Acid Gas Removal Options for Minimizing Methane Emissions

Lessons Learned from Natural Gas STAR

Occidental Petroleum Corporation and California Independent Petroleum Association

Producers Technology Transfer Workshop
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dpa.gov/gasstar
Acid Gas Removal: Agenda

- Methane Losses
- Methane Recovery
- Is Recovery Profitable?
- Industry Experience
- Discussion
Methane Losses from Acid Gas Removal

- There are 287 acid gas removal (AGR) units in the natural gas industry\(^1\)
  - Emit 634 million cubic feet (MMcf) annually\(^1\)
  - 6 thousand cubic feet per day (Mcf/day) emitted by the average AGR unit\(^1\)
  - Most AGR units use an amine process or Selexol\(^\text{TM}\) process
  - Several new processes remove acid gas with lower methane emissions and other associated benefits

1 – Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990 - 2005
What is the Problem?

- 1/3 of U.S. gas reserves contain carbon dioxide (CO$_2$) and/or nitrogen (N$_2$)$^1$
- Wellhead natural gas may contain acid gases
  - Hydrogen sulfide (H$_2$S), CO$_2$ are corrosive to gathering/boosting and transmission lines, compressors, pneumatic instruments, and distribution equipment
- Acid gas removal processes have traditionally used an aqueous amine solution to absorb acid gas
- Amine regeneration strips acid gas (and absorbed methane)
  - CO$_2$ (with methane) is typically vented to the atmosphere, flared, or recovered for enhanced oil recovery (EOR)
  - H$_2$S is typically flared in low concentrations or sent to sulfur recovery

$^1$ – Daiminger and Lind, Engelhard Corporation. Adsorption Processes for Natural Gas Treatment
Typical Amine Process

- Sweet Gas
- Sour Gas
- Contactor (Absorber)
- Lean Amine
- Rich Amine
- Flash Tank
- Fuel/Recycle
- Exchanger
- Filter
- Booster Pump
- Reboiler
- Reflux Pump
- Condenser
- Stripper - Diethanol Amine (DEA)
- H₂S to sulfur plant or flare
- CO₂ / methane to atmosphere / flare / thermal oxidizer

- Contact (Absorber)
- Fuel/Recycle
- Lean Amine
- Flash Tank
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Methane Recovery - New Acid Gas Removal Technologies

- GTI & Uhde Morphysorb® Process
- Kvaerner Membrane Process
- Guild / Engelhard Molecular Gate® Process

Primary driver is process economics, not methane emissions savings

Reduce methane venting by 50 to 100%
Morphysorb® Process
Morphysorb® Process

- Morphysorb® absorbs acid gas but also absorbs some methane
  - Methane absorbed is 66% to 75% lower than competing solvents¹

- Flash vessels 1 & 2 recycled to absorber inlet to minimize methane losses

- Flash vessels 3 & 4 at lower pressure to remove acid gas and regenerate Morphysorb®

¹ – Oil and Gas Journal, July 12, 2004, p 57
Is Recovery Profitable?

- Morphysorb® can process streams with high (>10%) acid gas composition
- Morphysorb® has a 30% to 40% operating cost advantage over DEA or Selexol™
  - 66% to 75% less methane absorbed than DEA or Selexol™
  - About 33% less total hydrocarbons (THC) absorbed
  - Lower solvent circulation volumes
- At least 25% capital cost advantage from smaller contactor and recycles
- Flash recycles 1 & 2 recover about 80% of methane that is absorbed

1 – Oil and Gas Journal, July 12, 2004, p 57, Fig. 7
2 – GTI
Industry Experience - Spectra Energy

- Kwoen plant does not produce pipeline-spec gas
  - Separates acid gas and reinjects it in reservoir
  - Frees gathering and processing capacity further downstream

- Morphysorb® retrofitted to a process unit designed for other solvent

- Morphysorb® chosen for acid gas selectivity over methane
  - Less recycle volumes; reduced gas compressor horsepower
Kvaerner Membrane Process

- Membrane separation of CO₂ from feed gas
  - Cellulose acetate spiral wound membrane
- High CO₂ permeate (effluent or waste stream) exiting the membrane is vented or blended into fuel gas
- Low CO₂ product exiting the membrane exceeds pipeline spec and is blended with feed gas

Adapted from “Trimming Residue CO₂ with Membrane Technology”, 2005
Kvaerner Membrane Technology

- CO₂ (and some methane) diffuse axially through the membrane
- High-CO₂ permeate exits from center of tube; enriched product exits from outer annular section
- One application for fuel gas permeate
  - Methane/CO₂ waste stream is added with fuel gas in a ratio to keep compressor emissions in compliance

Design requirements
- Upstream separators remove contaminants which may foul membrane
- Line heater may be necessary
Industry Experience – DCP Midstream

- Kvaerner process installed at Mewborn processing plant in Colorado, 2003
- Problem: sales gas CO₂ content increasing above the 3% pipeline spec

Evaluated options

- Blend with better-than-spec gas
  - Not enough available
- Use cryogenic natural gas liquids (NGL) recovery to reject CO₂
  - Infrastructure/capital costs too high
- Final choice: membrane or amine unit
Industry Experience - Continued

- Membrane chosen for other advantages; zero emissions is added benefit
  - 65% less capital cost than amine unit
  - About 10% operating cost (compared to amine)
  - About 10% operator man hours (compared to amine)
  - 1/3 footprint of amine unit

- Less process upsets
- Less noise
- Less additional infrastructure construction

Typical process conditions

<table>
<thead>
<tr>
<th>Flow Into Membrane</th>
<th>Membrane Residue (Product)</th>
<th>Membrane Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.3 MMcf/day</td>
<td>21</td>
<td>1.3</td>
</tr>
<tr>
<td>70 to 110 degrees Fahrenheit</td>
<td>70 to 110</td>
<td>70 to 110</td>
</tr>
<tr>
<td>800 to 865 psia</td>
<td>835</td>
<td>55</td>
</tr>
<tr>
<td>3% CO₂</td>
<td>2%</td>
<td>16%</td>
</tr>
<tr>
<td>84% C₁</td>
<td>89%</td>
<td>77%</td>
</tr>
<tr>
<td>13% C₂+</td>
<td>9%</td>
<td>7%</td>
</tr>
<tr>
<td>~0% H₂O</td>
<td>~0%</td>
<td>~0%</td>
</tr>
<tr>
<td>~0% H₂S</td>
<td>~0%</td>
<td>~0%</td>
</tr>
</tbody>
</table>
Is Recovery Profitable?

Costs

- Conventional DEA AGR would cost $4.5 to $5 million capital, $0.5 million operation and maintenance (O&M) per year
- Kvaerner Membrane process cost $1.5 to $1.7 million capital, $0.02 to $0.05 million O&M per year

Optimization of permeate stream

- Permeate mixed with fuel gas, $5/Mcf fuel credit
- Only installed enough membranes to take feed from >3% to >2% CO₂, and have an economic supplemental fuel supply for compressors

In operation since 2005

Offshore Middle East using NATCO membrane process on gas with 90% CO₂, achieving pipeline spec quality
Methane Recovery - Molecular Gate®
CO₂ Removal

- Adsorbs acid gas (CO2 and H2S) in fixed bed

- Molecular sieve application selectively adsorbs acid gas molecules of smaller diameter than methane

- Bed regenerated by depressuring
  - ~10% of feed methane lost in “tail gas” depressuring
  - Route tail gas to fuel
Molecular Gate® Applicability

- Lean gas
  - Gas wells, coal bed methane

- Associated gas
  - Tidelands Oil Production Company
    - 1.4 MMcf/day
    - 18% to 40% CO₂
    - Water saturated, rich gas
  - Design options for C₄+ in tail gas stream
    - Heavy hydrocarbon recovery before Molecular Gate®
    - Recover heavies from tail gas in adsorber bed
    - Use as fuel for process equipment
Molecular Gate® CO₂ Removal

17 psi pressure drop

Product
90 - 95% of C₁
80 - 90% of C₂
50% of C₃

Tail Gas
5 - 10% of C₁
10 - 20% of C₂
50% of C₃
C₄+
CO₂
H₂S
H₂O

Optional Enriched C₁ Recycle

Pressure Swing Adsorption

Vacuum Compressor

C₄+ Recovery

Dehydration

High Pressure Feed
C₁
C₂
C₃
C₄+
CO₂
H₂S
H₂O
Industry Experience - Tidelands Molecular Gate® Unit

- First commercial unit started in May 2002
- Process up to 1.4 MMcf/day
- No glycol system is required
- Heavy hydrocarbons and water removed with CO₂
- Tail gas used for fuel is a key optimization: no process venting
- 18% to 40% CO₂ removed to pipeline specifications (2%)
- Eliminated flaring
# Molecular Gate Performance at Tidelands

<table>
<thead>
<tr>
<th></th>
<th>Design Feed</th>
<th>Actual Feed</th>
<th>Design Product</th>
<th>Actual Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow, MMcf/day</td>
<td>1.0</td>
<td>1.4</td>
<td>0.52</td>
<td>0.54</td>
</tr>
<tr>
<td>Pressure, psig</td>
<td>65</td>
<td>70</td>
<td>63</td>
<td>68</td>
</tr>
<tr>
<td>Temperature, F</td>
<td>60-80</td>
<td>60-80</td>
<td>60-80</td>
<td>60-80</td>
</tr>
<tr>
<td>Composition, Mol %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>71.25</td>
<td>48.35</td>
<td>95.09</td>
<td>94.17</td>
</tr>
<tr>
<td>O2</td>
<td>400 ppm</td>
<td>800 ppm</td>
<td>700 ppm</td>
<td>1500 ppm</td>
</tr>
<tr>
<td>N2</td>
<td>2.18</td>
<td>1.34</td>
<td>3.74</td>
<td>2.40</td>
</tr>
<tr>
<td>CO2</td>
<td>18.82</td>
<td>37.58</td>
<td>0.19</td>
<td>1.90</td>
</tr>
<tr>
<td>C2</td>
<td>2.35</td>
<td>2.96</td>
<td>0.90</td>
<td>0.68</td>
</tr>
<tr>
<td>C3</td>
<td>2.12</td>
<td>3.77</td>
<td>0.20</td>
<td>0.03</td>
</tr>
<tr>
<td>C4</td>
<td>1.75</td>
<td>3.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C5</td>
<td>0.76</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C6+</td>
<td>0.72</td>
<td>1.41</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H2O</td>
<td>saturated</td>
<td>saturated</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

F = Fahrenheit  
psig = pounds per square inch, gauge  
ppm = parts per million
Tidelands Gas Revenue & Associated Volume

Gas Revenue

Gas Volume

Gas Price ($/Million British Thermal Unit)
Is Recovery Profitable?

- Molecular Gate® costs are 20% less than amine process
  - 9 to 35 ¢ / Mcf product depending on scale
- Fixed-bed tail gas vent can be used as supplemental fuel
  - Eliminates venting from acid gas removal
- Other Benefits
  - Allows wells with high acid gas content to produce
    (alternative is shut-in)
  - Can dehydrate and remove acid gas to pipeline specs in one step
  - Less operator attention
Other Molecular Gate Applications

- Nitrogen removal from natural gas
- Dew point control by heavy hydrocarbon and water removal
- Removal of $\text{C}_2$ (<6%), $\text{C}_3^+$ (<3%) and $\text{C}_6^+$ (<0.2%) for California Air Resources Board compressed natural gas
- Removal of heavy hydrocarbons from CO$_2$ in amine plant vents to eliminate flaring
## Comparison of AGR Alternatives

<table>
<thead>
<tr>
<th></th>
<th>Amine (or Selexol™) Process</th>
<th>Molecular Gate® CO₂</th>
<th>Morphysorb® Process</th>
<th>Kvaerner Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorbent or Adsorbent</strong></td>
<td>Water &amp; Amine (Selexol™)</td>
<td>Titanium Silicate</td>
<td>Morpholine Derivatives</td>
<td>Cellulose Acetate</td>
</tr>
<tr>
<td><strong>Methane Savings Compared to Amine Process</strong></td>
<td>--</td>
<td>Methane in tail gas combusted for fuel</td>
<td>66 to 75% less methane absorption</td>
<td>Methane in permeate gas combusted for fuel</td>
</tr>
<tr>
<td><strong>Regeneration</strong></td>
<td>Reduce Pressure &amp; Heat</td>
<td>Reduce Pressure to Vacuum</td>
<td>Reduce Pressure</td>
<td>Replace Membrane about 5 years</td>
</tr>
<tr>
<td><strong>Primary Operating Costs</strong></td>
<td>Amine (Selexol™) &amp; Steam</td>
<td>Electricity</td>
<td>Electricity</td>
<td>Nil</td>
</tr>
<tr>
<td><strong>Capital Cost</strong></td>
<td>100%</td>
<td>&lt;100%</td>
<td>75%</td>
<td>35%</td>
</tr>
<tr>
<td><strong>Operating Cost</strong></td>
<td>100%</td>
<td>80%</td>
<td>60% to 70%</td>
<td>&lt;10%</td>
</tr>
</tbody>
</table>
Discussion

- Industry experience applying these technologies and practices
- Limitations on application of these technologies and practices
- Actual costs and benefits