Carbon Dioxide: Generation and Capture

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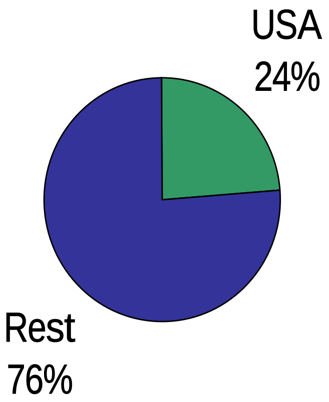
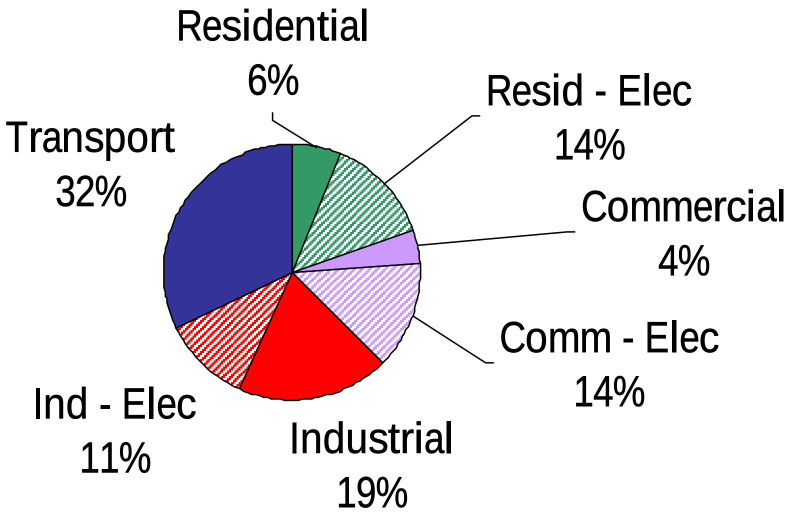
Carbon Dioxide Emissions 2001

In Million Metric Tons of Carbon Equivalent

World – 6582 MMT



USA– 1579 MMT



Industrial – Non-Electricity / Non-Steam	
Cement Production	11.4
Ammonia Synthesis	11.0
Lime Production & Use	5.6
CO2 from natural Gas	5.0
Hydrogen Production	~3.0
Aluminum Production	1.0
Soda Ash Production & Use	0.6
Ethylene Oxide	0.2
Other Chemical Processes	<1.0
TOTAL	~38 MMT

from S. Barnicki (Eastman)

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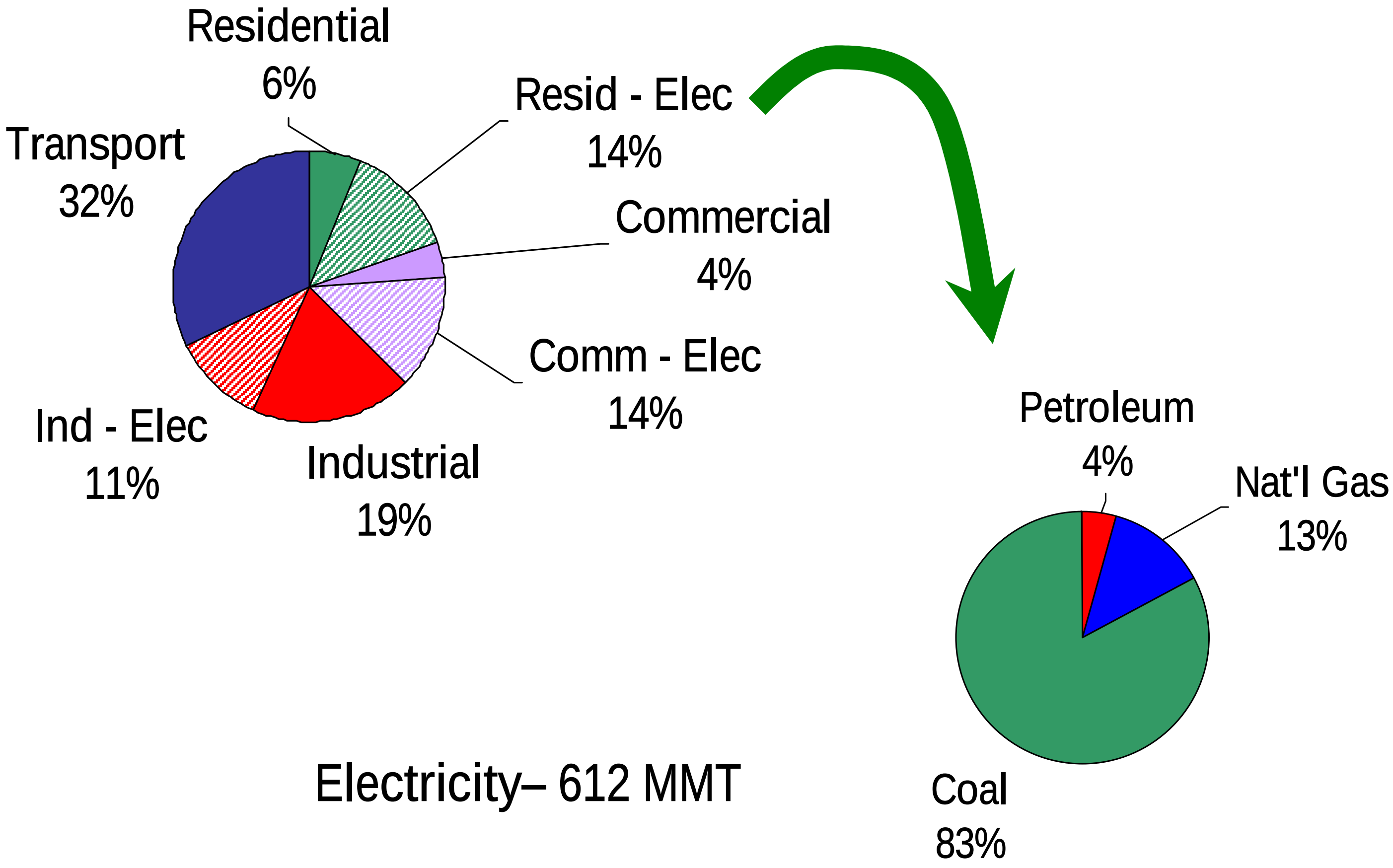


Electricity– 612 MMT

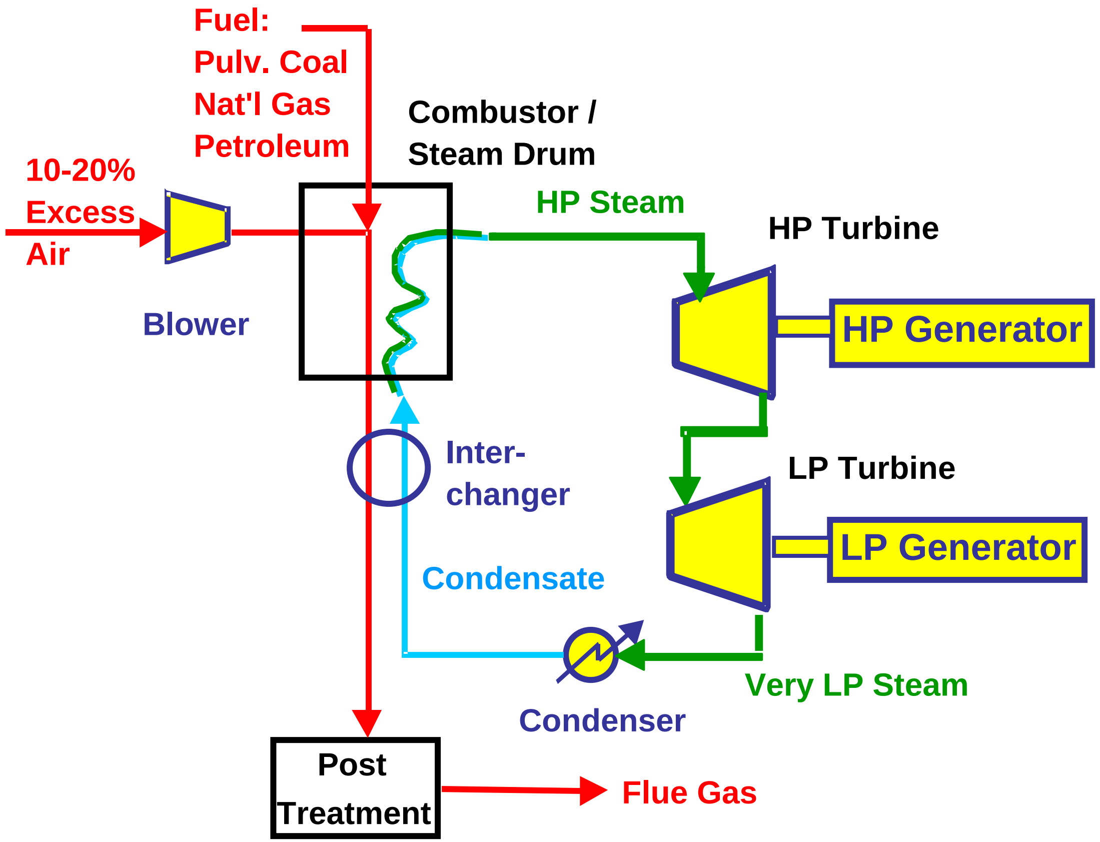
from S. Barnicki (Eastman)

Representative CO_2 Emission Sources

	Source Type	**% US Emissions**	**Mole % CO_2 in Source**	**Typical Pressure (psig)**	**Typical Capture Methods**
Auto/Diesel	Diffuse	33%	~ 13%	0	NONE
Pulverized Coal Power	Point	32%	~15%	0	NONE, Chem Abs
Nat'l Gas Power	Point	5%	~ 8%	0	NONE
Integ. Gas Combined Cycle (IGCC)	Point	Small	15-65%	800-1000	Phys Abs; Chem Abs
Cement Manufacture	Point	0.7%	9-15%	0	NONE
Ammonia Synthesis	Point	0.7%	17-20%	400-550	Phys Abs; Chem Abs
Nat'l Gas Sweetening	Point	0.3%	0.5%-10%	300-1200	Phys Abs; Chem Abs; Membrane, < 5 MSFD
H_2 Synthesis	Point	0.2%	17-20%	400-550	Phys Abs; Chem Abs P-Swing Ads
Ethylene Oxide	Point	0.015%	10-15%	200-250	Chem Abs

from S. Barnicki (Eastman)

Conventional Fossil Fuel Steam Power Cycle



Fuel:
Pulv. Coal
Nat'l Gas
Petroleum

10-20%
Excess
Air

Blower

Combustor /
Steam Drum

HP Steam

HP Turbine

HP Generator

LP Turbine

LP Generator

Inter-
changer

Condensate

Condenser

Very LP Steam

Post
Treatment

Flue Gas

- Rankine Cycle - 25-30% efficiency
- Energy in very LP steam is lost - condensed w/o energy recovery
- Difficult to control pollution
- Flue gas at low pressure ~1 atm

	CO_2	H_2O	N_2	O_2
COAL	15 %	5 %	76 %	4 %
NAT'L GAS	8 %	16 %	73 %	3 %

from S. Barnicki (Eastman)

CO_2 Capture From Conventional Power Plant

- Recovery from low pressure (~1 atm) flue gas
- Low CO_2 partial pressure (~1-1.5 psia)
- Oxygen-containing gas (~2-5%)
- Hot flue gas - 400-800 °C
- May contain NO_x, Hg, SO_2, H_2S, other sulfur species & particulates

from S. Barnicki (Eastman)

Conventional Methods for CO_2 Capture

Method	**Principle of Separation**	**Separating Agent**
Physical Absorption	Preferential Solubility	Liquid
Chemical Absorption	Preferential Reactivity	Reacting liquid
Adsorption	Difference in affinity for solid	Solid adsorbent
Gas Permeation	Diffusion through membrane; pressure gradient	membrane

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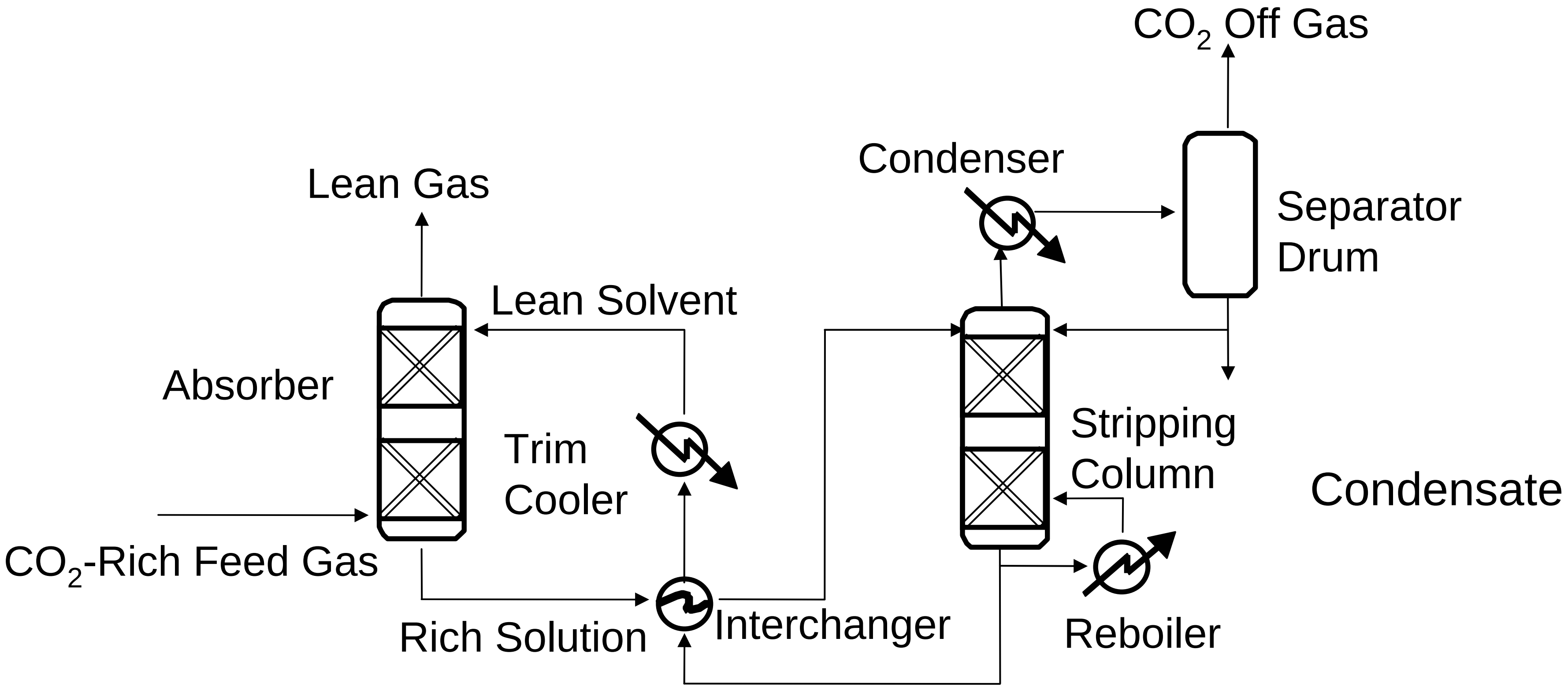
Typical CO_2 Capture Process



- Many variations possible
- Physical absorbent may not require extensive heat input for regeneration
- CO_2 off-gas often at low pressure
- May require pre-compression, depending on feed gas pressure

from S. Barnicki (Eastman)

Physical Absorption

- Solubility of CO_2 in solvent - NO reaction
- Typical absorbents:
  - Methanol, N-methyl-2-pyrrolidone, methyl glymes of EG oligomers, tri-n-butyl phosphate, propylene carbonate, water (not very good)
- Regeneration often can be accomplished with Δ P, limited (or no) ΔT
- Under optimal conditions generally much less energy usage than chemical absorption

from S. Barnicki (Eastman)

Chemical Absorption

- Chemical reaction of absorbed CO_2 with solvent
- Typical absorbents:
  - Primary, secondary, tertiary, hindered amines
    - MEA, DEA, MDEA, TEA, 2-AMP
  - Alkali metal hydroxides or carbonates
    - NaOH, K_2CO_3 , Na_2CO_3
- 1st, 2nd amines limited ~0.5 mol CO_2/mol Amine
- Tert & hindered can reach ~1.0 mol/mol
- Regeneration by ΔT & often Δ P
- Solution concentration limited by solubility, corrosion and/or reactivity with O_2, contaminants

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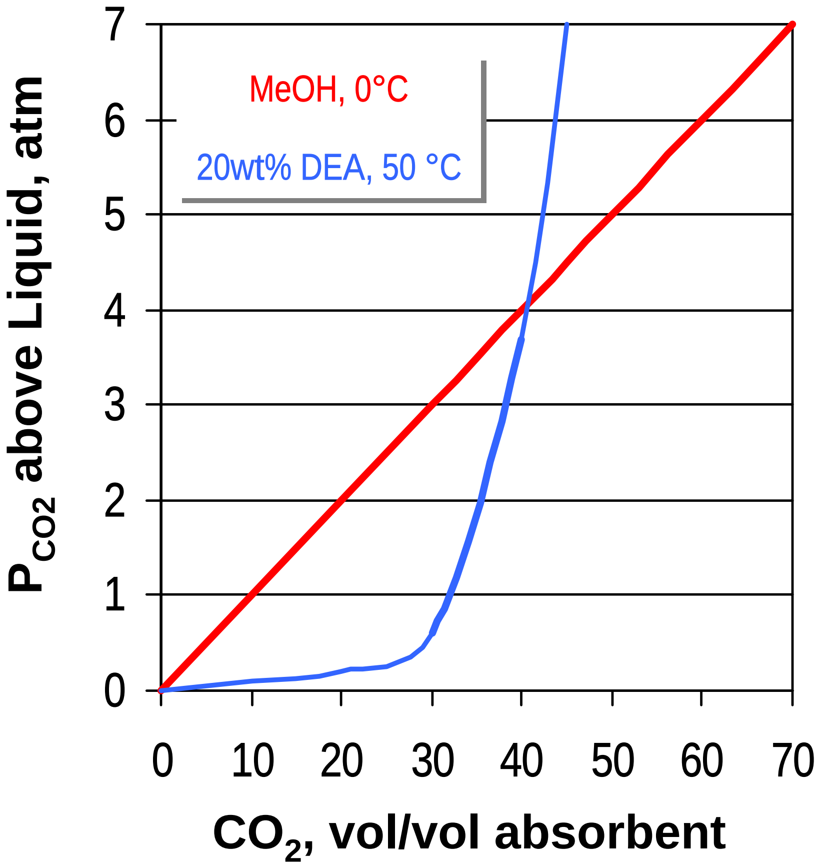
Chemical vs Physical Equilibrium



Chemical solvent

- Good at low inlet P_{CO_2}
- Can reach very low outlet P_{CO_2} i.e., < 10 ppm possible
- Sharp rise in outlet P_{CO_2} when loading reaches rxn stoichiometry

Physical solvent

- Better at high inlet P_{CO_2}
- Loading proportional to P_{CO_2}
- Cannot reach very low outlet P_{CO_2} i.e., usually 0.1-2%, but some can reach ppm levels

from S. Barnicki (Eastman)

Range of Applicability For H_2S & CO_2 Removal

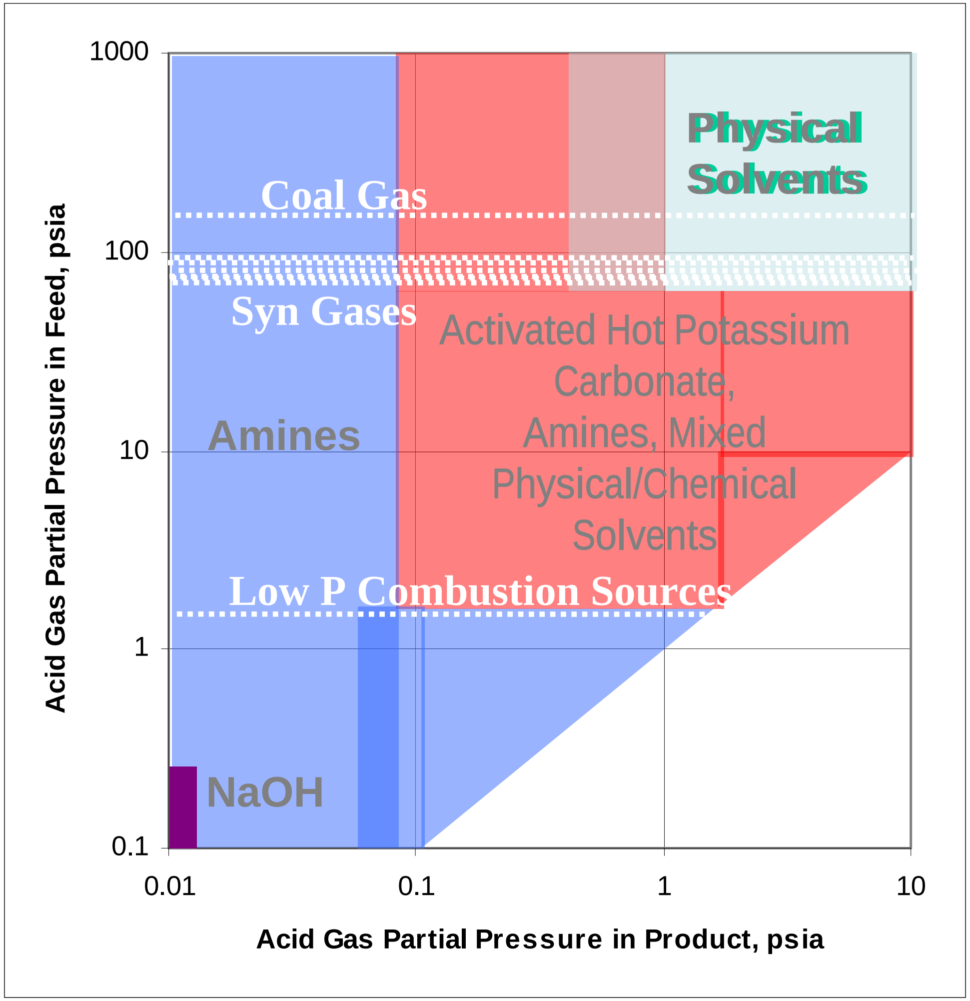
Within optimized region, costs about equivalent between methods

Low P Combustion Sources

Auto/Diesel
Nat'l Gas Power Plant
Pulverized Coal Power Plant
Cement Kilns

Syn Gases

Ammonia
H_2



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Amine Processes

- Reacts with CO_2 to form carbamate complex
- Many commercially available processes
- Choice dictated by removal requirements, stability to stream components
- Generally can be selective between for H_2S / CO_2
- Good for $\mathbf{P_{CO_2}}$ ~ 0.1 psi or higher
- Susceptible to O_2 degradation, other contaminants – can be controlled
- Good stage efficiencies

from S. Barnicki (Eastman)

Carbonate Processes

- Basic idea similar for many akali- & alkali earth hydroxides & carbonates
- Choice dictated by cost & solubility in water
- Non-selective between H_2S / CO_2
- Very best for $\mathbf{P_{CO_2}}$ above ~ 10 psi, but can work at lower $P_{\mathbf{CO_2}}$
- Vacuum stripping for CO_2 removal to less than ~ 1000 ppm
- Poor stage efficiencies – tall absorption towers
- Improved with amine as catalyst

from S. Barnicki (Eastman)

Components of Energy Balance in Absorptive Capture

Absorber

- Remove heat of absorption & reaction
- Cool lean recycle solvent - sensible heat

Stripper

- Heat rich solvent to boiling point
- Supply heat of desorption & reaction
- Generate stripping/reflux vapors

Possible Power Plant Capture Add-ons

- Cool flue gas to absorber conditions
- Compress feed gas to overcome pressure drop in Absorber
- Post compression of CO_2 to desired product pressure

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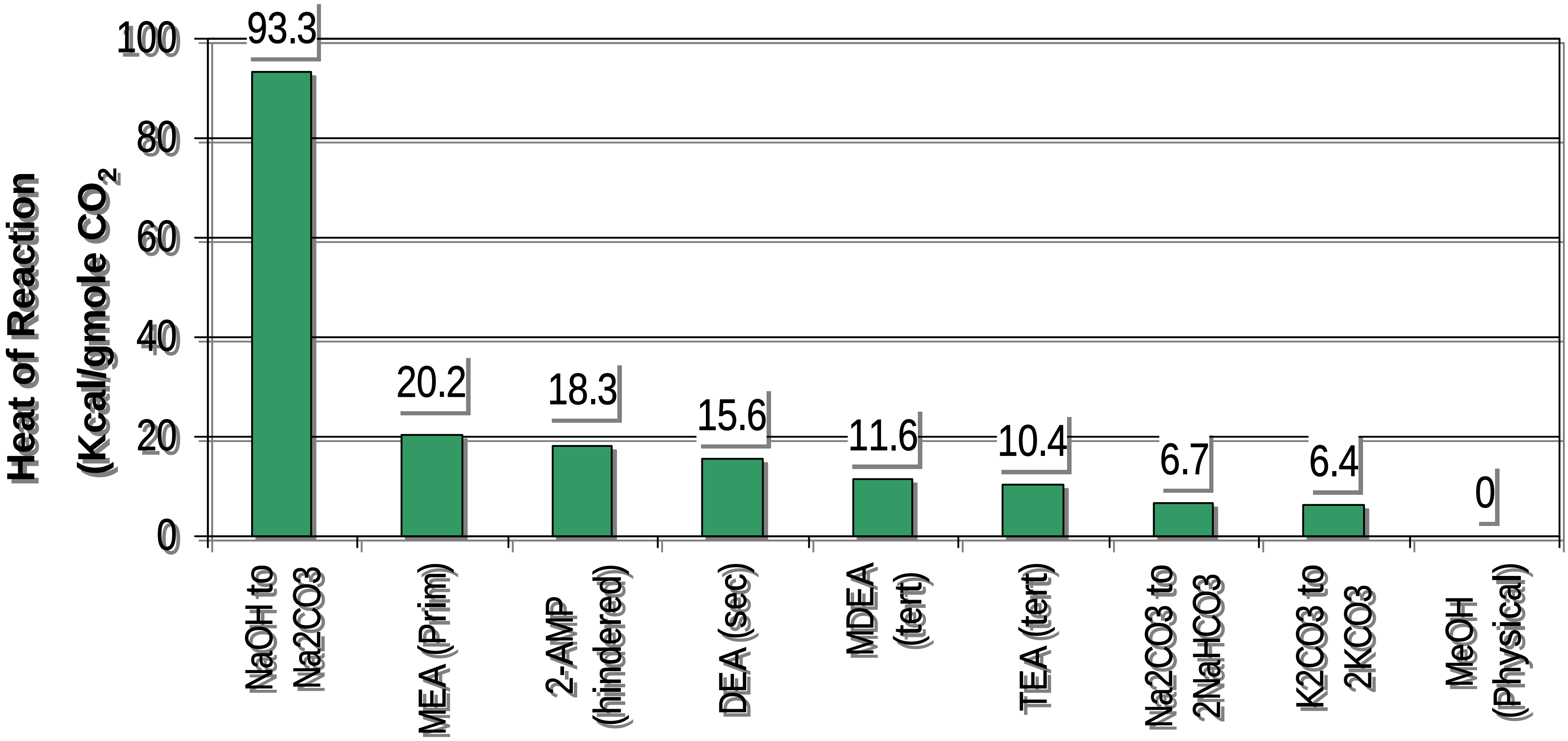
Heat of Reaction: Representative Absorbents



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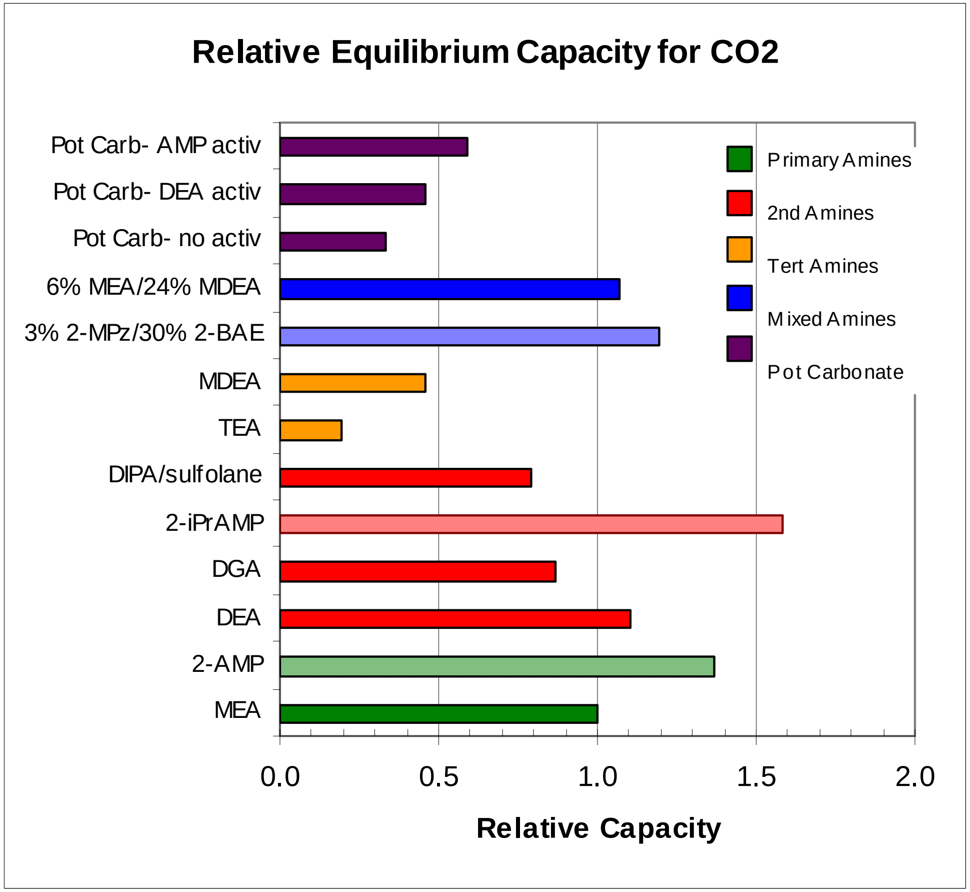
Potential Absorbents For Flue Gases

Primary Amines	MEA (25 wt%)
Secondary Amines	DEA (35 wt%), DIPA (40 wt%), DGA (40 wt%),
Tertiary Amines	TEA (40 wt%), , MDEA (40 wt%),
Hindered Amines	2-AMP (40 wt%), 2- iPrAMP (40 wt%), 30 wt% 2-BAE / 3 wt% 2-MP
Mixed Amines	24 wt% MDEA / 6 wt% MEA
Hot Potassium Carbonate	30 wt% Unactiv. or activ. w/ DEA, AMP
Ionic Liquids	

from S. Barnicki (Eastman)

Conventional Power Plant Capture: Solvent Loading



- Depends on reaction equilibrium
- Secondary effect of solution concentration
- Large effect on energy usage and equipment size

from S. Barnicki (Eastman)

Energy Usage Analysis

- 15% CO_2 in flue gas at ~1 atm absolute pressure
- 90% recovery of CO_2 in flue gas
- Pre-compression of flue gas to overcome pressure drop in absorber (14.7 psia to 18 psia)
- Post-compression of recovered CO_2 to 10 and 100 atm in two stages, w/ interstage cooling

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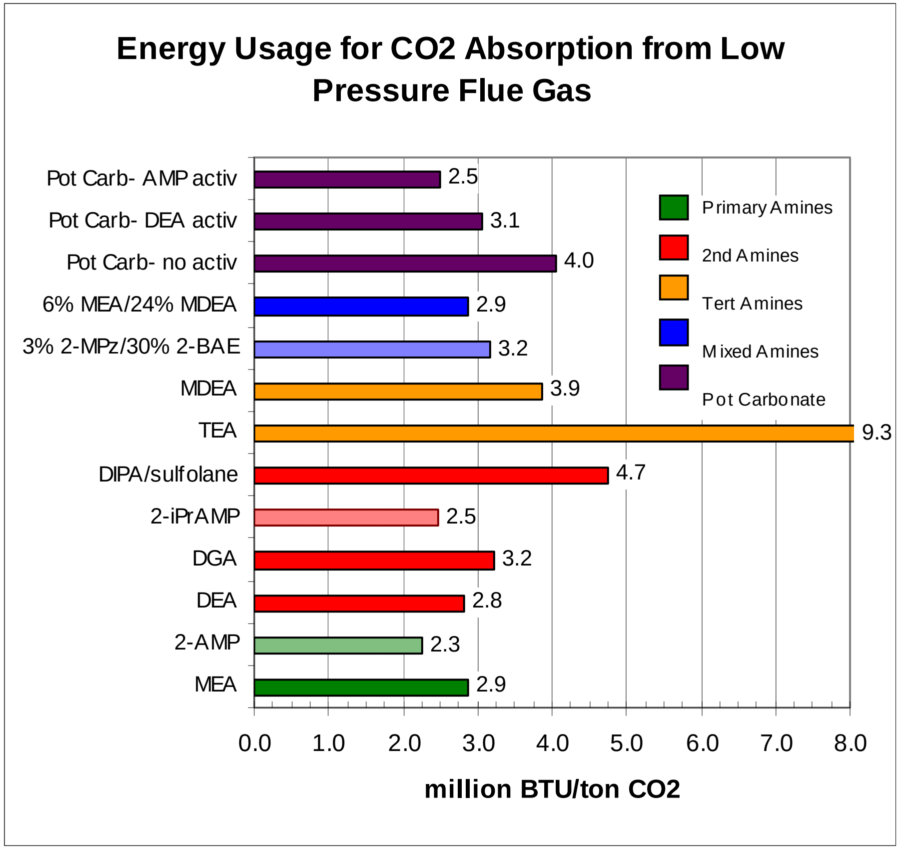
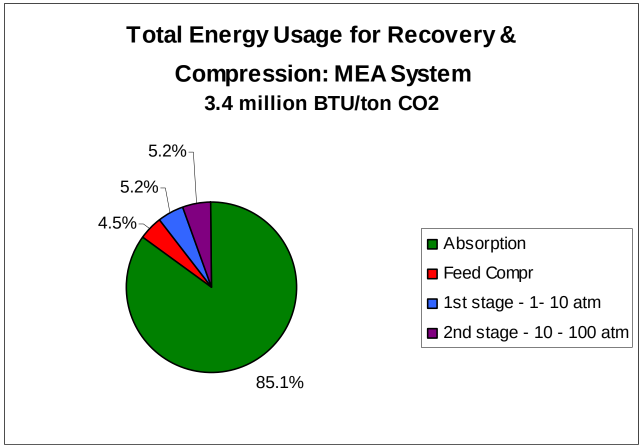
Energy Usage: CO_2 Capture - Compression

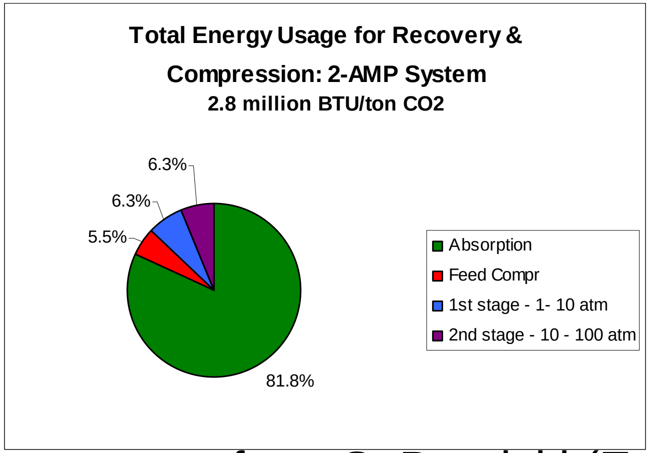
Absorption Step



MEA - 3.4 M BTU / Ton CO_2



2-AMP - 2.8 M BTU / Ton CO_2



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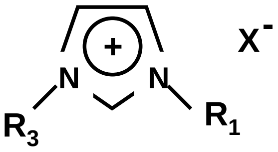
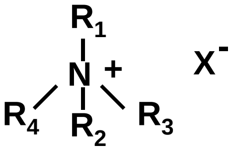
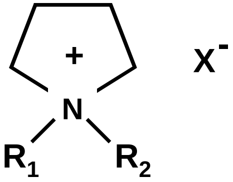
Alternative solvents: Ionic Liquids



imidazolium

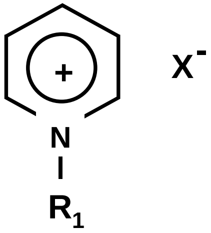


tetra alkylammonium

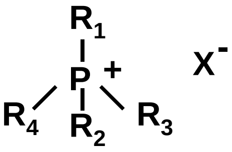


pyrrolidinium

X = PF_6
BF_4
$(CF_3SO_2)_2N$
Cl
NO_3
CH_3CO_2
CF_3CO_2
CF_3SO_3



pyridinium



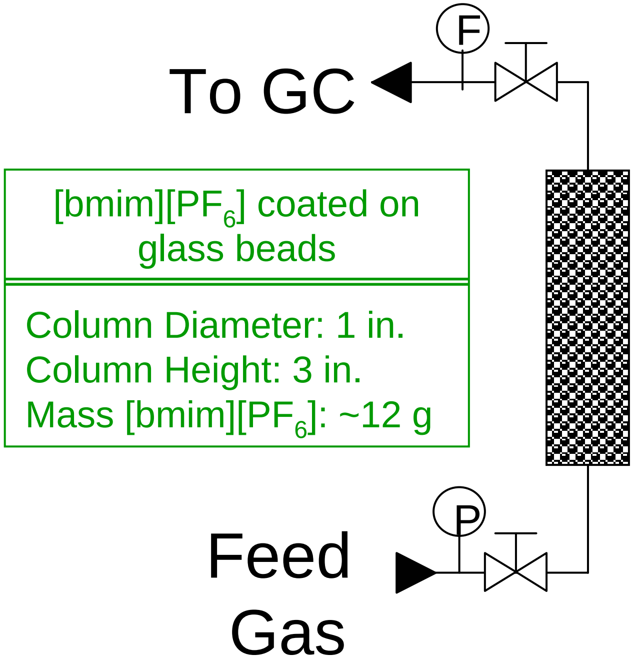
tetra alkylphosphonium

Example:
1-n-butyl-3-methylimidazolium
hexafluorophosphate
[bmim][PF_6]

- **Organic salts**
- **Liquid at ambient conditions**
- **Negligible vapor pressure**
- **Water stable ILs (Wilkes and Zaworotko, 1992)**
- **Solvent for a variety of industrial reactions**

Using [bmim][PF_6] to Separate Gas Mixtures

Conventional Absorber

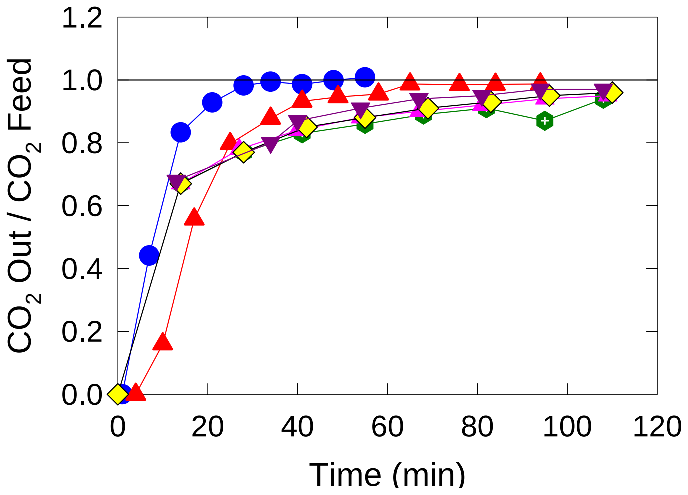


[bmim][PF_6] coated on glass beads

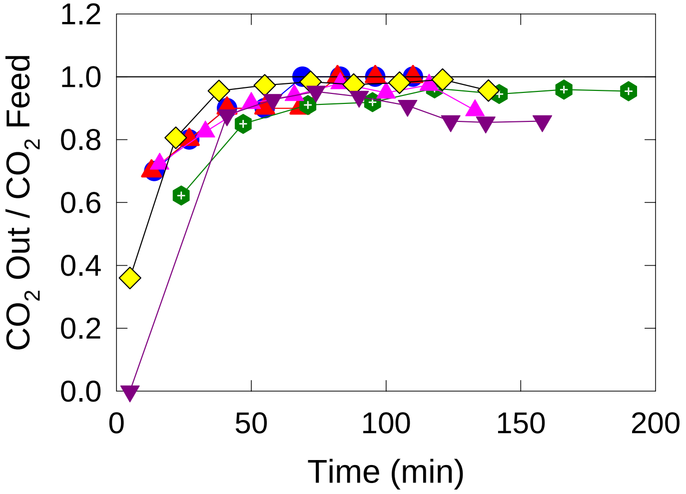
Column Diameter: 1 in.
Column Height: 3 in.
Mass [bmim][PF_6]: ~12 g

Breakthrough Curves

Feed Gas:
10% CO_2 in N_2



Feed Gas:
10% CO_2 in CH_4



- Proof-of-concept experiments show ILs have potential as a gas separation media
- Should not contaminate gas phase (non-volatile)
- Also worked in supported-liquid membrane configuration

Comparison of MEA and [bmim][PF$_6$]

Monoethanolamine	[bmim][PF$_6$]
High absorbing capacity	Lower absorbing capacity
Low hydrocarbon solubility	Low hydrocarbon solubility
High volatility	No volatility
Limited temperatures	Stable at high temperatures
High Δh_{rxn} with CO_2	Lower Δh_{abs} with CO_2
Low viscosity	Relatively high viscosity

Energy using MEA to Capture CO_2

- Total energy: **3.4 million BTU/ton CO_2**
  - Slightly compress the feed gas to 1.2 bar

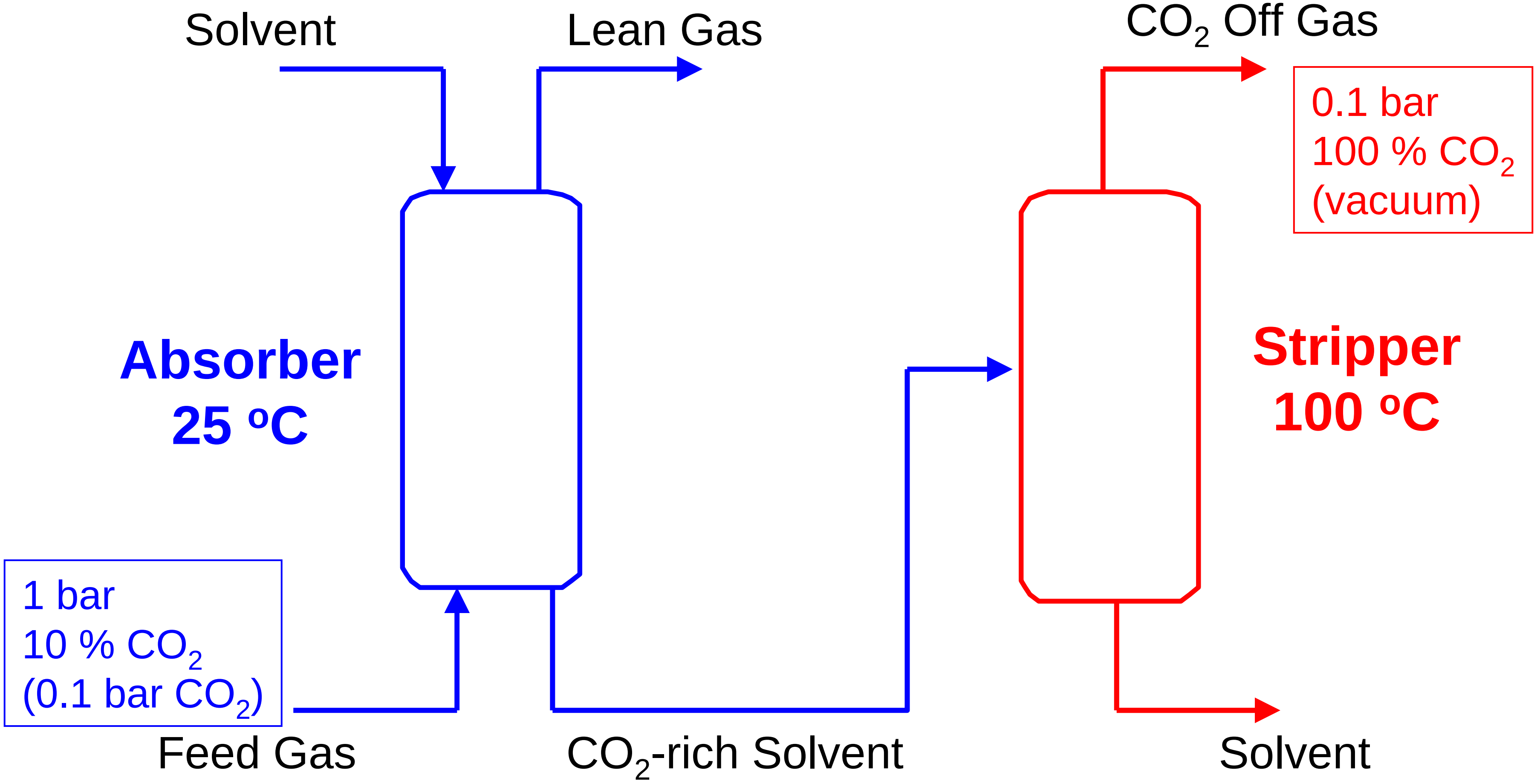
    0.15 million BTU/ton CO_2
  - Desorb the CO_2 in the stripper

    2.9 million BTU/ton CO_2
  - Compress the CO_2 off-gas to 100 bar

    2 stages at 0.18 million BTU/ton CO_2 each

from S. Barnicki (Eastman)

Simplified Temperature-Swing Process



Solvent

Lean Gas

CO_2 Off Gas

0.1 bar
100 % CO_2
(vacuum)

Absorber
25 ºC

Stripper
100 ºC

1 bar
10 % CO_2
(0.1 bar CO_2)

Feed Gas

CO_2-rich Solvent

Solvent

Energy Balance

$$Q = -\Delta h_{abs} + m * Cp * \Delta T$$

Q: energy needed for desorption

Δh_{abs}: enthalpy of absorption for [bmim][PF_6] or the enthalpy of reaction for MEA

m: mass of solvent to absorb 1 kg CO_2

Cp: heat capacity of the solvent

ΔT: temperature difference between the absorption and desorption step

Parameters

Δh_{rxn} (30 wt% MEA in H_2O) = - 85.4 kJ / mol CO_2

Δh_{abs} ([bmim][PF_6]) = -16.1 kJ / mol CO_2

m (30 wt% MEA in H_2O) = 17 kg / kg CO_2

m ([bmim][PF_6]) = 5914 kg / kg CO_2

Cp (30 wt% MEA in H_2O) = 4.18 kJ / kg K

Cp ([bmim][PF_6]) = 1.0 kJ / kg K (low)
= 2.5 kJ / kg K (high)

Actual Cp for [bmim][PF_6]:
At 25 °C: 1.40 kJ/kg*K
At 100 °C: 1.48 kJ/kg*K

Energy for CO_2 Absorption and Recovery

Temperature-swing (25 °C to 100 °C)
CO_2 partial pressure = 0.1 bar

	[bmim][PF_6]		MEA (30 wt%)
	(low *Cp*)	(high *Cp*)	
mass solvent/kg CO_2	5914		17
Cp (kJ/kg K)	1.0	2.5	4.18
$-\Delta h_{abs}$ or $-\Delta h_{rxn}$ (kJ/kg CO_2)	**$3.7*10^2$**		**$1.9*10^3$**
m*Cp*ΔT (kJ/kg CO_2)	**$4.4*10^5$**	**$1.1*10^6$**	**$5.2*10^3$**
***Q* (kJ/kg CO_2)**	**$4.4*10^5$**	**$1.1*10^6$**	**$7.1*10^3$**
***Q* (million BTU/ton CO_2)**	**382**	**954**	**6.1**

$$\approx 2.9 \frac{millionBTU}{tonCO_2}$$

$$Q = -\Delta h_{abs} + m * Cp * \Delta T$$

Energy for CO_2 Absorption and Recovery

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Q (kJ/kg CO_2)	**4.4×10^5**	**1.1×10^6**	**7.1×10^3**
Q (million BTU/ton CO_2)	**382**	**954**	**6.1**

Chemical Absorbent
Determined by Stoichiometry
0.5 mol CO_2/mol MEA

Energy for CO_2 Absorption and Recovery

Temperature-swing (25 °C to 100 °C)

CO_2 partial pressure = 0.1 bar

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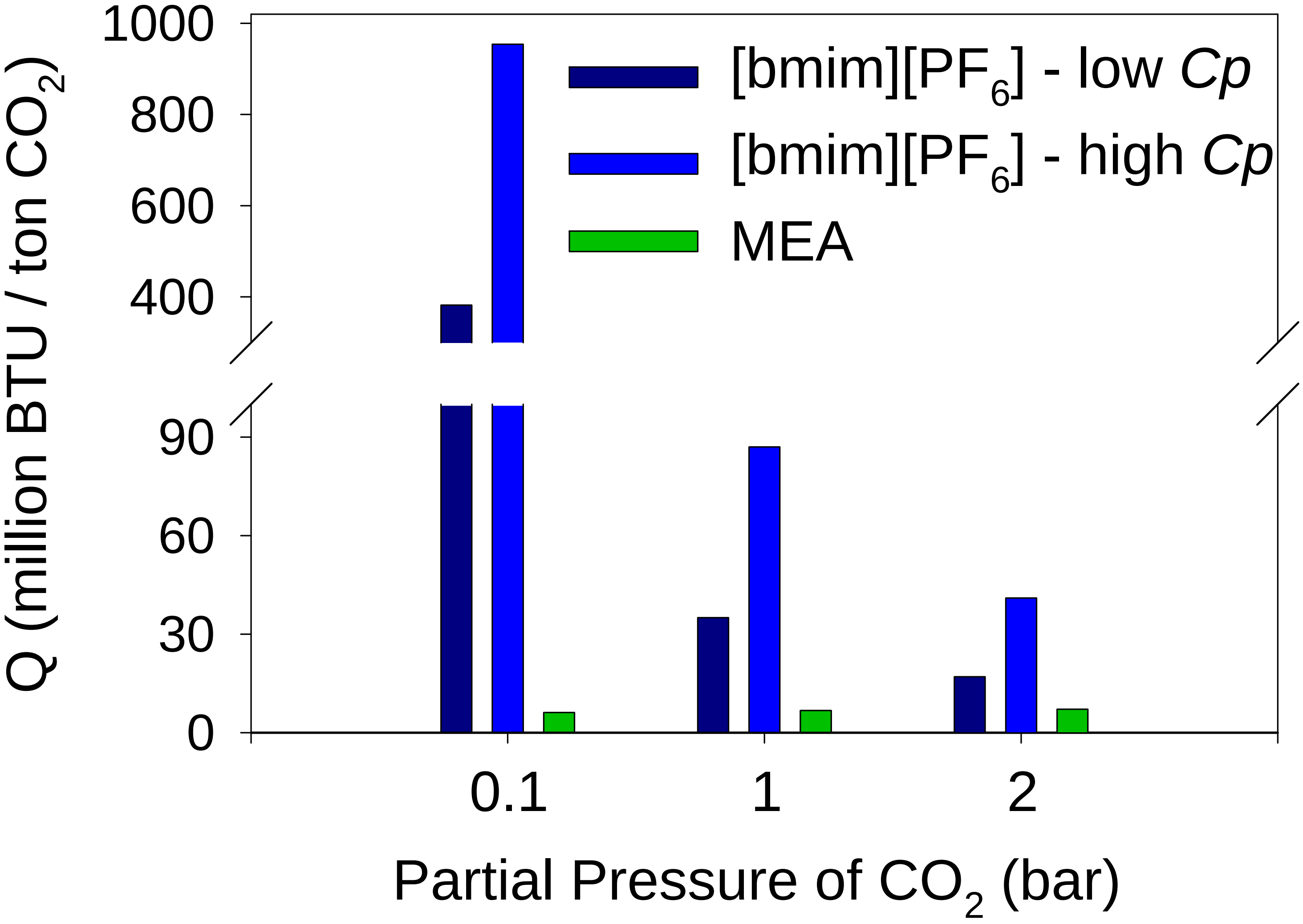
***Q* (million BTU/ton CO_2)**	**382**	**954**	**6.1**

Physical Absorbent
P_{CO2} dependent

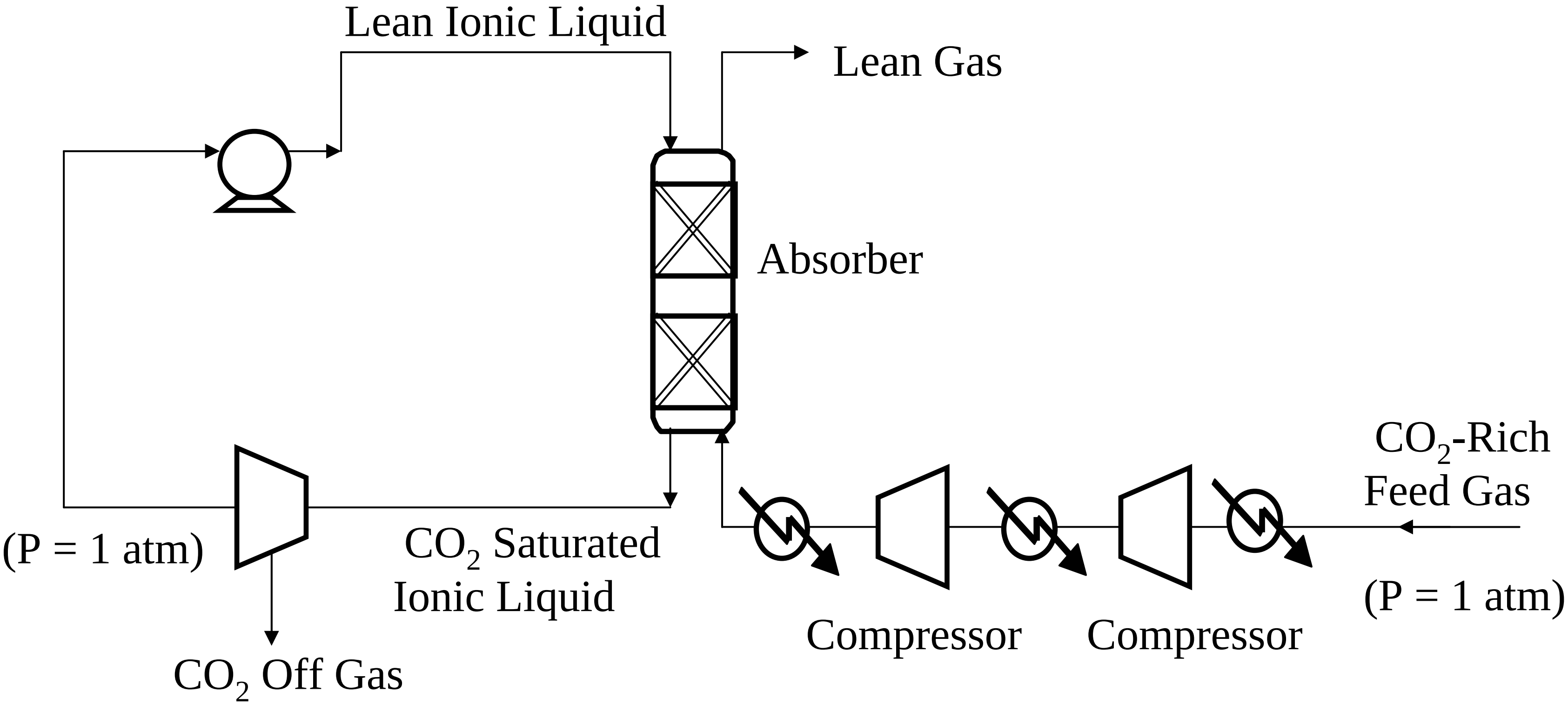
Chemical Absorbent
Limited by Stoichiometry
0.5 mol CO_2/mol MEA

Feed Pressure Effects

Temperature-swing calculations but with varying CO_2 partial pressures



Pressure Swing Absorber



Using MEA to Capture CO_2

- Total energy: **3.4 million BTU/ton CO_2**
  - Slightly compress the feed gas to 1.2 bar

    0.15 million BTU/ton CO_2
  - Desorb the CO_2 in the stripper

    2.9 million BTU/ton CO_2
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    2 stages at 0.18 million BTU/ton CO_2 each

from S. Barnicki (Eastman)

Ideal IL Henry's Constant to Compete with MEA

[bmim][PF_6] @ 25 ^{o}C:
H ~ 53 bar

Temperature-swing (25 ^{o}C to 100 ^{o}C)

	P_{CO2} = 0.1 bar		**P_{CO2} = 1 bar**		**P_{CO2} = 2 bar**	
	(low *Cp*)	(high *Cp*)	(low *Cp*)	(high *Cp*)	(low *Cp*)	(high *Cp*)
mass solvent / kg CO_2	90	36	90	36	90	36
Cp (kJ/kg K)	1.0	2.5	1.0	2.5	1.0	2.5
H (bar) at 25 ^{o}C	**1.1**	**0.5**	**11**	**5.2**	**23**	**11**
H (bar) at 100 ^{o}C	**4.2**	**2.0**	**42**	**19**	**84**	**39**

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	P_{CO2} = 0.1 bar		P_{CO2} = 1 bar		P_{CO2} = 2 bar	
	(low *Cp*)	(high *Cp*)	(low *Cp*)	(high *Cp*)	(low *Cp*)	(high *Cp*)
mass solvent / kg CO_2	90	36	90	36	90	36
Cp (kJ/kg K)	1.0	2.5	1.0	2.5	1.0	2.5
H (bar) at 25 ^oC	**1.1**	**0.5**	**11**	**5.2**	**23**	**11**
H (bar) at 100 ^oC	**4.2**	**2.0**	**42**	**19**	**84**	**39**

[bmim][Tf_2N] @ 25 ^oC: H ~ 30 bar

Jim Davis TSIL with amine on cation: H ~ 3 bar

Conclusions

- [bmim][PF_6] not capable of replacing MEA
- Need higher CO_2 carrying capacity
- Combination temperature-swing and pressure-swing for CO_2 capture and solvent regeneration could decrease energy usage
- Necessary improvement seems within reason