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
Long Beach, California
August 21, 2007

epa.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™ process
  - Several new processes remove acid gas with lower methane emissions and other associated benefits

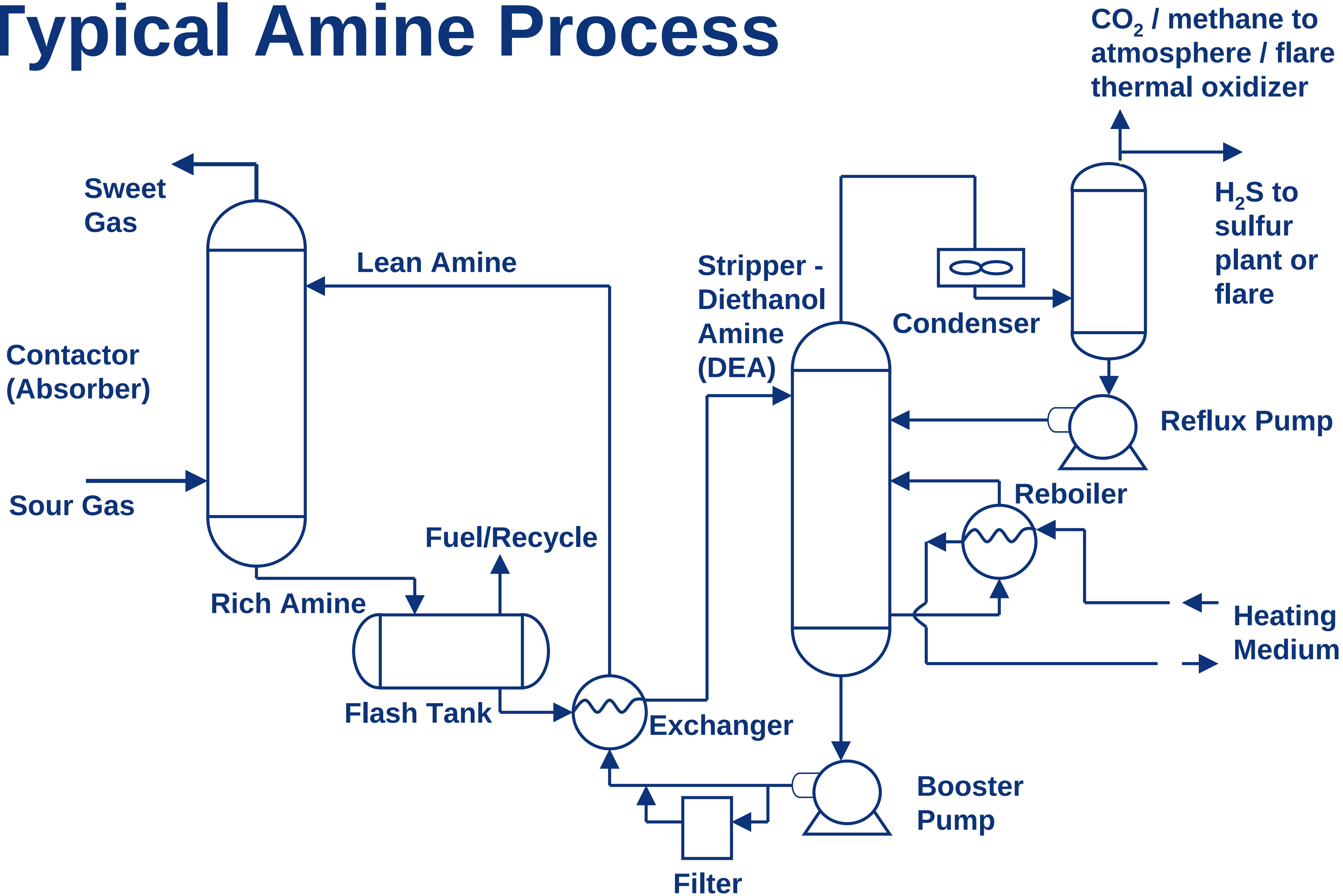
1 – Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990 - 2005

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_2S), 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_2S is typically flared in low concentrations or sent to sulfur recovery

1 – Daiminger and Lind, Engelhard Corporation. *Adsorption Processes for Natural Gas Treatment*

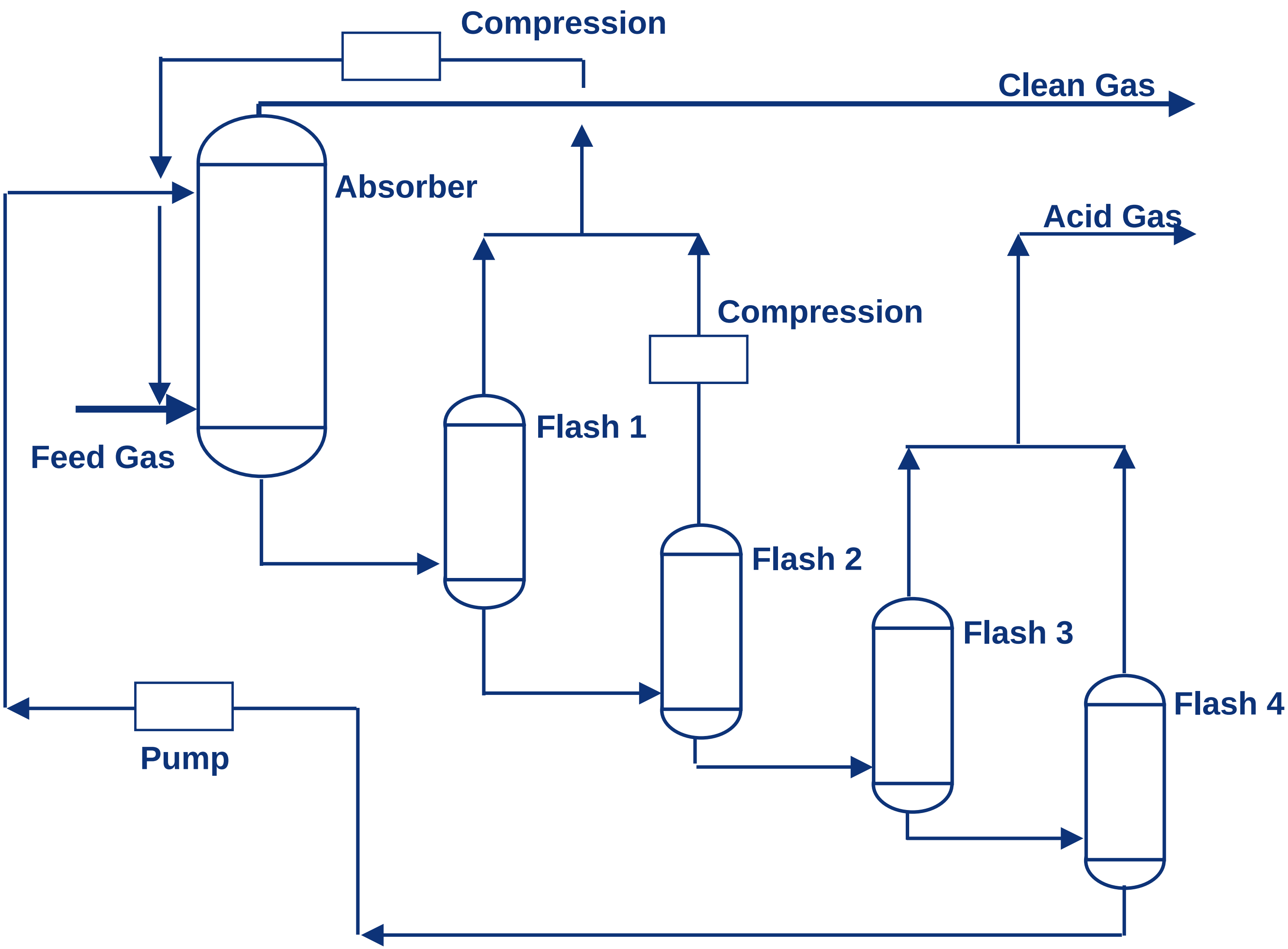
Typical Amine Process



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 solvents[1]
- 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™ [2]
  - 66% to 75% less methane absorbed than DEA or Selexol™
  - About 33% less total hydrocarbons (THC) absorbed[2]
  - Lower solvent circulation volumes
- At least 25% capital cost advantage from smaller contactor and recycles[2]
- Flash recycles 1 & 2 recover about 80% of methane that is absorbed[1]

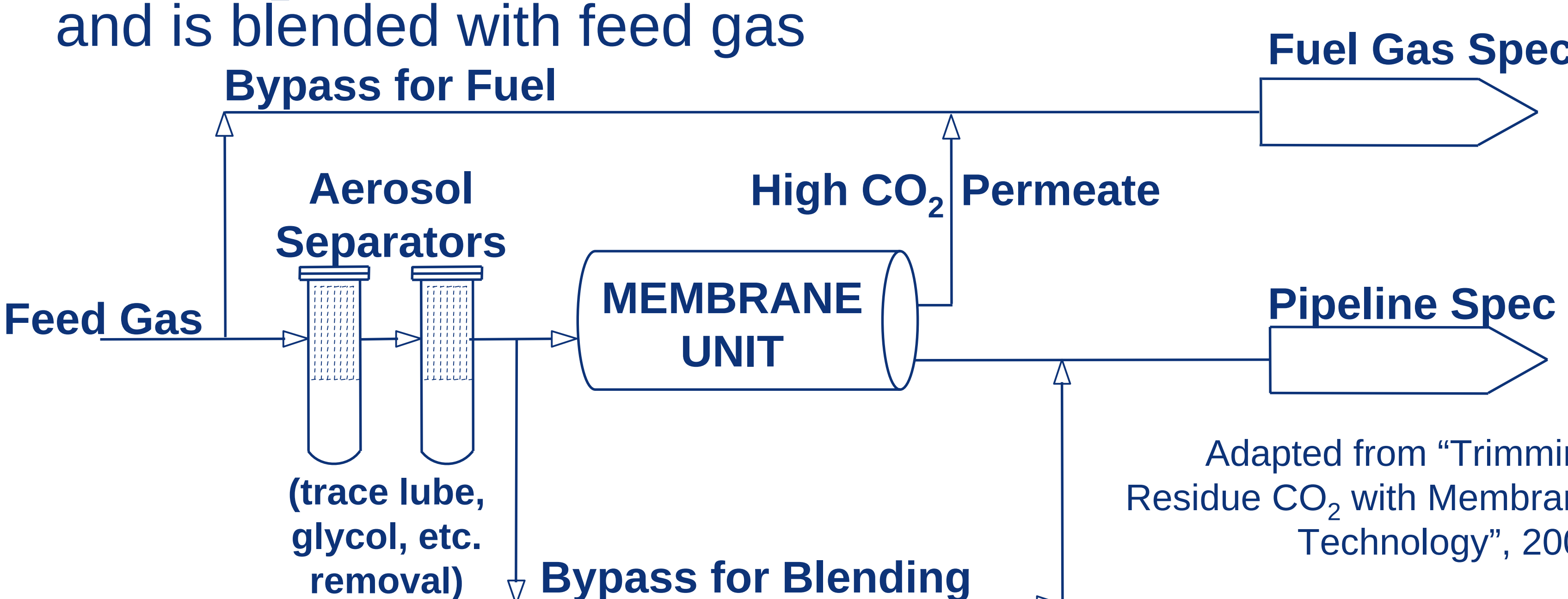
1 – Oil and Gas Journal, July 12, 2004, p 57, Fig. 7
2 – GTI

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

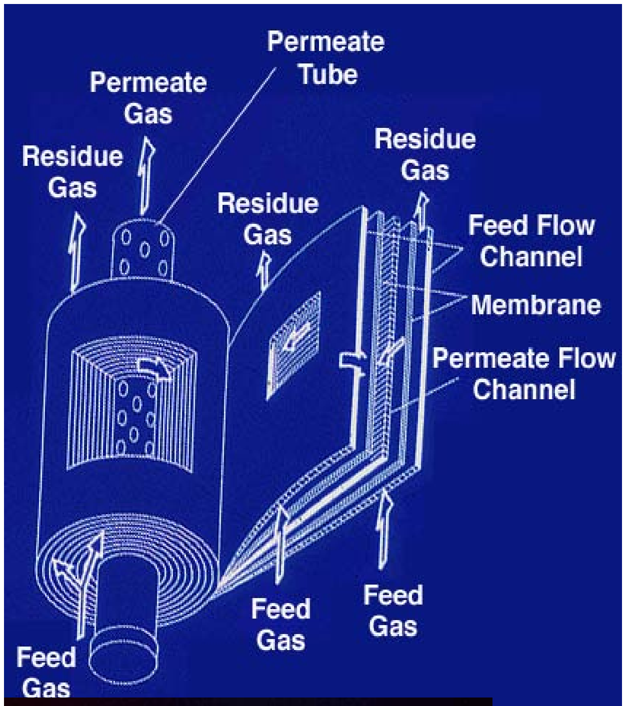
Kvaerner Membrane Process

- Membrane separation of CO_2 from feed gas
  - Cellulose acetate spiral wound membrane
- High CO_2 permeate (effluent or waste stream) exiting the membrane is vented or blended into fuel gas
- Low CO_2 product exiting the membrane exceeds pipeline spec and is blended with feed gas



Adapted from "Trimming Residue CO_2 with Membrane Technology", 2005

Kvaerner Membrane Technology



- CO_2 (and some methane) diffuse axially through the membrane
- High-CO_2 permeate exits from center of tube; enriched product exits from outer annular section
- One application for fuel gas permeate
  - Methane/CO_2 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 CO_2 content increasing above the 3% pipeline spec

DCP Midstream

- Evaluated options
  - Blend with better-than-spec gas
    - Not enough available
  - Use cryogenic natural gas liquids (NGL) recovery to reject CO_2
    - 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

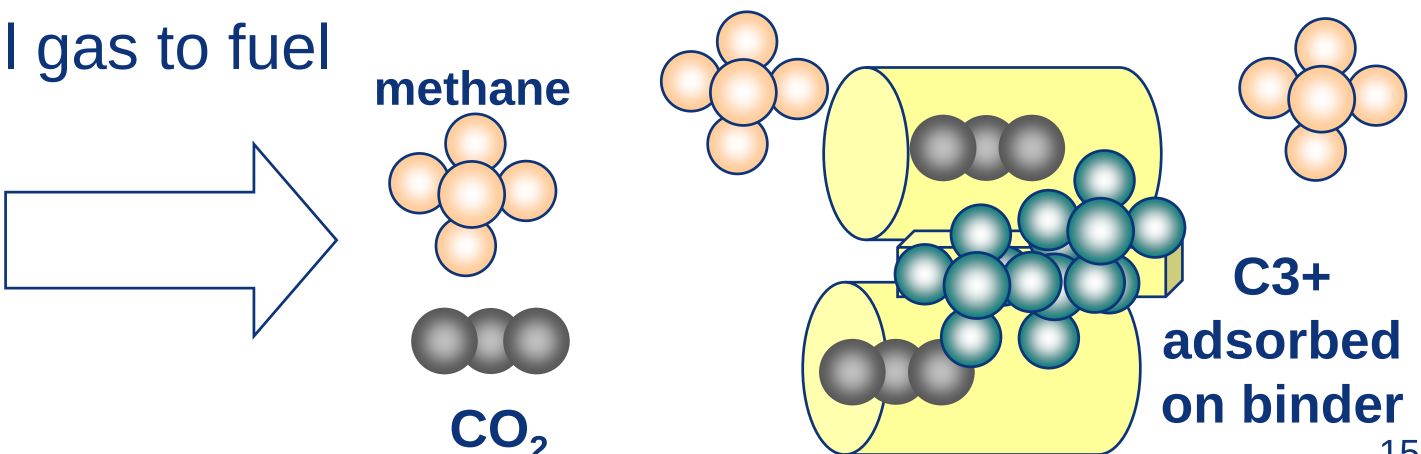
Flow Into Membrane	Membrane Residue (Product)	Membrane Permeate
22.3 MMcf/day	21	1.3
70 to 110 degrees Fahrenheit	70 to 110	70 to 110
800 to 865 psia	835	55
3% CO_2	2%	16%
84% C_1	89%	77%
13% C_2+	9%	7%
~0% H_2O	~ 0%	~0%
~0% H_2S	~0%	~0%

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% CO_2, and have an economic supplemental fuel supply for compressors
- In operation since 2005
- Offshore Middle East using NATCO membrane process on gas with 90% CO_2, achieving pipeline spec quality

Methane Recovery - Molecular Gate® CO_2 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

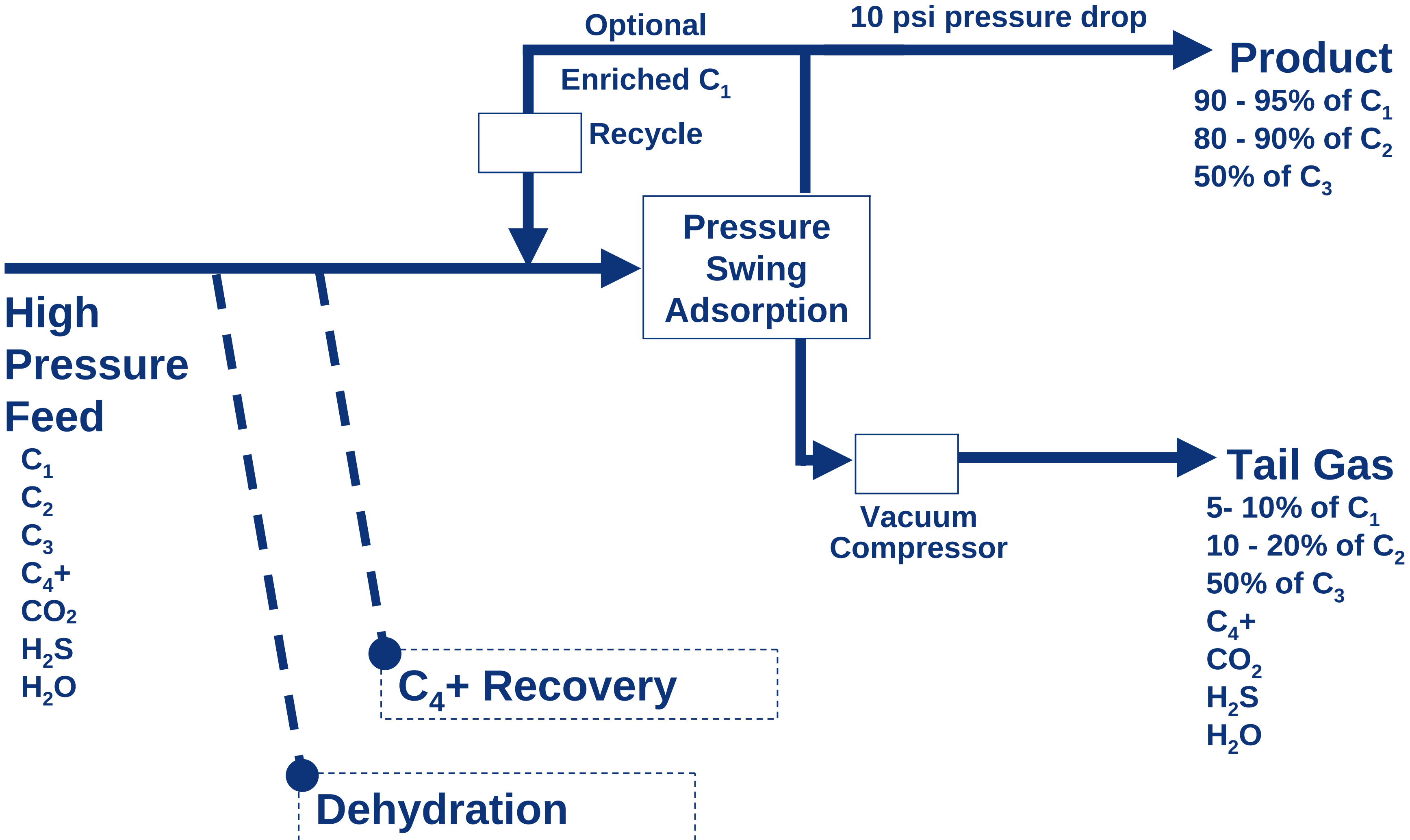


Molecular Gate® Applicability

- Lean gas
  - Gas wells, coal bed methane
- Associated gas
  - Tidelands Oil Production Company
    - 1.4 MMcf/day
    - 18% to 40% CO_2
    - Water saturated, rich gas
  - Design options for C_4+ in tail gas stream
    - Heavy hydrocarbon recovery before Molecular Gate®
    - Recover heavies from tail gas in adsorber bed
    - Use as fuel for process equipment

Coal bed methane System in Illinois
www.moleculargate.com

Molecular Gate® CO_2 Removal



Industry Experience - Tidelands Molecular Gate® Unit

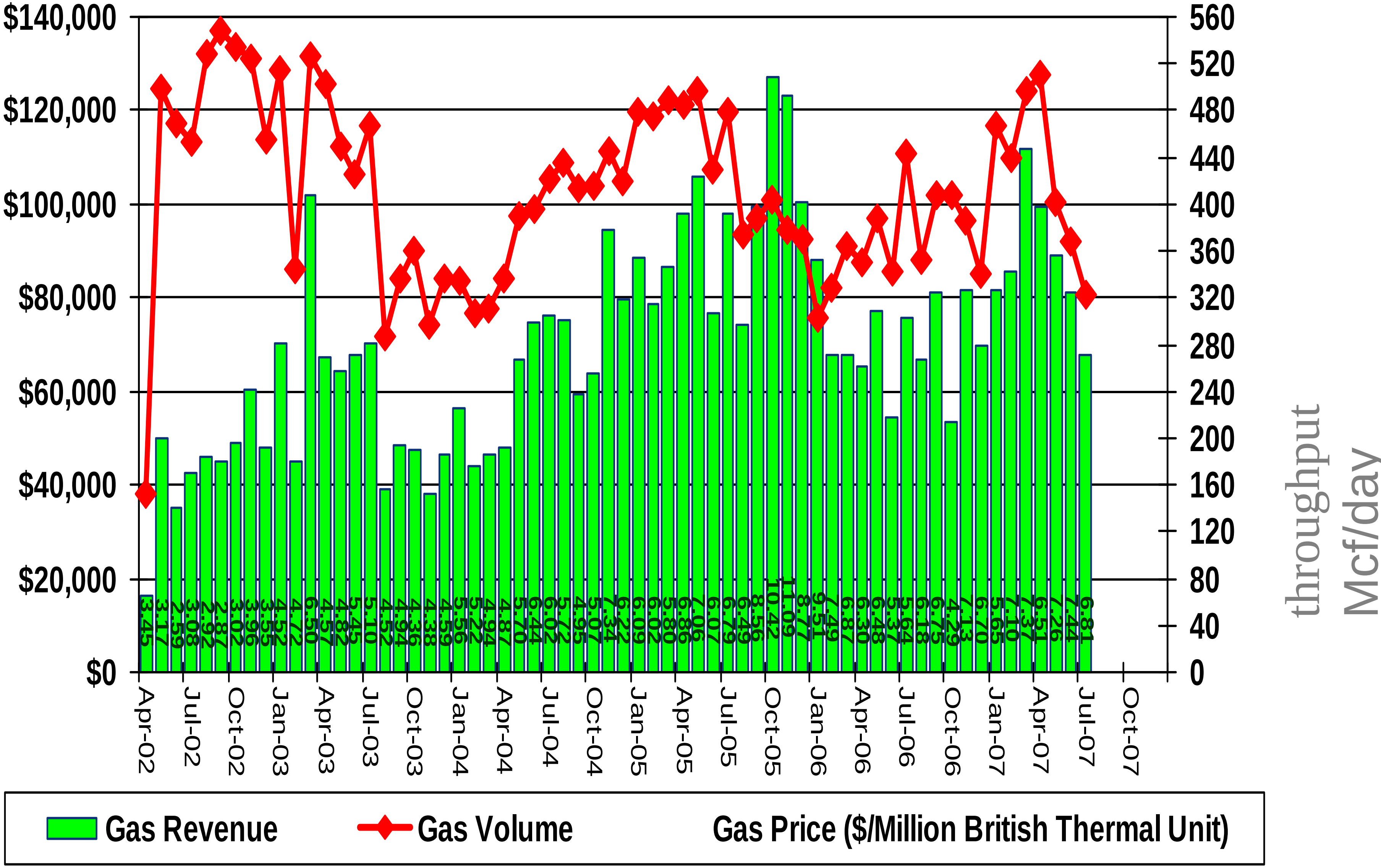
- First commercial unit started in May 2002
- Process up to 1.4 MMcf/day
- No glycol system is required
- Heavy hydrocarbons and water removed with CO_2
- Tail gas used for fuel is a key optimization: no process venting
- 18% to 40% CO_2 removed to pipeline specifications (2%)
- Eliminated flaring

Molecular Gate Performance at Tidelands

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

F = Fahrenheit
psig = pounds per square inch, gauge
ppm = parts per million

Tidelands Gas Revenue & Associated Volume



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 C_2 (<6%), C_3+ (<3%) and 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

	Amine (or Selexol™) Process	Molecular Gate® CO_2	Morphysorb® Process	Kvaerner Membrane
Absorbent or Adsorbent	Water & Amine (Selexol™)	Titanium Silicate	Morpholine Derivatives	Cellulose Acetate
Methane Savings Compared to Amine Process	--	Methane in tail gas combusted for fuel	66 to 75% less methane absorption	Methane in permeate gas combusted for fuel
Regeneration	Reduce Pressure & Heat	Reduce Pressure to Vacuum	Reduce Pressure	Replace Membrane about 5 years
Primary Operating Costs	Amine (Selexol™) & Steam	Electricity	Electricity	Nil
Capital Cost	100%	<100%	75%	35%
Operating Cost	100%	80%	60% to 70%	<10%

Discussion

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