containing an attrition catalyst (Chapter 6; Speight, 2000, 2014a), may be placed ahead of the molecular sieves to remove the sulfur compounds. Downflow reactors are commonly used for adsorption processes, with an upward flow regeneration of the adsorbent and cooling using gas flow in the same direction as adsorption flow.

Solid desiccant units generally cost more to buy and operate than glycol units. Therefore, their use is typically limited to applications such as gases having a high hydrogen sulfide content, very low water dew point requirements, simultaneous control of water, and hydrocarbon dew points. In processes where cryogenic temperatures are encountered, solid desiccant dehydration is usually preferred over conventional methanol injection to prevent hydrate and ice formation (Kidnay and Parrish, 2006).
16.4.3 Membranes

Membrane separation process are very versatile and are designed to process a wide range of feedstocks and offer a simple solution for the removal and recovery of higher-boiling hydrocarbons (natural gas liquids) from natural gas (Figure 16.3; Foglietta, 2004; Abdel-Aal et al., 2016). The separation process is based on high-flux membranes that selectively permeate higher-boiling hydrocarbons (compared to methane) and are recovered as a liquid after recompression and condensation. The residue stream from the membrane is partially depleted of higher-boiling hydrocarbons and is then sent to sales gas stream. Gas permeation membranes are usually made with vitreous polymers that exhibit good selectivity but, to be effective, the membrane must be very permeable with respect to the separation process.

16.5 LIQUID REMOVAL

Natural gas coming directly from a well contains higher-molecular-weight hydrocarbons, often referred to as natural gas liquids (NGLs) that, in most instances (depending upon the market demand), have a higher value as separate products and making it worthwhile to remove these constituents from the gas stream (Mokhatab et al., 2006; Speight, 2007; Abdel Aal et al., 2016). The removal of natural gas liquids usually takes place in a relatively centralized processing plant and uses techniques similar to those used to dehydrate natural gas. There are two basic steps to the treatment of natural gas liquids in the natural gas stream. In the first step, the liquids must be extracted from the natural gas and in the second step the natural gas liquids must be separated into the base constituents. These two processes account for approximately 90% v/v of the total production of natural gas liquids.

In many cases, before pipelining, condensate liquids are most often removed from the gas stream at the wellhead through the use of mechanical separators. In most instances, the gas flow into the separator comes directly from the wellhead, since the gas–oil separation process is not needed. The gas stream enters the processing plant at high pressure (≥600 psi) through an inlet slug catcher where free water is removed from the gas, after which it is directed to a condensate separator. Extracted condensate is routed to on-site storage tanks.

FIGURE 16.3 Membrane separation process.
16.5.1 Extraction

There are two principle techniques for removing natural gas liquids from the natural gas stream: the absorption method and the cryogenic expander process. In the process, a turboexpander is used to produce the necessary refrigeration and very low temperatures and high recovery of light components, such as ethane and propane, can be attained. The natural gas is first dehydrated using a molecular sieve followed by the cooling of the dry stream (Figure 16.4). The separated liquid containing most of the heavy fractions is then demethanized, and the cold gases are expanded through a turbine that produces the desired cooling for the process. The expander outlet is a two-phase stream that is fed to the top of the demethanizer column. This serves as a separator in which (1) the liquid is used as the column reflux and the separator vapors combined with vapors stripped in the demethanizer are exchanged with the feed gas and (2) the heated gas, which is partially recompressed by the expander compressor, is further recompressed to the desired distribution pressure in a separate compressor.

The extraction of natural gas liquids from the natural gas stream produces both cleaner, purer natural gas, as well as the valuable hydrocarbons that are the natural gas liquids themselves. This process allows for the recovery of approximately 90%–95% v/v of the ethane originally in the gas stream. In addition, the expansion turbine is able to convert some of the energy released when the natural gas stream is expanded into recompressing the gaseous methane effluent, thus saving energy costs associated with extracting ethane.

16.5.2 Absorption

The absorption method of extraction is very similar to using absorption for dehydration. The main difference is that, in the absorption of natural gas liquids, absorbing oil is used as opposed to glycol. This absorbing oil has an affinity for natural gas liquids in much the same manner as glycol has an affinity for water. Before the oil has picked up any natural gas liquids, it is termed lean absorption oil.

The oil absorption process involves the countercurrent contact of the lean (or stripped) oil with the incoming wet gas with the temperature and pressure conditions programmed to maximize the dissolution of the liquefiable components in the oil. The rich absorption oil (sometimes referred to as

as *fat oil*), containing natural gas liquids, exits the absorption tower through the bottom. It is now a mixture of absorption oil, propane, butanes, pentanes, and other higher-boiling hydrocarbons. The rich oil is fed into lean oil stills, where the mixture is heated to a temperature above the boiling point of the natural gas liquids but below that of the oil. This process allows for the recovery of around 75% v/v of the butane isomers and 85%–90% v/v of the pentane isomers and higher-boiling constituents from the natural gas stream.

The basic absorption process is subject to modifications that improve process effectiveness and even target the extraction of specific natural gas liquids. In the refrigerated oil absorption method, where the lean oil is cooled through refrigeration, propane recovery can be in the order of 90%+ v/v, and approximately 40% v/v of the ethane can be extracted from the natural gas stream. Extraction of the other, higher-boiling natural gas hydrocarbons is typically near quantitative using this process.

The AET process (Figure 16.5) for the recovery of liquefied petroleum gas utilizes noncryogenic absorption to recover ethane, propane, and higher-boiling constituents from natural gas streams. The absorbed gases in the rich solvent from the bottom of the absorber column are fractionated in the solvent regenerator column that separates gases (as an overhead fraction) and lean solvent (as a bottoms fraction). After heat recuperation, the lean solvent is presaturated with absorber overhead gases. The chilled solvent flows in the top of the absorber column. The separated gases are sent to storage. Depending upon the economics of ethane recovery, the operation of the plant can be switched online from ethane plus recovery to propane plus recovery without affecting the propane recovery levels. The AET-liquefied petroleum gas plant uses lower-boiling lean oils. For most applications, there are no solvent makeup requirements.

### 16.5.3 Fractionation of Natural Gas Liquids

After separation of the natural gas liquids from the natural gas stream, they must be separated (fractionated) into the individual constituents prior to sales. The process of fractionation (which is based on the different boiling points of the hydrocarbons that constitute the natural gas liquids) occurs in stages with each stage involving the separation of the hydrocarbons as individual products. The process commences with the removal of the lower-boiling hydrocarbons from the feedstock. The particular fractionators are used in the following order: (1) the deethanizer, which is used to separate the ethane from the stream of natural gas liquids; (2) the depentanizer, which is used to separate
the propane from the deethanized stream; (3) the debutanizer, which is used to separate the butane isomers, leaving the pentane isomers and higher-boiling hydrocarbons in the stream; and (4) the butane splitter or deisobutanizer, which is used to separate \( n \)-butane and \( iso \)-butane.

### 16.6 Nitrogen Removal

Nitrogen may often occur in sufficient quantities in natural gas and, consequently, lower the heating value of the gas. Thus, several plants for nitrogen removal from natural gas have been built, but it must be recognized that nitrogen removal requires liquefaction and fractionation of the entire gas stream, which may affect process economics. In some cases, the nitrogen-containing natural gas is blended with a gas having a higher heating value and sold at a reduced price depending upon the thermal value (Btu/ft\(^3\)).

For high-flow-rate gas streams, a cryogenic process is typical and involves the use of the different volatilities of methane (b.p. \(-161.6^\circ\text{C} / -258.9^\circ\text{F}\)) and nitrogen (b.p. \(-195.7^\circ\text{C} / -320.3^\circ\text{F}\)) to achieve separation. In the process, a system of compression and distillation columns drastically reduces the temperature of the gas mixture to a point where methane is liquefied and the nitrogen is not. On the other hand, for smaller volumes of gas, a system utilizing pressure swing adsorption (PSA) is a more typical method of separation. In pressure swing adsorption method, methane and nitrogen can be separated by using an adsorbent with an aperture size very close to the molecular diameter of the larger species (the methane), which allows nitrogen to diffuse through the adsorbent. This results in a purified natural gas stream that is suitable for pipeline specifications. The adsorbent can then be regenerated, leaving a highly pure nitrogen stream. The pressure swing adsorption method is a flexible method for nitrogen rejection, being applied to both small and large flow rates.

### 16.7 Acid Gas Removal

In addition to water and natural gas liquids removal, one of the most important parts of gas processing involves the removal of hydrogen sulfide and carbon dioxide, which are generally referred to as contaminants. Natural gas from some wells contains significant amounts of hydrogen sulfide and carbon dioxide and is usually referred to as sour gas. Sour gas is undesirable because the sulfur compounds it contains can be extremely harmful, even lethal, to breathe and the gas can also be extremely corrosive. The process for removing hydrogen sulfide from sour gas is commonly referred to as sweetening the gas.

The primary process (Figure 16.6) for sweetening sour natural gas is quite similar to the processes of glycol dehydration and removal of natural gas liquids by absorption. In this case, however, amine (olamine) solutions are used to remove the hydrogen sulfide (the amine process). The sour gas is run through a tower, which contains the amine solution. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from natural gas as it passes through. The effluent gas is virtually free of sulfur compounds and thus loses its sour gas status. Like the process for the extraction of natural gas liquids and glycol dehydration, the amine solution used can be regenerated for reuse. Although most sour gas sweetening involves the amine absorption process, it is also possible to use solid desiccants like iron sponge to remove hydrogen sulfide and carbon dioxide (Mokhatab et al., 2006; Speight, 2007; Abdel-Aal et al., 2016).

Treatment of gas to remove the acid gas constituents (hydrogen sulfide and carbon dioxide) is most often accomplished by the contact of the natural gas with an alkaline solution. The most commonly used treating solutions are aqueous solutions of the ethanolamine (Table 16.3) or alkali carbonates, although a considerable number of other treating agents have been developed in recent years. Most of these newer treating agents rely upon physical absorption and chemical reaction. When only carbon dioxide is to be removed in large quantities or when only partial removal is necessary, a hot carbonate solution or one of the physical solvents is the most economical selection.
The most well-known hydrogen sulfide removal process is based on the reaction of hydrogen sulfide with iron oxide (often also called the iron sponge process or the dry box method) in which the gas is passed through a bed of wood chips impregnated with iron oxide.

The iron oxide process (which was implemented during the nineteenth century and also referred to as the iron sponge process) is the oldest and still the most widely used batch process for sweetening natural gas and natural gas liquids (Zapffe, 1963; Duckworth and Geddes, 1965; Anerousis and Whitman, 1984; Mokhatab et al., 2006; Speight, 2014a). In the process (Figure 16.7), the sour gas is passed down through the bed. In the case where continuous regeneration is to be utilized, a small concentration of air is added to the sour gas before it is processed. This air serves to continuously regenerate the iron oxide, which has reacted with hydrogen sulfide, which serves to extend the onstream life of a given tower but probably serves to decrease the total amount of sulfur that a given weight of bed will remove.

The process is usually best applied to gases containing low to medium concentrations (300 ppm) of hydrogen sulfide or mercaptan derivatives. This process tends to be highly selective and does not
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normally remove significant quantities of carbon dioxide. As a result, the hydrogen sulfide stream from the process is usually of high purity. The use of iron oxide process for sweetening sour gas is based on the adsorption of the acid gases on the surface of the solid sweetening agent followed by the chemical reaction of ferric oxide (Fe₂O₃) with hydrogen sulfide:

$$2\text{Fe}_2\text{O}_3 + 6\text{H}_2\text{S} \rightarrow 2\text{Fe}_2\text{S}_3 + 6\text{H}_2\text{O}$$

The reaction requires the presence of slightly alkaline water and a temperature below 43°C (110°F) and bed alkalinity (pH +8 to 10) should be checked regularly, usually on a daily basis. The pH level is be maintained through the injection of caustic soda with the water. If the gas does not contain sufficient water vapor, water may need to be injected into the inlet gas stream.

The ferric sulfide produced by the reaction of hydrogen sulfide with ferric oxide can be oxidized with air to produce sulfur and regenerate the ferric oxide:

$$2\text{Fe}_2\text{S}_3 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 6\text{S}$$

$$\text{S}_2 + 2\text{O}_2 \rightarrow 2\text{SO}_2$$

The regeneration step is exothermic and air must be introduced slowly so that the heat of reaction can be dissipated. If air is introduced quickly, the heat of reaction may ignite the bed. Some of the elemental sulfur produced in the regeneration step remains in the bed. After several cycles this sulfur will cake over the ferric oxide, decreasing the reactivity of the bed. Typically, after 10 cycles the bed must be removed and a new bed introduced into the vessel.

The iron oxide process is one of several metal oxide-based processes that scavenge hydrogen sulfide and organic sulfur compounds (mercaptan derivatives) from gas streams through reactions with the solid-based chemical adsorbent (Kohl and Riesenfeld, 1985). They are typically nonregenerable, although some are partially regenerable, losing activity upon each regeneration cycle. Most of the processes are governed by the reaction of a metal oxide with hydrogen sulfide to form the metal sulfide. For regeneration, the metal oxide is reacted with oxygen to produce elemental sulfur and the regenerated metal oxide. In addition to iron oxide, the primary metal oxide used for dry sorption processes is zinc oxide.

In the zinc oxide process, the zinc oxide media particles are extruded cylinders 3–4 mm in diameter and 4–8 mm in length (Kohl and Nielsen, 1997; Mokhatab et al., 2006; Speight, 2007; Abdel-Aal et al., 2016) and react readily with the hydrogen sulfide:

$$\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$$

At increased temperatures (205°C–370°C, 400°F–700°F), zinc oxide has a rapid reaction rate, thereby providing a short mass transfer zone, resulting in a short length of the unused bed and improved efficiency.

Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the Ferrox process or the Stretford process. The Ferrox process is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The Stretford process employs a solution containing vanadium salts and anthraquinone disulfonic acid (Maddox, 1974; Abdel-Aal et al., 2016). Most hydrogen sulfide removal processes return the hydrogen sulfide unchanged, but if the quantity involved does not justify the installation of a sulfur recovery plant (usually a Claus plant), it is necessary to select a process that directly produces elemental sulfur. In the Beavon–Stretford process, a hydrotreating reactor converts sulfur dioxide in the off-gas to hydrogen sulfide, which is contacted with Stretford solution (a mixture of vanadium salt, anthraquinone disulfonic acid, sodium carbonate, and sodium hydroxide) in a liquid–gas absorber. The hydrogen sulfide reacts stepwise with sodium carbonate and anthraquinone disulfonic acid to produce elemental...
sulfur, with vanadium serving as a catalyst. The solution proceeds to a tank where oxygen is added to regenerate the reactants. One or more froth or slurry tanks are used to skim the product sulfur from the solution, which is recirculated to the absorber.

The processes using ethanalamine and potassium phosphate are now widely used. The ethanalamine process, known as the Girbotol process, removes acid gases (hydrogen sulfide and carbon dioxide) from liquid hydrocarbons as well as from natural and from refinery gases. The Girbotol process uses an aqueous solution of ethanalamine (H₃NCH₂CH₂OH) that reacts with hydrogen sulfide at low temperatures and releases hydrogen sulfide at high temperatures. The ethanalamine solution fills a tower called an absorber through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanalamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanalamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanalamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator.

The process using potassium phosphate is known as phosphate desulfurization, and it is used in the same way as the Girbotol process to remove acid gases from liquid hydrocarbons as well as from gas streams. The treatment solution is a water solution of potassium phosphate (K₃PO₄), which is circulated through an absorber tower and a reactivator tower in much the same way as the ethanalamine is circulated in the Girbotol process; the solution is regenerated thermally.

Moisture may be removed from hydrocarbon gases at the same time as hydrogen sulfide is removed. Moisture removal is necessary to prevent harm to anhydrous catalysts and to prevent the formation of hydrocarbon hydrates (e.g., C₃H₆·18H₂O) at low temperatures. A widely used dehydration and desulfurization process is the glycolamine process, in which the treatment solution is a mixture of ethanalamine and a large amount of glycol. The mixture is circulated through an absorber and a reactivator in the same way as ethanalamine is circulated in the Girbotol process. The glycol absorbs moisture from the hydrocarbon gas passing up the absorber; the ethanalamine absorbs hydrogen sulfide and carbon dioxide. The treated gas leaves the top of the absorber; the spent ethanalamine–glycol mixture enters the reactivator tower, where heat drives off the absorbed acid gases and water.

Other processes include the Alkazid process for the removal of hydrogen sulfide and carbon dioxide using concentrated aqueous solutions of amino acids. The hot potassium carbonate process decreases the acid content of natural and refinery gas from as much as 50% to as low as 0.5% and operates in a unit similar to that used for amine treating. The Giammarco–Vetrocoke process is used for hydrogen sulfide and/or carbon dioxide removal. In the hydrogen sulfide removal section, the reagent consists of sodium carbonate (Na₂CO₃) or potassium carbonate (K₂CO₃) or a mixture of the carbonates, which contain a mixture of arsenite derivatives and arsenate derivatives; the carbon dioxide removal section utilizes hot aqueous alkali carbonate solution activated by arsenic trioxide (As₂O₃) or selenous acid (H₂SeO₃) or tellurous acid (H₂TeO₃). A word of caution might be added about the last three chemicals, which are toxic and can involve stringent environmental-related disposal protocols.

Molecular sieves are highly selective for the removal of hydrogen sulfide (as well as other sulfur compounds) from gas streams and over continuously high absorption efficiency. They are also an effective means of water removal and thus offer a process for the simultaneous dehydration and desulfurization of gas. Gas that has excessively high water content may require upstream dehydration, however (Mokhatab et al., 2006; Speight, 2007, 2014a; Abdel-Aal et al., 2016). The molecular sieve process is similar to the iron oxide process. Regeneration of the bed is achieved by passing heated clean gas over the bed. As the temperature of the bed increases, it releases the adsorbed hydrogen sulfide into the regeneration gas stream. The sour effluent regeneration gas is sent to a flare stack, and up to 2% v/v of the gas seated can be lost in the regeneration process. A portion of the natural gas may also be lost by the adsorption of hydrocarbon components by the sieve (Mokhatab et al., 2006; Speight, 2007, 2014a).
In this process, unsaturated hydrocarbon components, such as olefins and aromatics, tend to be strongly adsorbed by the molecular sieve. Molecular sieves are susceptible to poisoning by such chemicals as glycols and require thorough gas cleaning methods before the adsorption step. Alternatively, the sieve can be offered some degree of protection by the use of guard beds in which a less expensive catalyst is placed in the gas stream before contact of the gas with the sieve, thereby protecting the catalyst from poisoning. This concept is analogous to the use of guard beds or attrition catalysts in the petroleum industry (Speight, 2000).

Other processes worthy of note include (1) the Selexol process, (2) the Sulfinol process, (3) the LOCAT process, and (4) the Sulferox process (Mokhatab et al., 2006; Abdel-Aal et al., 2016).

The Selexol process uses a mixture of the dimethyl ether of propylene glycol as a solvent. It is nontoxic and its boiling point is not high enough for amine formulation. The selectivity of the solvent for hydrogen sulfide (H₂S) is much higher than that for carbon dioxide (CO₂), so it can be used to selectively remove these different acid gases, minimizing carbon dioxide content in the hydrogen sulfide stream sent to the sulfur recovery unit (SRU) and enabling the regeneration of solvent for carbon dioxide recovery by economical flashing. In the process, a stream of natural gas is injected in the bottom of the absorption tower operated at 1000 psi. The rich solvent is flashed in a flash drum (flash reactor) at 200 psi where methane is flashed and recycled back to the absorber and joins the sweet (low-sulfur or no-sulfur) gas stream. The solvent is then flashed at atmospheric pressure and acid gases are flashed off. The solvent is then stripped by steam to completely regenerate the solvent, which is recycled back to the absorber. Any hydrocarbons are condensed, and any remaining acid gases are flashed from the condenser drum. This process is used when there is a high acid gas partial pressure and no heavy hydrocarbons. Diisopropanolamine (DIPA) can be added to this solvent to remove carbon dioxide to a level suitable for pipeline transportation.

The Sulfinol process uses a solvent that is a composite solvent, consisting of a mixture of diisopropanolamine (30%–45% v/v) or methyl diethanolamine (MDEA), sulfolane (tetrahydrothiophene dioxide) (40%–60% v/v), and water (5%–15% v/v). The acid gas loading of the Sulfinol solvent is higher, and the energy required for its regeneration is lower than those of purely chemical solvents. At the same time, it has the advantage over purely physical solvents that severe product specifications can be met more easily and coabsorption of hydrocarbons is relatively low. Aromatic compounds, higher-molecular-weight hydrocarbons, and carbon dioxide are soluble to a lesser extent. The process is typically used when the hydrogen sulfide–carbon dioxide ratio is greater than 1:1 or where carbon dioxide removal is not required to the same extent as hydrogen sulfide removal. The process uses a conventional solvent absorption and regeneration cycle in which the sour gas components are removed from the feed gas by countercurrent contact with a lean solvent stream under pressure. The absorbed impurities are then removed from the rich solvent by stripping with steam in a heated regenerator column. The hot lean solvent is then cooled for reuse in the absorber. Part of the cooling may be by heat exchange with the rich solvent for partial recovery of heat energy. The solvent reclaimer is used in a small ancillary facility for recovering solvent components from higher-boiling products of alkanolamine degradation or from other high-boiling or solid impurities.

The LOCAT process uses an 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, sour gas is contacted with the chelating reagent in the absorber and H₂S reacts with the dissolved iron to form elemental sulfur:

\[
\text{H}_2\text{S} + 2\text{Fe}^{3+} \rightarrow \text{S} + 2\text{Fe}^{2+} + 2\text{H}^+ 
\]

The sulfur is removed from the regenerator to centrifugation and melting. Application of heat is not required because of the exothermic reaction. The reduced iron ion is regenerated in the regenerator by air blowing:

\[
4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^- 
\]
In the Sulferox process, chelating iron compounds are the heart of the process. Sulferox is a redox technology, as is the LOCAT; however, in this case, a concentrated iron solution is used to oxidize hydrogen sulfide to elemental sulfur. 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 becomes small. As in the LOCAT process, there are two basic reactions: the first takes place in the absorber and the second takes place in the regenerator, as in reaction. The key to the Sulferox technology is the ligand used in the process that allows the process to use high total iron concentrations (>1% w/w). In the process, the acid gas enters the contactor, where hydrogen sulfide is oxidized to produce 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 ferrous iron (Fe$^{2+}$) is oxidized by air to ferric iron (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. A makeup Sulferox solution is added to replace the degradation of the ligands. Control of this degradation rate and purging of the degradation products ensures smooth operation of the process.

### 16.8 FRACTIONATION

Fractionation processes are very similar to those processes classed as liquids removal processes but often appear to be more specific in terms of the objectives: hence the need to place the fractionation processes into a separate category. The fractionation processes are those processes that are used (1) to remove the more significant product stream first or (2) to remove any unwanted light ends from the heavier liquid products.

In the general practice of natural gas processing, the first unit is a deethanizer followed by a depropanizer, then by a debutanizer, and finally, by a butane fractionator. Thus, each column can operate at a successively lower pressure, thereby allowing the different gas streams to flow from column to column by virtue of the pressure gradient, without necessarily the use of pumps.

The purification of hydrocarbon gases by any of these processes is an important part of refinery operations, especially in regard to the production of liquefied petroleum gas (LPG). This is actually a mixture of propane and butane, which is an important domestic fuel, as well as an intermediate material in the manufacture of petrochemicals (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a). The presence of ethane in liquefied petroleum gas must be avoided because of the inability of this lighter hydrocarbon to liquefy under pressure at ambient temperatures and its tendency to register abnormally high pressures in the liquefied petroleum gas containers. On the other hand, the presence of pentane in liquefied petroleum gas must also be avoided, since this particular hydrocarbon (a liquid at ambient temperatures and pressures) may separate into a liquid state in the gas lines.

### 16.9 CLAUS PROCESS

The Claus process is not so much a gas cleaning process but a process for the disposal of hydrogen sulfide, a toxic gas that originates in natural gas as well as during crude oil processing such as in the coking, catalytic cracking, hydrotreating, and hydrocracking processes. Burning hydrogen sulfide as a fuel gas component or as a flare gas component is precluded by safety and environmental considerations since one of the combustion products is the highly toxic sulfur dioxide (SO$_2$), which is also toxic. As described earlier, hydrogen sulfide is typically removed from the refinery light end gas streams through an olamine process after which the application of heat regenerates the olamine and forms an acid gas stream. Following from this, the acid gas stream is treated to convert the hydrogen sulfide elemental sulfur and water. The conversion process utilized in most modern refineries is the Claus process, or a variant thereof.
The Claus process (Figure 16.8) involves combustion of approximately one-third of the hydrogen sulfide to sulfur dioxide and then reaction of the sulfur dioxide with the remaining hydrogen sulfide in the presence of a fixed bed of activated alumina, cobalt molybdenum catalyst resulting in the formation of elemental sulfur:

\[
2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O
\]

\[
2H_2S + SO_2 \rightarrow 3S + 2H_2O
\]

Different process flow configurations are used to achieve the correct hydrogen sulfide/sulfur dioxide ratio in the conversion reactors.

In a split-flow configuration, one-third split of the acid gas stream is completely combusted and the combustion products are then combined with the noncombusted acid gas upstream of the conversion reactors. In a once-through configuration, the acid gas stream is partially combusted by only providing sufficient oxygen in the combustion chamber to combust one-third of the acid gas. Two or three conversion reactors may be required depending on the level of hydrogen sulfide conversion required. Each additional stage provides incrementally less conversion than the previous stage.

Overall, conversion of 96%–97% v/v of the hydrogen sulfide to elemental sulfur is achievable in a Claus process. If this is insufficient to meet air quality regulations, a Claus process tail gas treater is utilized to remove essentially the entire remaining hydrogen sulfide in the tail gas from the Claus unit. The tail gas treater may employ a proprietary solution to absorb the hydrogen sulfide followed by conversion to elemental sulfur.

The SCOT (Shell Claus Off-Gas Treating) unit is a very common type of tail gas unit and uses a hydrotreating reactor followed by amine scrubbing to recover and recycle sulfur, in the form of hydrogen, to the Claus unit (Nederland, 2004). In the process (Figure 16.9), tail gas (containing hydrogen sulfide and sulfur dioxide) is contacted with hydrogen and reduced in a hydrotreating reactor to form hydrogen sulfide and water. The catalyst is typically cobalt/molybdenum on alumina. The gas is then cooled in a water contractor. The hydrogen sulfide–containing gas enters an amine absorber that is typically in a system segregated from the other refinery amine systems.
The purpose of segregation is twofold: (1) the tail gas treater frequently uses a different amine than the rest of the plant and (2) the tail gas is frequently cleaner than the refinery fuel gas (with regard to contaminants) and segregation of the systems reduces maintenance requirements for the SCOT® unit. Amines chosen for use in the tail gas system tend to be more selective for hydrogen sulfide and are not affected by the high levels of carbon dioxide in the off-gas.

The hydrotreating reactor converts sulfur dioxide in the off-gas to hydrogen sulfide that is then contacted with a Stretford solution (a mixture of a vanadium salt, anthraquinone disulfonic acid, sodium carbonate, and sodium hydroxide) in a liquid–gas absorber (Abdel-Aal et al., 2016). The hydrogen sulfide reacts stepwise with sodium carbonate and the anthraquinone sulfonic acid to produce elemental sulfur, with vanadium serving as a catalyst. The solution proceeds to a tank where oxygen is added to regenerate the reactants. One or more froths or slurry tanks are used to skim the sulfur product from the solution, which is recirculated to the absorber. Other tail gas treating processes include (1) caustic scrubbing, (2) polyethylene glycol treatment, (3) the Selectox process, and (4) sulfite/bisulfite tail gas treatment (Table 16.10; Mokhatab et al., 2006; Speight, 2007, 2014a).

**TABLE 16.10**

**Tail Gas Processes**

*Caustic scrubbing:* An incinerator converts trace sulfur compounds in the off-gas to sulfur dioxide, which is contacted with caustic, which is sent to the wastewater treatment system.

*Polyethylene glycol:* Off-gas from the Claus unit is contacted with this solution to generate an elemental sulfur product; unlike the Beavon–Stretford process, no hydrogenation reactor is used to convert sulfur dioxide to hydrogen sulfide.

*Selectox:* A hydrogenation reactor converts sulfur dioxide in the off-gas to hydrogen sulfide; a solid catalyst in a fixed-bed reactor converts the hydrogen sulfide to elemental sulfur that is recovered for sales.

*Sulfite/bisulfite tail gas treating unit:* Following Claus reactors, an incinerator converts trace sulfur compounds to sulfur dioxide, which is then contacted with sulfite solution in an absorber, where the sulfur dioxide reacts with the sulfite to produce a bisulfite solution. The gas is then sent to the stack, the bisulfite is regenerated and liberated, and sulfur dioxide is sent to the Claus units for recovery.

**FIGURE 16.9** The SCOT process.
REFERENCES


