CO_2 Capture by Amine Scrubbing

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Roadmap

- Research on Amine Scrubbing
  - Objectives and Scope
  - Goals
- Conclusions on Energy
  - Amine Scrubbing is THE Process
- Conclusions on Solvent Management
  - Amine Scrubbing is THE Process
- R&D needs for amine scrubbing

Objectives of the Luminant Program

- Train graduate & undergraduate students
- Create understanding, data, & methods to facilitate deployment of CO_2 capture
- Create innovations to enhance performance and reduce cost of CO_2 capture

• Strategy

- Apply ChE science to understand & quantify the performance of MEA absorption/stripping
  - Energy Performance
  - Solvent Management

- Develop evolutionary innovations
  - Better Processes
  - Better Solvents

Annual Funding by Important Sponsors

Current

- $500k Luminant Energy
- $800k 29 companies
- $800k State of Texas – ovhd & faculty
- $2100k Total Annual Program Funding

Pending

- $350k NRG/DOE, pilot & tech support
- $325k CO_2 capture pilot plant project (C2P3)
- $1000k DOE (w URS & Trimeric), pilot testing

Energy Science

- Thermo and Rates
  - FTIR: P_{CO2}, P_{amine}: 30-70C, 120-160C
  - P_t : 120-160C
  - Wetted Wall Column: P_{CO2}, k'_g: 40-100C
  - – C_p by DSC, Speciation by NMR
- Packing Characterization in 18-inch column
  - – a (CO_2), K_ga (SO_2), k_la (toluene)
- AspenPlus Process Modeling
  - – Thermo by Electrolyte NRTL
  - – Diffusion & kinetics by RateSep
  - – Dynamics by ACM
- Validation by 18-inch absorber/stripper
  - – Air/CO_2

Science of Solvent Management

- Oxidative Degradation
  - With FTIR – 1-5 days – 40-70C
  - 1-4 weeks, low gas flow, 40-70C
  - Cyclic: 2 weeks, 70-130C
- Thermal degradation - cylinders at 100-175C
- Nitrosoamine production & analysis
- Amine Volatility by FTIR
- Reclaiming: Thermal, Sulfate Crystallization
- Analytical tools
  - HPLC: cation, anion, aminoacid, molecule
  - MS with HPLC, cation, GC

Process Innovation Goals

- Use Heat rather than mechanical compression
  - Strip at 120-150^{o}C, limited by degradation
- Reversible Stripping – high lean ldg, 0.3-0.4
- Maximize Heat Reversibility at stripper
  - Cross Exchanger & Reboiler $\Delta T=5^{o}C$
  - 2-stage flash, matrix, multiP, or interheat
  - Vapor recompression
- Minimize T of Absorption, 30-40^{o}C
  - Precooling & intercooling Gas & Solvent
  - Control water balance
- Simplify

Solvent Innovation Goals

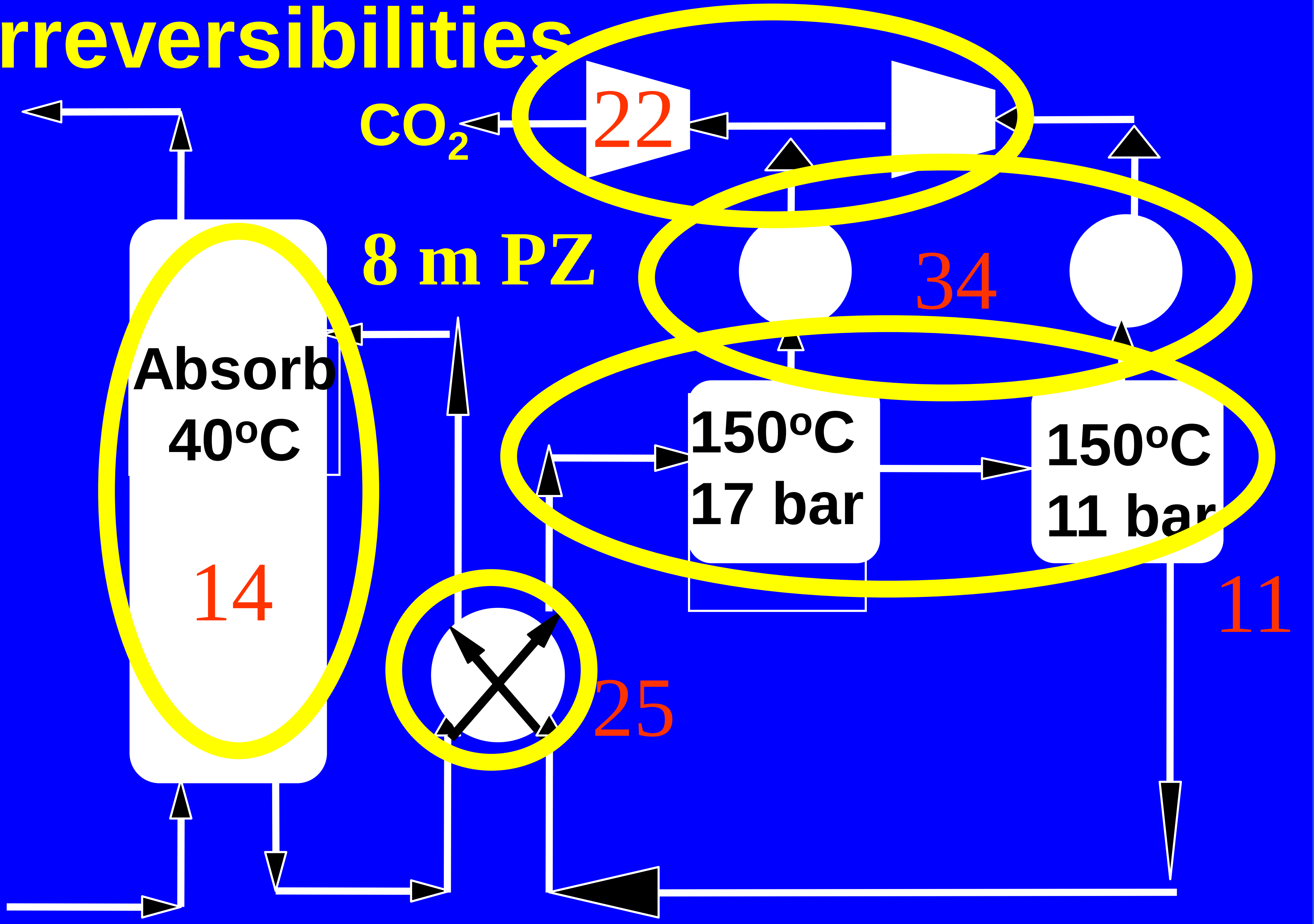
- Cost <$5/lb, one step past MEA
- CO_2 Rate >MEA
- Heat of Absorption >70 kJ/mole
- T Stability >140^{o}C
- Reversible Capacity >0.8 mole/kg
- Viscosity <15 cP
- No solid or liquid phase separation
- Low oxidative degradation
- Volatility=10-30 ppm, allows reclaiming

Solvents

- Intense Work
  - 7 to 11 m (30-40%) MEA
  - 8 m (40%) Piperazine (PZ)
  - 7 m MDEA/2 m PZ (50 wt)
  - Piperazine Derivatives
- Screening
  - Aminoacids
  - Hindered amines
  - DGA, EDA, MAPA

Conclusions on Energy

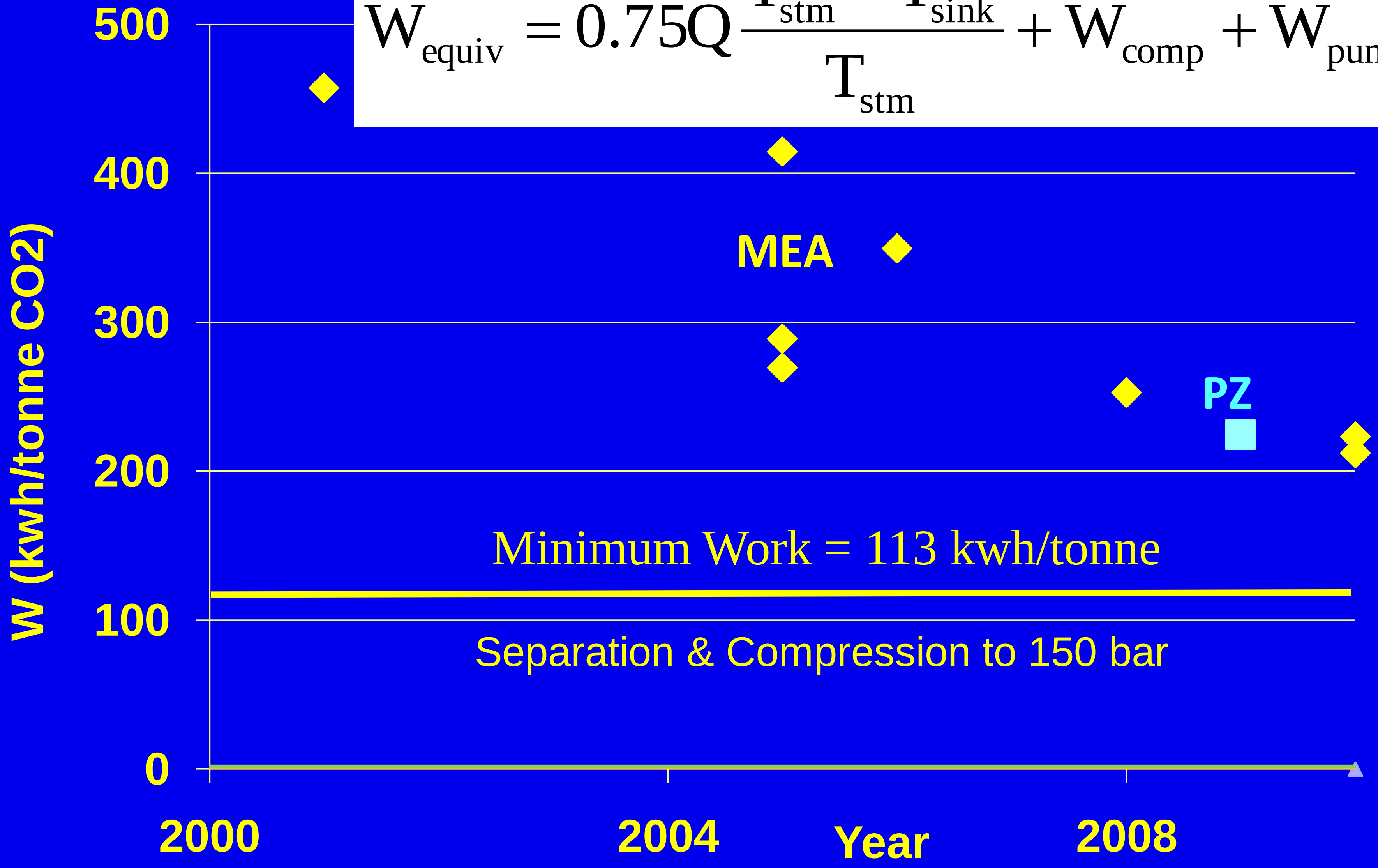
Irreversibilities



W_{ideal}= 113 kwh/tonne, W_{real}=219 kwh/tonne

Equivalent Work of Amine Scrubbing

$$W_{equiv} = 0.75Q \frac{T_{stm} - T_{sink}}{T_{stm}} + W_{comp} + W_{pump}$$



Separation Efficiency, W_{min}/W (%)

CO_2 capture by 8 m PZ (2-stage regeneration at 150°C)	50
Cryogenic air separation (Darde et al., 2008)	25
Hydrocarbon Distillation (relative volatility=1.1 to 5)	10-36
Desalination by reverse osmosis (Semiat, 2008)	21

Capture processes driven by mechanical compression are not competitive

	Work (kwh/tonne)	**Efficiency (%)**
Minimum Work (Isothermal, ideal compression)	111	100
PZ with 2-stage regeneration at 150C	219	50
Ideal process driven by real compression 72% eff, 40^{o}C cooling, P_j/P_{j-1} =2 (Ideal Membranes or PSA)	206+	55
Oxycombustion with Ideal air separation Real compressors for Air & CO_2 1.35 moles O_2/mole CO_2	217+	52
Real Oxycombustion (Darde et al., 2008)	284	40

Thermal Swing Regeneration of solids requires difficult equipment.

- Low absorption T with high heat of absorption
- Solids regeneration at high pressure
- “Cross exchange” at $\Delta T = 5^oC$
- And low cost, robust solids

Conclusions
Research on Solvent Management

MEA is inexpensive & stable to 120C
but degrades readily with O_2 or high T

PZ is more expensive
but stable to 150C & oxidizes slowly

Both are reclaimed by evaporation

High cost reagents or materials may not survive coal flue gas

- Continuous & intermittent impurities
  - SO_3, SO_2, HCl, fly ash, NO_x, O_2, H_2O
  - Fe^{+2}, Cr^{+3}, gypsum, $CaCO_3$, T excursions
- High cost materials must be reclaimable
- High cost materials will require costly pretreating
- Most likely a fatal flaw for anything >$5/lb
  - Designer amines
  - Enzymes
  - Ionic liquids
  - Membranes
  - Most organic & inorganic adsorbents/absorbents
  - Nanomaterials

Some R&D Needs for Amine Scrubbing

- Solvent Management
  - Nitrosamines, aldehydes, land other toxics
  - Oxidative Degradation
  - Reclaiming
  - Pilot plant testing with coal flue gas
- Energy
  - Inexpensive solvents with greater heat of absorption
  - Inexpensive solvents stable to higher T
- Scale-up
  - Advanced strippers
  - Absorbers
  - Exchangers: Reboilers, Exchangers
  - Steam Extraction
  - Pretreating & water balance

History Repeats
$CaCO_3$ Slurry:::Amine Scrubbing

$CaCO_3$	Event	Amine
1948	1st commercial plant	1980
1970	Too commercial for Gov. support But too costly, too dirty to use	1990
1970-82	Government funds advanced alts	1995-
1975-85	Govern. & EPRI fund test facilities	2010-
1977	Power Industry deploys 500+ MW	2016?
2009	First choice dominates	2030 ?

A Newer System to Reduce cost by 10-20%
8 m (40 wt%) Piperazine

- 10-20% less energy than 30 wt% MEA
  - 2 x CO_2 mass transfer rate
  - 1.8 x capacity
  - High P (6 – 15 atm) Stripper, stable to 150°C
- Oxidatively stable, esp. with Inhibitor A
- Less volatile than 7 m MEA
- Good Opportunities for Reclaiming

Economic Perspective

- Capture is \$50-75/tonne CO2 (\$50-75/MWH)
  - Wholesale power doubles (\$50 to 100/MWH)
- Breakeven w Gas at \$70/MWH (capture \$50)
  - Existing plants, fuel + capture
  - Coal @\$2/MMBtu
  - Gas @ \$4.50/MMBtu
- Gasoline @ \$0.40/gal = \$50/Tonne CO_2

Aqueous Abs/Str: Near commercial

- 100's of plants for treating H_2 & natural gas
  - MEA and other amine solvents
- 10's of plants with natural gas combustion
  - Fluor, 30% MEA
  - MHI, KS-1
- A few plants with coal combustion
  - Abb-Lummus, 20% MEA, 6, 8, & 33 MW
  - Fluor, 30% MEA, (6 MW)
  - MHI, KS-1 (7 & 25 MW)
- Still need coal on 800 MW

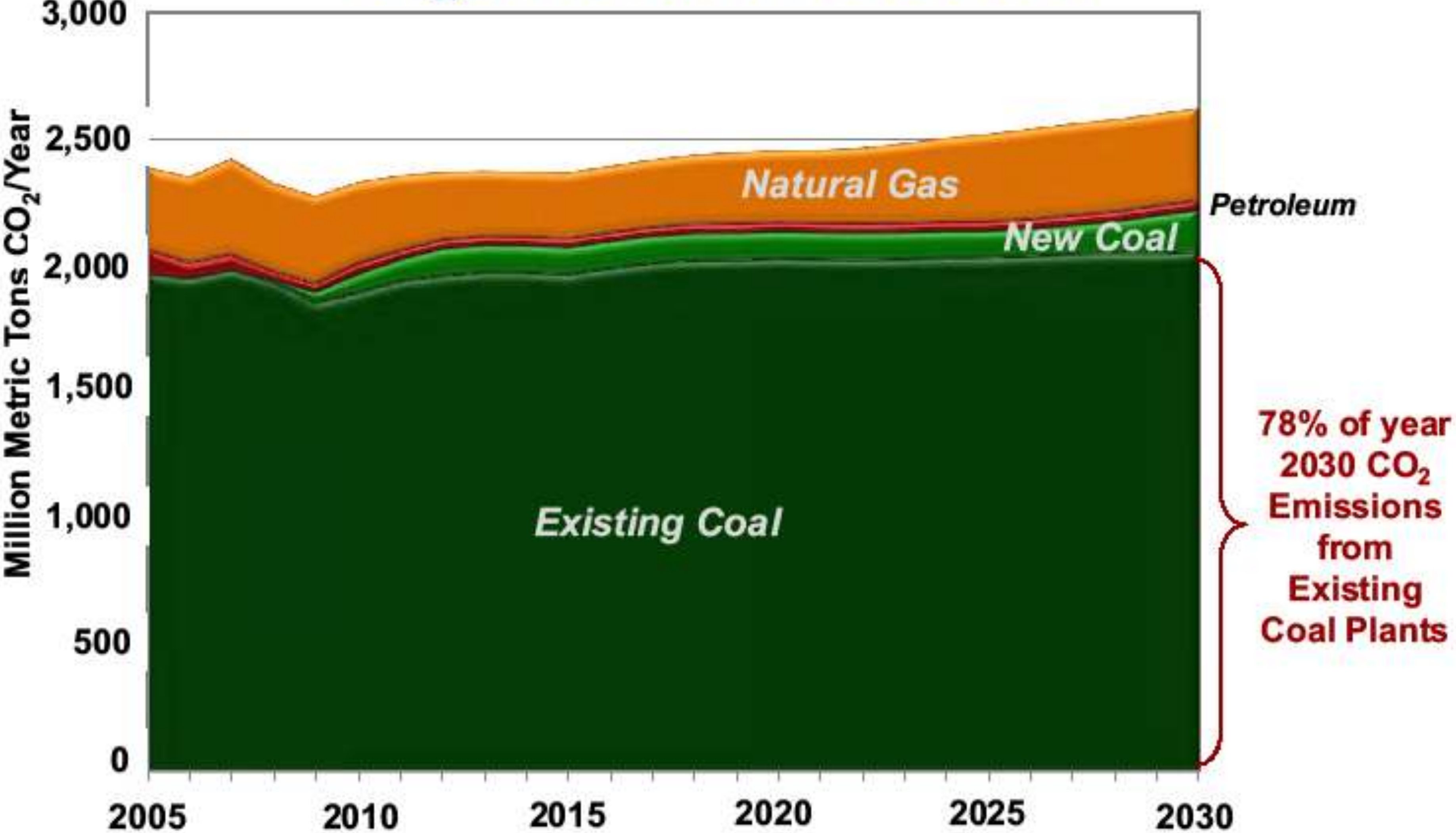
One Conclusion on Energy
8 m PZ (40 wt%) with 2-stage Flash at 150oC

- 10-20% less energy than 30 wt% MEA
  - 2 x CO_2 mass transfer rate
  - 1.8 x capacity
  - Stable to 150^{o}c
    - Stripping at 11 & 17 atm
- W_{min}/W_{actual} = 50% efficiency

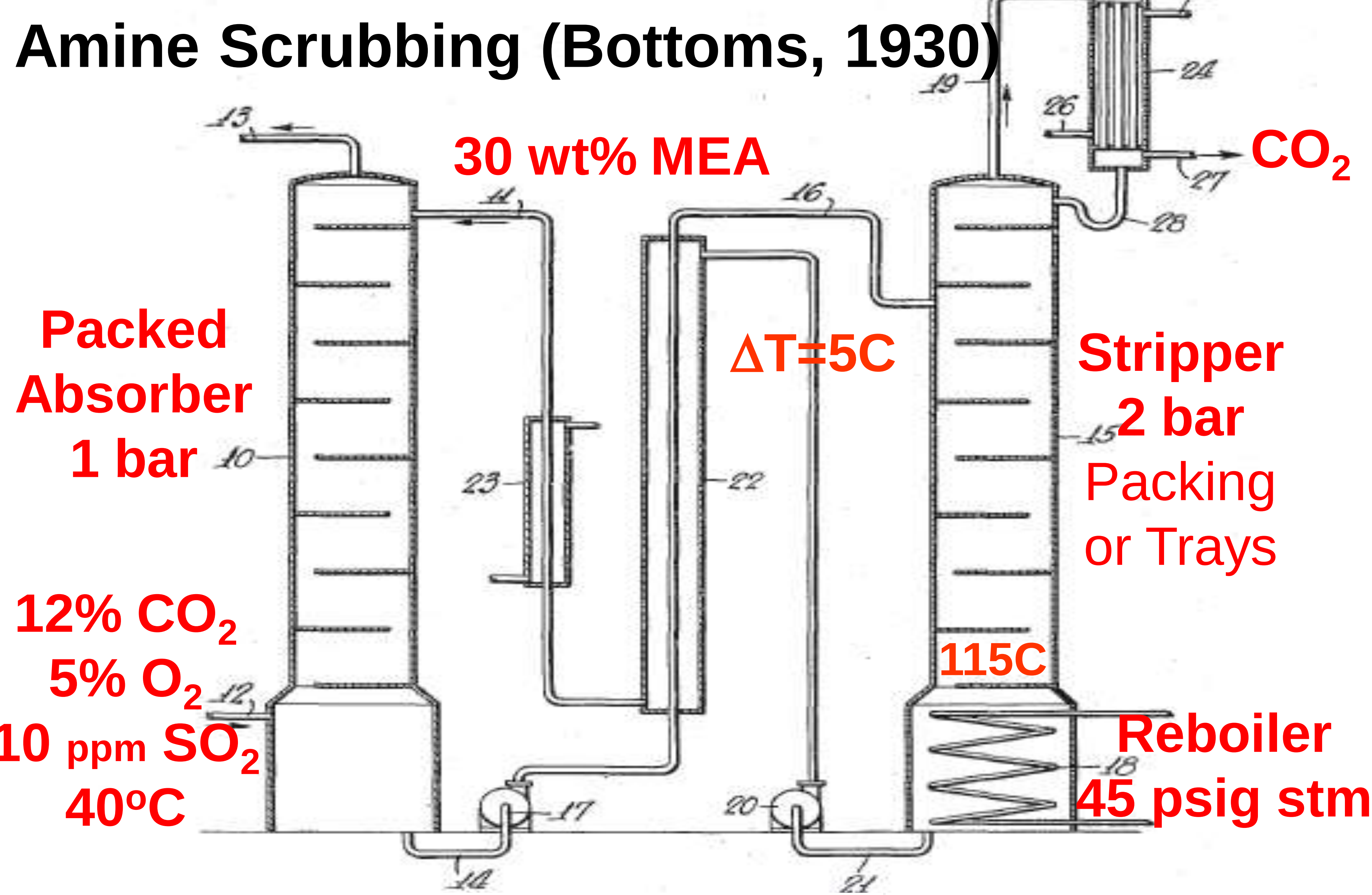
Tail End Technology Ideal for Development, Demonstration, & Deployment

- Low risk
  - Independent, separable, add-on systems
  - Failures impact only Capture and Sequestration
  - Permits on/off operation to address peak load
- Low cost & less calendar time
  - Develop and demonstrate with add-on systems
  - Less demo cost than integrated systems
  - Resolve problems in small pilots with real gas
  - Demo Full-scale absorbers w 100-200 MW gas
    - Ultimately 800 MW absorbers

U.S. Electricity Generation CO_2 Emissions Forecast



Amine Scrubbing (Bottoms, 1930)



Dec. 2, 1930. R. R. BOTTOMS 1,783,901

PROCESS FOR SEPARATING ACIDIC GASES

Filed Oct. 7, 1930