Minor constituents

Nitrogen Rejection (Chapter 13)
Trace-Component Recovery or Removal (Chapter 14)

Based on presentation by Prof. Art Kidnay
Plant Block Schematic

Gas & liquids from wells

Field liquids removal

Field acid gas removal

Field dehydration

Field compression

Inlet receiving

Inlet compression

Gas Treating

Hydrocarbon recovery

Dehydration

Nitrogen rejection

Helium recovery

Outlet compression

Liquification

LNG

NGLs

Sales gas

Crude Helium

CO2

Elemental Sulfur

Sulfur recovery

Liquids processing

Water & solids

Natural gasoline

Adapted from Figure 7.1, Fundamentals of Natural Gas Processing, 2nd ed. Kidnay, Parrish, & McCartney
Topics

Nitrogen Rejection (NRU)
- Nitrogen Rejection for Gas Upgrading
- Nitrogen Rejection for EOR

Trace-Component Recovery or Removal
- H₂, O₂, NORM, As
- Helium
- Mercury
  - Amalgam Formation
  - Removal Processes
- BTEX
Nitrogen Rejection (NRU)
Nitrogen Removal / Rejection

Nitrogen rejection required to:

- Lower N$_2$ level to meet pipeline specifications
- Recover N$_2$ for use in enhanced oil recovery (EOR)
- Obtain raw N$_2$ / He stream for He recovery
Subquality gas and EOR

16% of the non-associated reserves (2000) were subquality in nitrogen and consequently require blending or processing to meet the 3 mol % total inerts specification for pipelines.

In 1998 EOR methods contributed about 12% of the total US oil production.

- about 55% from thermal methods,
- 28% from carbon dioxide flooding,
- 12% from natural gas flooding,
- 4.5% was from nitrogen flooding.
Removing $N_2$ from natural gas

<table>
<thead>
<tr>
<th>Process</th>
<th>Flow range MMscfd (MMs3/d)</th>
<th>Complexity</th>
<th>Heavy hydrocarbon recovery</th>
<th>Stage of development</th>
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</thead>
<tbody>
<tr>
<td>Distillation</td>
<td>&gt; 15</td>
<td>Complex</td>
<td>In product gas</td>
<td>Mature</td>
</tr>
<tr>
<td>Pressure Swing Adsorption (PSA)</td>
<td>2 – 15</td>
<td>Simple: batch operation</td>
<td>In regeneration gas</td>
<td>Early Commercial</td>
</tr>
<tr>
<td>Membrane</td>
<td>0.5 – 2.5</td>
<td>Simple: continuous operation</td>
<td>In product gas</td>
<td>Early Commercial</td>
</tr>
</tbody>
</table>
Conventional Cryo Process

Adapted from Figure 12.15, *Fundamentals of Natural Gas Processing*, 2nd ed. Kidnay, Parrish, & McCartney

Cold C₃ Vapor

Feed Gas

Gas-Gas Exchangers

Cold C₃ Liquid

Turboexpander

Cold Separator

Reboilers

Demethanizer

NGL

Residue Gas to Outlet Compression

Adapted from Figure 12.15, *Fundamentals of Natural Gas Processing*, 2nd ed. Kidnay, Parrish, & McCartney

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Conventional Cryo Process

- Cold C$_3$ Vapor
- Feed Gas
- Gas-Gas Exchangers
- Cold C$_3$ Liquid
- Turboexpander
- Cold Separator
- Reboilers
- Demethanizer
- Cryogenic distillation
- NGL
Distillation

nitrogen + methane feed → VERY COLD → nitrogen

nitrogen

normal boiling point, °F

N₂ -320

CH₄ -259

methane
Two-column cryogenic distillation

Adapted from Figure 13.1, *Fundamentals of Natural Gas Processing*, 2nd ed.
Kidnay, Parrish, & McCartney

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Adsorption – Modes of Regeneration

Temperature Swing Adsorption (TSA)
- Increase temperature for regeneration
- Good for trace impurities with high heat of adsorption

Pressure Swing Adsorption (PSA)
- Decrease pressure for regeneration
- Good for enriching streams
- Components have low heat of adsorption
- Rapid cycles (seconds to few minutes)
Adsorption

Four steps in one complete cycle
1> Bed 1 pressurized with feed, Bed 2 is depressurized
2> Feed flow started through Bed 1, Bed 2 purged with small product gas slipstream
3> Bed 2 pressurized with feed, Bed 1 is depressurized
4> Feed flow started through Bed 2, Bed 1 is purged with small product gas slipstream

Closed
Open
Slipstream
Main flow
Adsorption

Four steps in one complete cycle
1> Bed 1 pressurized with feed, Bed 2 is depressurized
2> Feed flow started through Bed 1, Bed 2 purged with small product gas slipstream
3> Bed 2 pressurized with feed, Bed 1 is depressurized
4> Feed flow started through Bed 2, Bed 1 is purged with small product gas slipstream

Key:
- ➔ closed
- ◄◄ open
- —— slipstream
- ——— main flow
Adsorption

Four steps in one complete cycle
1> Bed 1 pressurized with feed, Bed 2 is depressurized
2> Feed flow started through Bed 1, Bed 2 purged with small product gas slipstream
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Adsorption

Four steps in one complete cycle
1> Bed 1 pressurized with feed, Bed 2 is depressurized
2> Feed flow started through Bed 1, Bed 2 purged with *small* product gas slipstream
3> Bed 2 pressurized with feed, Bed 1 is depressurized
4> Feed flow started through Bed 2, Bed 1 is purged with *small* product gas slipstream

- closed
- open
- slipstream
- main flow
Membranes

Composite membrane structure used to separate nitrogen from natural gas

- Membrane is a silicone rubber/polyetherimide (PEI) composite
Membranes

Membrane unit to treat gas containing 8 - 16% N₂ to bring it to Btu gas specifications and 5 to 10% N₂ in the treated stream.

Adapted from Figure 13.2, Fundamentals of Natural Gas Processing, 2nd ed. Kidnay, Parrish, & McCartney
Trace-Component Recovery or Removal
Possible trace components

Hydrogen
- Rare unless refinery cracked gas is fed to plant

Oxygen
- Not naturally occurring. Major source – leaks in sub-atmospheric gathering systems

Radon (NORM)
- Solids collect on pipe walls & inlet filters

Arsenic
- Toxic nonvolatile solid

Helium
- Valuable!

Mercury
- Mechanical damage to brazed aluminum exchangers

BTEX (benzene, toluene, ethylbenzene, and xylene)
- Aromatic emissions from TEG & amine vents
Oxygen

Oxygen issues

- Enhances pipeline corrosion
- Forms heat stable salts (HSS) with amines
- Forms corrosive acidic compounds with glycols
- Forms water with heavy hydrocarbons during reactivation of adsorbent beds

Oxygen removal techniques

- Non-regenerative scavengers
- Catalytic reaction to form water and CO₂ (H₂O removed in dehydration process)
  - Sulfur compounds poison oxidation catalysts
Radon (NORM)

Naturally Occurring Radioactive Material

Natural gas contains Radon (Ra$_{222}$) at low concentrations

- gas is rarely health problem
- half-life of about 3.8 days

Radon gas $\rightarrow$ radioactive solids

\[
\begin{align*}
\text{Ra}_{222} & \rightarrow \text{Po}_{218} & \rightarrow \text{Pb}_{214} & \rightarrow \text{Bi}_{214} & \rightarrow \text{Po}_{214} & \rightarrow \text{Pb}_{210} & \rightarrow \text{Bi}_{210} & \rightarrow \text{Po}_{210} & \rightarrow \text{Pb}_{206} \\
3.8 \text{ d} & \quad 3.0 \text{ m} & \quad 27 \text{ m} & \quad 20 \text{ m} & \quad 164 \text{ ms} & \quad 22.3 \text{ yr} & \quad 5.0 \text{ d} & \quad 138 \text{ d}
\end{align*}
\]

Solids collect on pipe walls & inlet filters

Scale generates large quantities of low-level radioactive waste which must be discarded in disposal wells.
Arsenic

Toxic nonvolatile solid

Predominately trimethylarsine (As(CH$_3$)$_3$)

Typically collects as fine grey dust

Removed from gas using nonregenerative adsorption

Facilities reduce concentrations in sweet raw gas from 1,000 to less than 1µg/m$^3$
Helium

Valuable!

Natural gas most viable source

“Helium-rich” gas > 0.3 vol% helium
  ▪ Rarely > 5 vol%

United States (2003) produced 84% of world production of Grade-A helium (99.995% purity)
  ▪ Remainder from Algeria, Poland & Russia.

New large helium plants:
  ▪ Qatar (2005)
  ▪ Darwin, Australia (2007)

Adapted from Figure 14.4, 2008 H3 Uses in the U.S., Fundamentals of Natural Gas Processing, 2nd ed. Kidnay, Parrish, & McCartney
# Feed compositions to Ladder Creek (mol %)

<table>
<thead>
<tr>
<th></th>
<th>He-Rich Gas</th>
<th>He-Lean Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>61.92</td>
<td>31.58</td>
</tr>
<tr>
<td>Helium</td>
<td>3.54</td>
<td>1.81</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.98</td>
<td>0.91</td>
</tr>
<tr>
<td>Methane</td>
<td>26.65</td>
<td>52.84</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.60</td>
<td>6.40</td>
</tr>
<tr>
<td>C3+</td>
<td>4.30</td>
<td>6.46</td>
</tr>
</tbody>
</table>

\[
\frac{N_2}{\text{He ratio}} \quad 17.49 \quad 17.45
\]
Helium recovery plant (Ladder Creek)

Adapted from Figure 14.5, *Fundamentals of Natural Gas Processing, 2nd ed.*, Kidnay, Parrish, & McCartney
Mercury

Two major problems of mercury in natural gas

- amalgam formation with aluminum
- environmental pollution - compounds readily absorbed by most biological systems

May be present as

- elemental mercury
  - Majority will condense in cryogenic section
- organometallic compounds, \(\text{CH}_3\text{HgCH}_3\) (dimethylmercury), \(\text{CH}_3\text{HgC}_2\text{H}_5\) (methylethylmercury), \(\text{C}_2\text{H}_5\text{HgC}_2\text{H}_5\) (diethylmercury)
  - Will concentrate in hydrocarbon liquids
- inorganic compounds such as \(\text{HgCl}_2\)
## Typical mercury levels

<table>
<thead>
<tr>
<th>Location</th>
<th>Elemental Mercury Concentration in micrograms/Nm3 (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>South America</td>
<td>69 – 119 (8 to 13)</td>
</tr>
<tr>
<td>Far East</td>
<td>58 – 93 (6 to 10)</td>
</tr>
<tr>
<td>North Africa</td>
<td>0.3 – 130 (0.03 to 15)</td>
</tr>
<tr>
<td>Gronigen (Germany)</td>
<td>180 (20)</td>
</tr>
<tr>
<td>Middle East</td>
<td>1 – 9 (0.1 to 1)</td>
</tr>
<tr>
<td>Eastern US Pipeline</td>
<td>0.019 - 0.44 (0.002 to 0.05)</td>
</tr>
<tr>
<td>Midwest US Pipeline</td>
<td>0.001 - 0.10 (0.0001 to 0.01)</td>
</tr>
<tr>
<td>North America</td>
<td>0.005 - 0.040 (0.0005 to 0.004)</td>
</tr>
</tbody>
</table>
Mercury removal processes

Nonregenerative chemisorption

- Removes elemental mercury to < 0.01μg/Nm³
- Typical bed capacities > 10%
- Most use sulfur impregnated on high surface area support

Regenerative chemisorption (1 process)

- Silver on mole sieve chemisorbs elemental mercury and dehydrates at the same time
- Can be added to existing dehydration unit
- Generates mercury waste stream
Mercury Recovery
No Treatment of Regeneration Gas

545 MMscfd, 70°F, 845 psia
27.67 lb H₂O/MMscf
2.5 micrograms Hg/Nm³

H₂O + regeneration gas
and 34.45 g/day Hg

H₂O + 0.154 g/day of Hg

34.4 MMscfd
regeneration gas

dry, Hg - free gas

adsorption
adsorption

Hg_removal_ENG
Mercury Recovery
Treatment of Regeneration Gas

545 MMscfd, 70°F, 845 psia
27.67 lb H₂O/MMscf
2.5 micrograms Hg/Nm³

Nonregenerated Hg bed
34.39 g/day accumulation

H₂O + 0.206 g/day of Hg

34.4 MMscfd regeneration gas
dry, Hg-free gas
BTEX: Benzene, Toluene, Ethylbenzene, Xylenes

Possible problems:

- Freeze out and plugging in cryogenic units
- Excessive aromatic hydrocarbon emissions
  - Venting from TEG regenerator largest source
  - Venting from amine regenerators lesser source
  - Recovery systems eliminate problem
BTEX Absorption in glycol dehydrators

TEG absorbs aromatic (BTEX) hydrocarbons

- Absorption enhanced at low temperatures, high TEG concentrations, and higher circulation rates
- Most of the absorbed BTEX vented with steam at top of regeneration column

BTEX Emission Control Methods

- Adjusting glycol unit operating conditions to minimize the quantity of BTEX absorbed
- Burning glycol still offgases prior to venting
- Condensing glycol offgases and recovering BTEX as a liquid product
- Adsorbing BTEX on a carbon adsorbent
Summary
Summary

Nitrogen removal to improve calorific value of gas and/or use for EOR gas injection

- Large scale removal by cryogenic distillation

Trace component removal

- Mercury removal upstream of brazed aluminum exchangers in cryogenic sections
- Control of BTEX in gas emissions – air quality concerns
- Helium recovery by cryogenic distillation
  - Even small concentrations could make the helium more valuable than the remaining natural gas & NGLs
Supplemental Slides
Commercial unit sold to Towne Exploration for treating gas containing 8-16% nitrogen.
Comparison Design & Actual Performance


<table>
<thead>
<tr>
<th>Feed Gas</th>
<th>Product Gas</th>
<th>Vent Gas</th>
<th>Recycle Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Design</td>
<td>Actual</td>
<td>Design</td>
</tr>
<tr>
<td>Btu/scf (daily average)</td>
<td>908.000</td>
<td>908.05</td>
<td>988</td>
</tr>
<tr>
<td>Btu/scf (actual)</td>
<td>908.000</td>
<td>908.05</td>
<td>988</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating Conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure (psig)</td>
<td>960.000</td>
<td>847.00</td>
<td>795.000</td>
</tr>
<tr>
<td>Temp (°F)</td>
<td>104</td>
<td>76</td>
<td>110</td>
</tr>
<tr>
<td>Volume (MMscfd)</td>
<td>2.00</td>
<td>1.738</td>
<td>1.65</td>
</tr>
<tr>
<td>Stream Compositions (daily average mol%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>16.054</td>
<td>15.34</td>
<td>9.060</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.225</td>
<td>0.26</td>
<td>0.260</td>
</tr>
<tr>
<td>Methane</td>
<td>78.992</td>
<td>80.70</td>
<td>85.222</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.095</td>
<td>1.95</td>
<td>2.421</td>
</tr>
<tr>
<td>Propane</td>
<td>1.086</td>
<td>0.95</td>
<td>1.264</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.261</td>
<td>0.24</td>
<td>0.307</td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.302</td>
<td>0.20</td>
<td>0.355</td>
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<tr>
<td>n-Pentane</td>
<td>0.086</td>
<td>0.07</td>
<td>0.101</td>
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<tr>
<td>Isopentane</td>
<td>0.201</td>
<td>0.08</td>
<td>0.237</td>
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<tr>
<td>n-Hexane</td>
<td>0.044</td>
<td>0.22</td>
<td>0.053</td>
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<tr>
<td>C₆+ Hydrocarbons</td>
<td>0.220</td>
<td>0.22</td>
<td>0.252</td>
</tr>
</tbody>
</table>

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