Processes to Recover and Purify Carbon Dioxide

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CHE 670 – Sustainability Seminar: Greenhouse Gases; Carbon Taxes and Trading; and Carbon Sequestration

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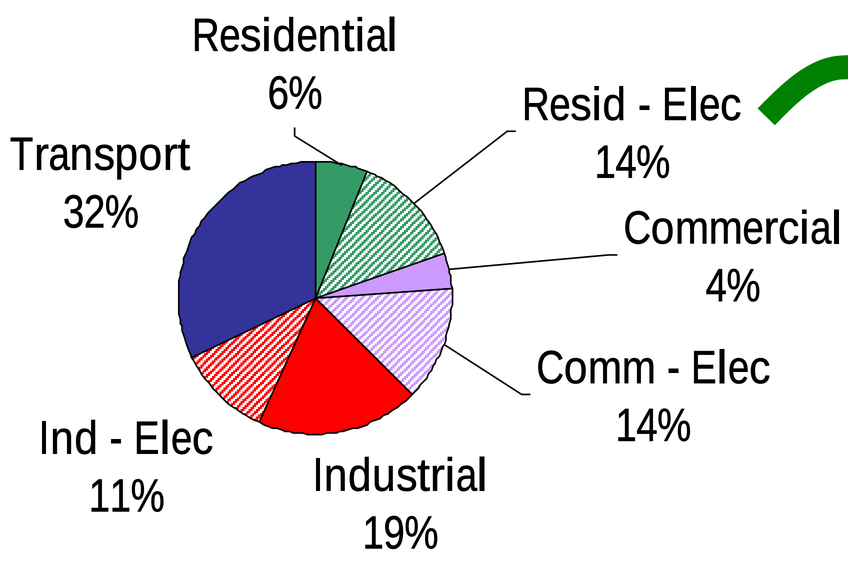
Presentation Outline

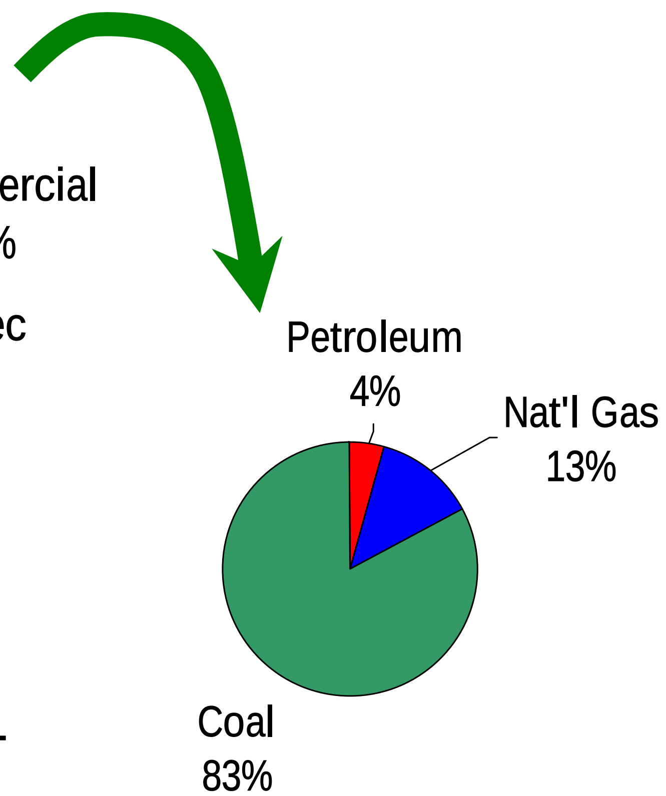
- Why CO_2 capture is important
- Generalized pathways for CO_2 capture
- Current state of the art technology
  - Limitations
- Emerging technologies
  - Challenges and opportunities

Carbon Dioxide Emissions 2001

In Million Metric Tons of Carbon Equivalent

USA– 1579 MMT





Electricity– 612 MMT

from S. Barnicki (Eastman)

Carbon Capture and Sequestration (CCS)

K-STATE ENGINEERING

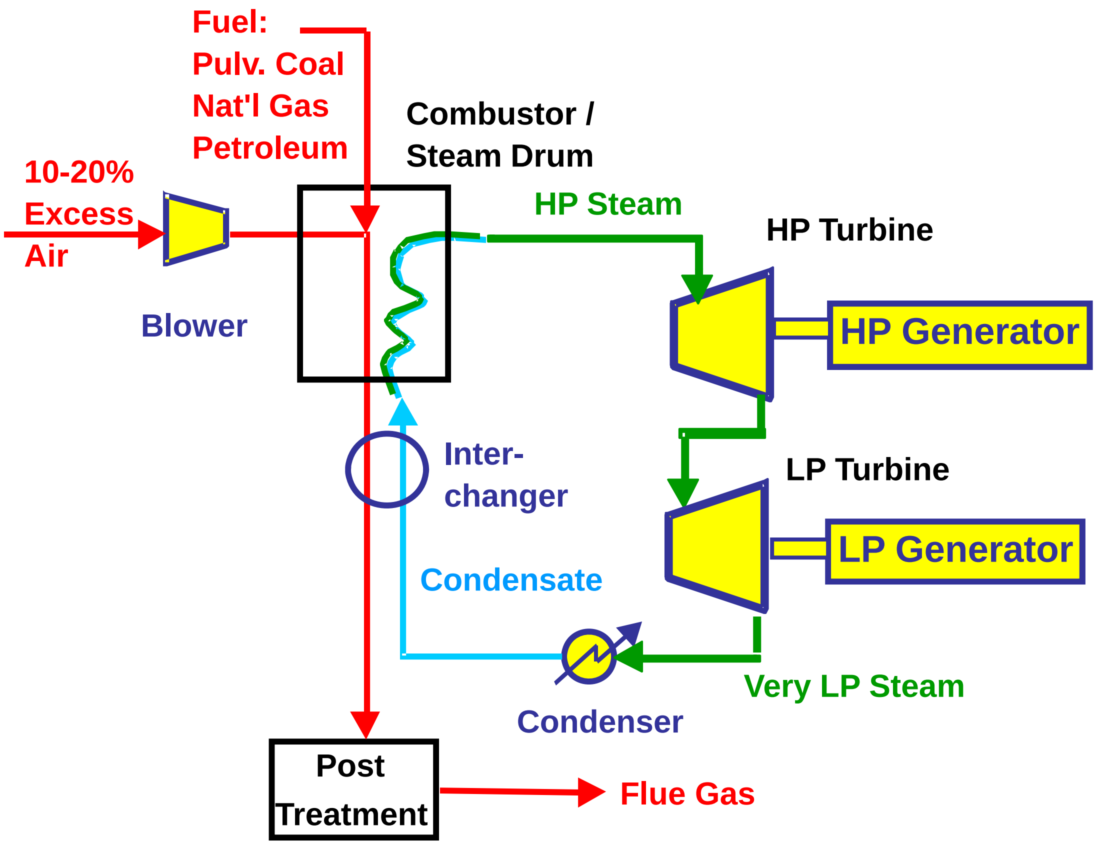
- Promising sequestration technologies, but all are limited by ability to capture & purify CO_2
- Separation costs generally the most significant portion of CSS costs
- Currently available technology not economically feasible for national implementation
  - Would reduce typical coal-fired power plant (generally ~33% efficient) net power output by 1/3
  - 20% power output reduction in state of the art power plant
- DOE Goal: Develop capture technologies by 2012 capable of 90% CO_2 capture at <10-20% increase in electricity costs

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

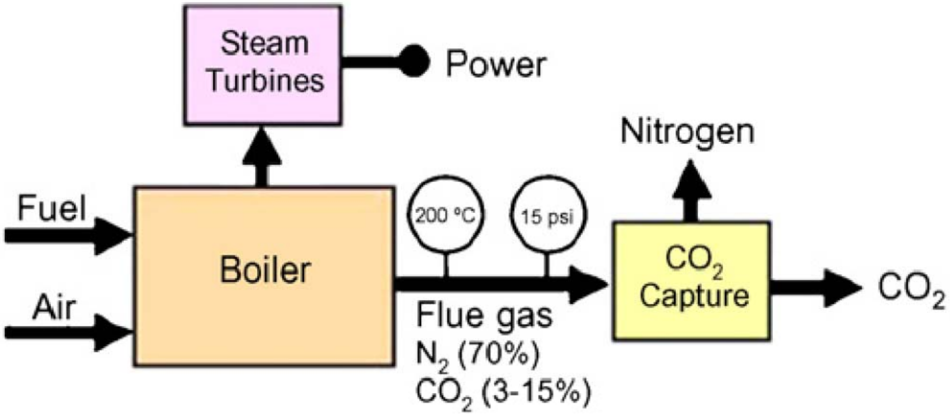


- Rankine Cycle - 25-30% efficiency
- Energy in very LP steam is lost - condensed w/o energy recovery
- Difficult to control pollution
- Flue gas at low pressure ~1 atm

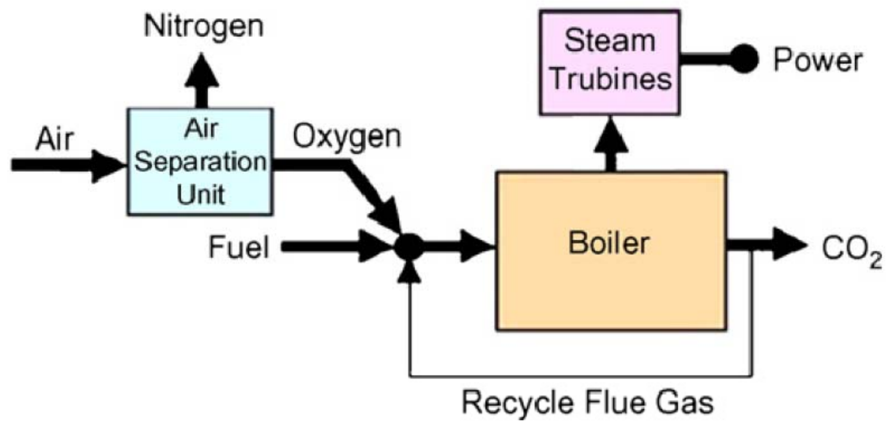
	CO_2	H_2O	N_2	O_2
COAL	15 %	5 %	76 %	4 %
NAT'L GAS	8 %	16 %	73 %	3 %

from S. Barnicki (Eastman)

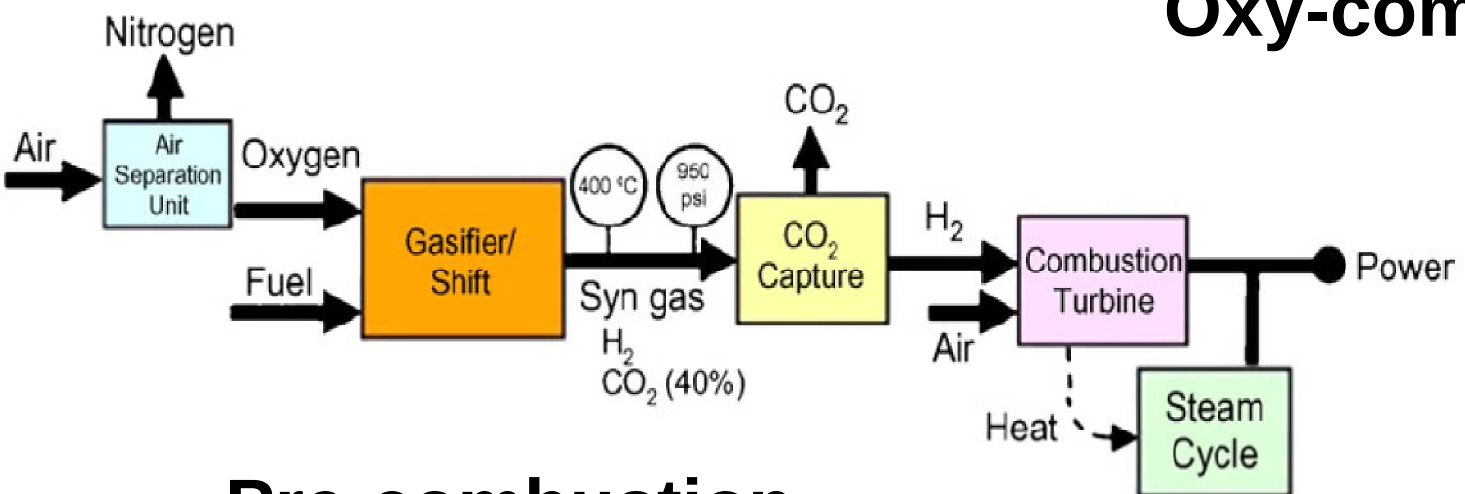
Carbon Capture Pathways



Post-combustion



Oxy-combustion



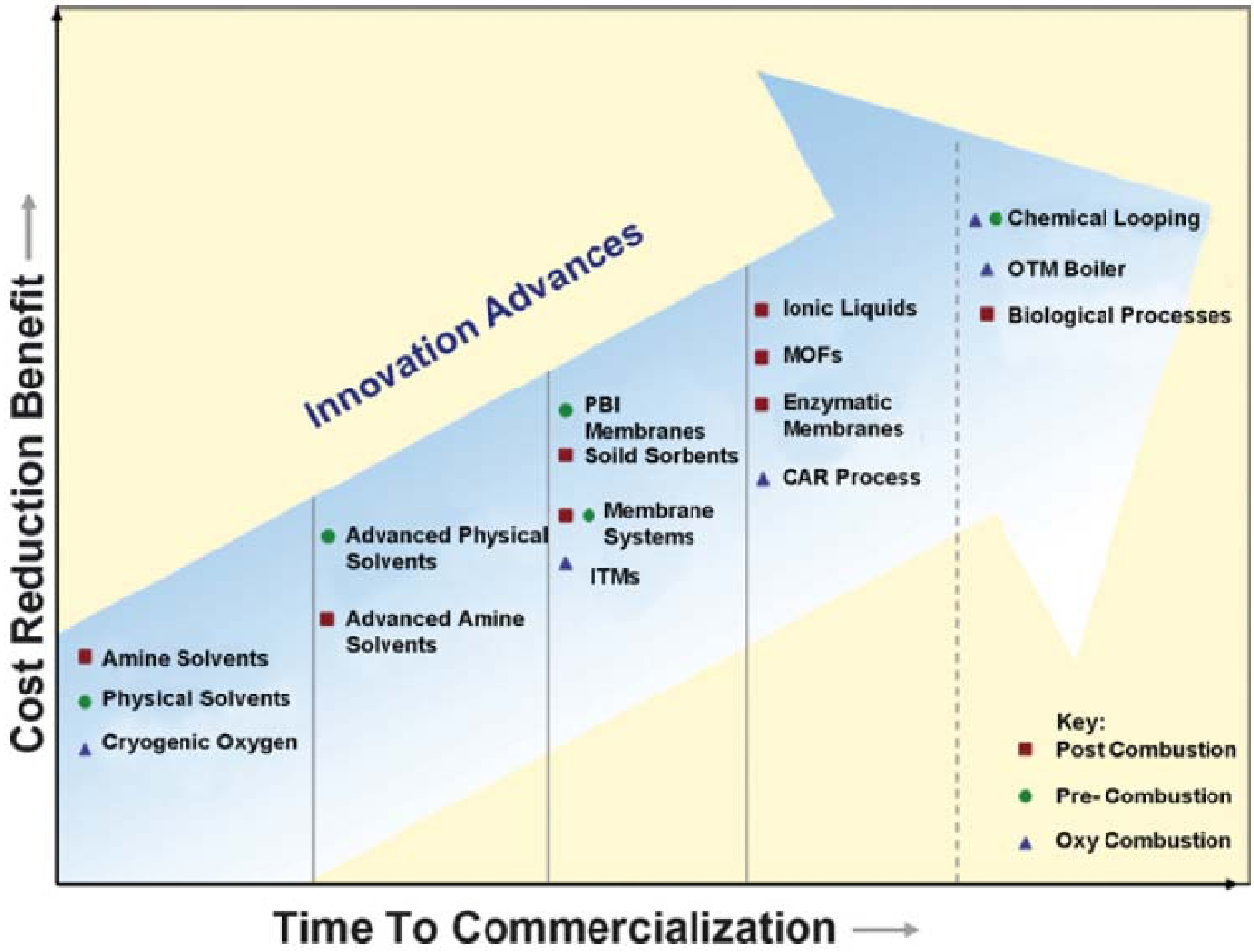
Pre-combustion

Int.J.Greenhouse Gas Control 2, 2008, 9-20.

Pathway Comparison

Pathway	Advantage	Barriers
Post-combustion	•Applicable to typical power plant •Retrofit option	•Flue gas dilute in CO_2 •Ambient pressure
Pre-combustion	•High CO_2 concentration •High pressure	•Few gasification plants in operation •Cost
Oxy-combustion	•High CO_2 concentration •Retrofit option	•Cryogenic O_2 production costly •Maintaining cooling temperatures

Cost Benefit of Emerging Technologies



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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

from S. Barnicki (Eastman)

Amine-Based Systems

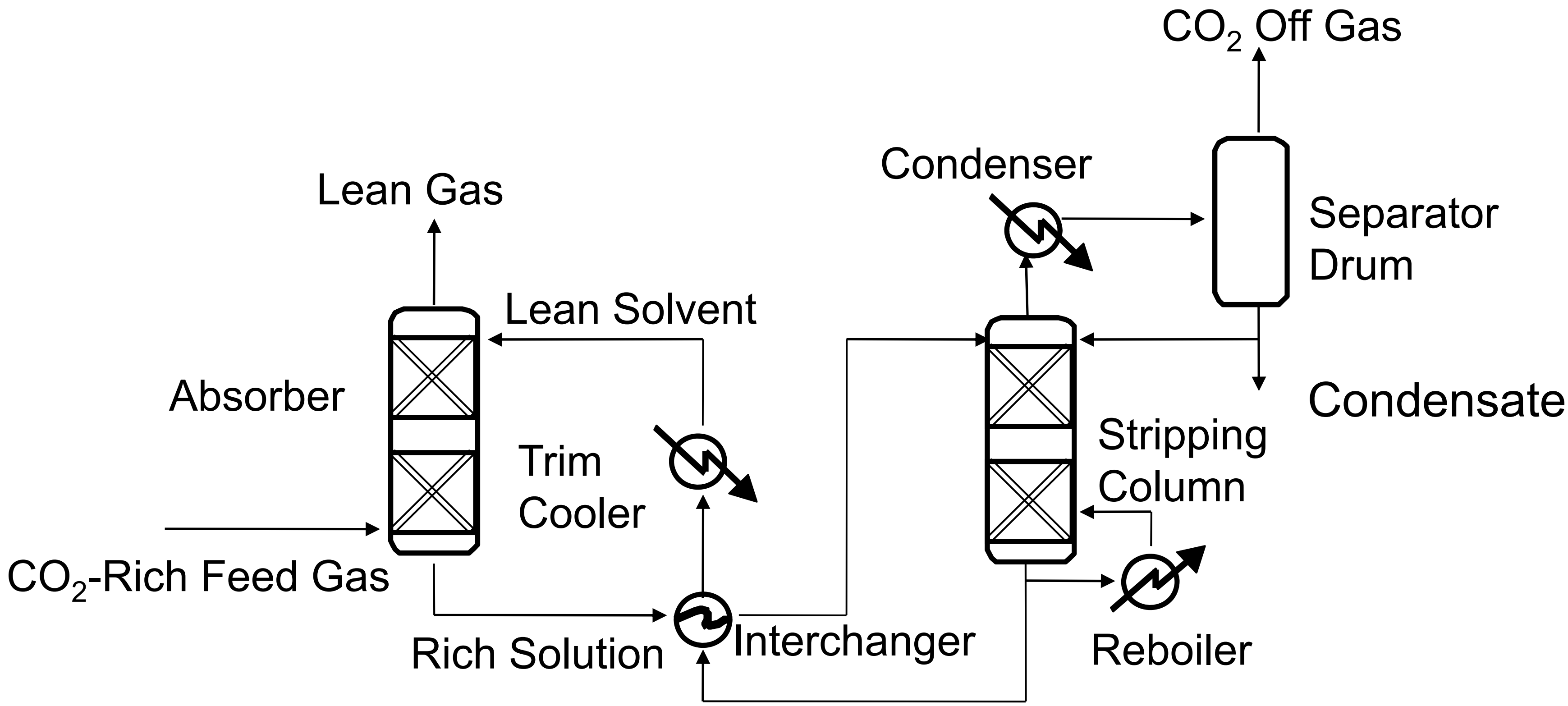
- Current state of the art for CO_2 removal
- Amine reacts with CO_2 to form stable compound

Strengths	Limitations
•High absorbing capacity •Low hydrocarbon solubility •Low viscosity	•High volatility •Corrosive (need to dilute) •Limited temperatures •High Δh_{rxn} with CO_2

R&D Opportunities: amine selection, column design, heat integration, additives to decrease corrosion, improved regeneration processes

Post-combustion capture

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)

Energy using MEA to Capture CO_2

Specifications for Energy Balance Calculation

- 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

- Total energy required: **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

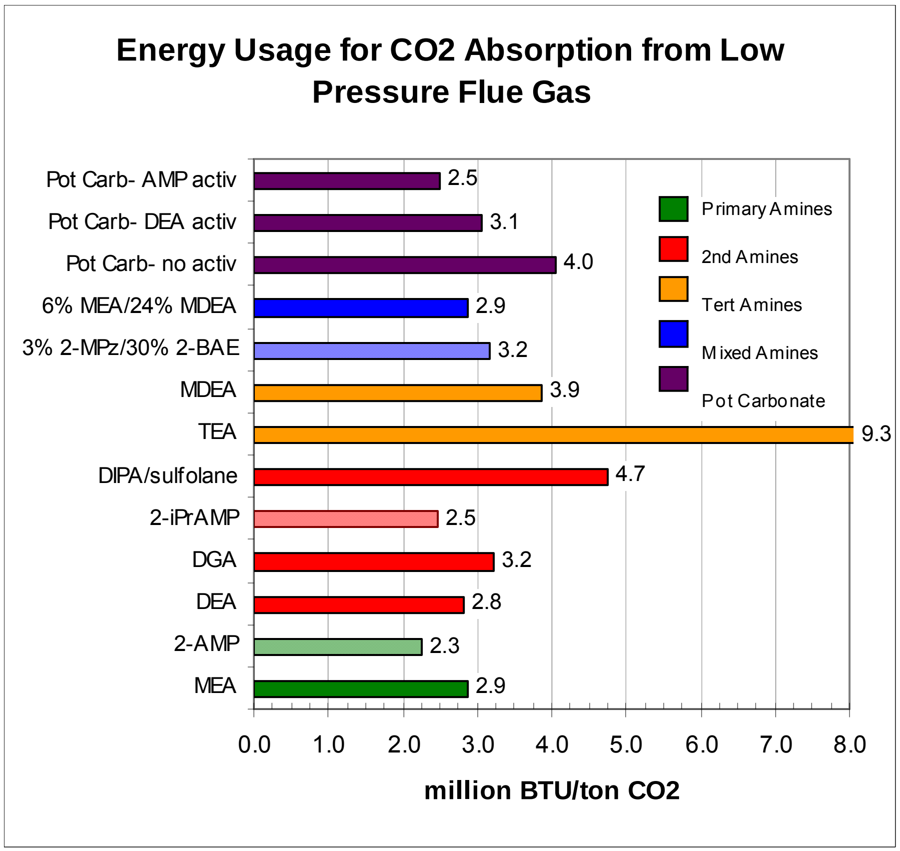
    2.9 million BTU/ton CO_2
  - Compress the CO_2 off-gas to 100 bar

    2 stages at 0.18 million BTU/ton CO_2 each

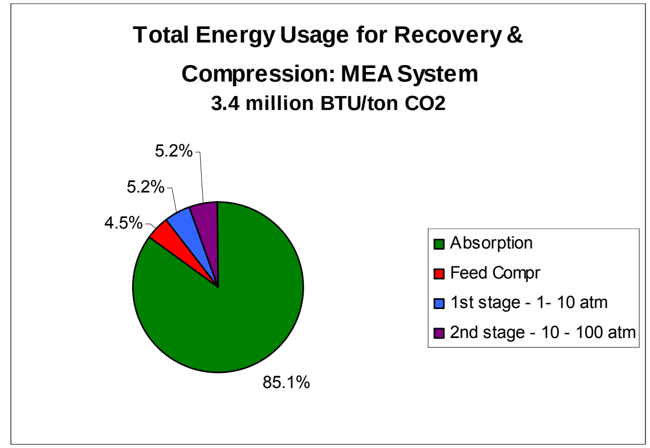
from S. Barnicki (Eastman)

Energy Usage for Other Amines

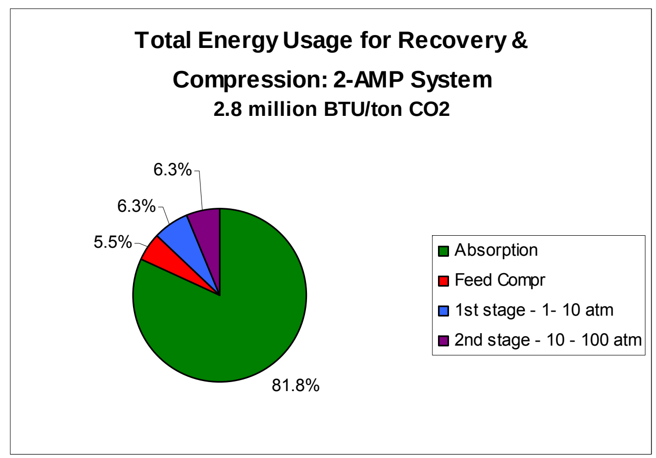
Absorption Step



MEA - 3.4 M BTU / Ton CO_2



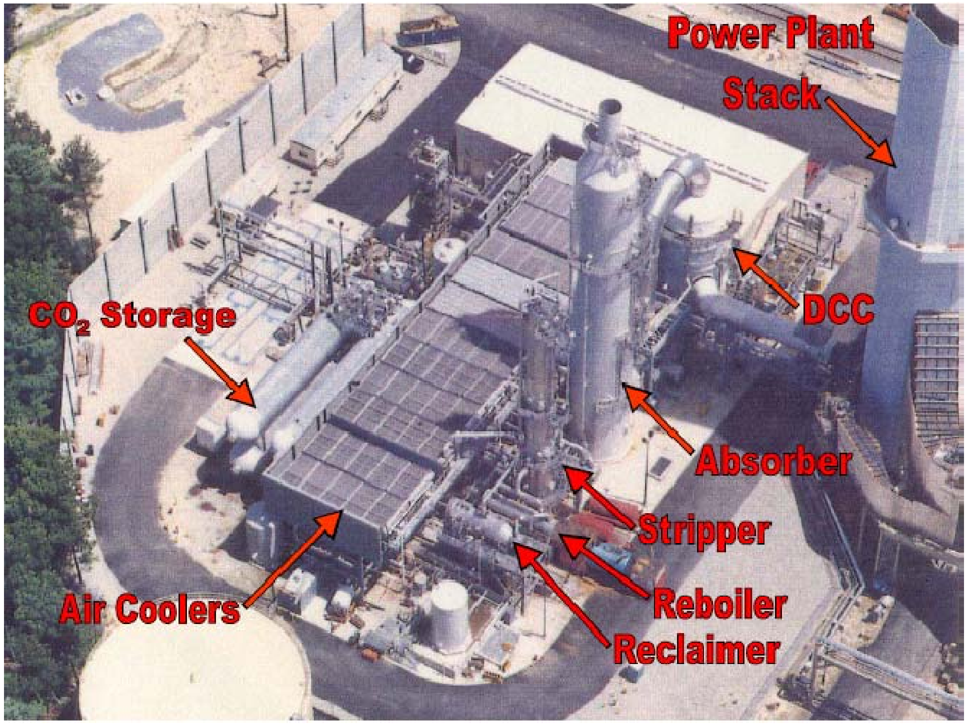
2-AMP - 2.8 M BTU / Ton CO_2



from S. Barnicki (Eastman)

Fluor Econamine FG Plus Process

- Uses proprietary acid gas removal system
- Requires 1400 BTU/lb CO_2 compared to 1700 BTU/lb CO_2 for 30% Monoethanolamine (MEA) solution
- Currently the standard commercial baseline for CO_2 removal



Bellingham, MA

Uthamaniyah, Saudia Arabia

Carbonate-Based Systems

- Soluble carbonate reacts with CO_2 to form bicarbonate compound, heat to regenerate
- Significantly lower energy requirements than amines

Research at UT-Austin (G. Rochelle):

K_2CO_3 system with catalytic piperazine

- Comparing to 30% MEA solution
  - 10-30% faster absorption rate
  - 5% lower energy use and higher loading (40%)
  - Proposed design changes expected to reduce energy 5-15%
  - Cost of piperazine cancels out cost of energy savings

Post-combustion capture

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Aqueous Ammonia

- Similar chemistry to amines → ammonia reacts with CO_2
- Lower heat of reaction, so easier to regenerate

Strengths	Limitations
•Potentially higher absorbing capacity •Lack of degradation during regeneration •Low cost •Possible to absorb other pollutants	•Even higher volatility •Loss of NH_3 during regeneration

Post-combustion capture

Chilled Ammonia Process

Alstrom Chilled Ammonia Process Implementation

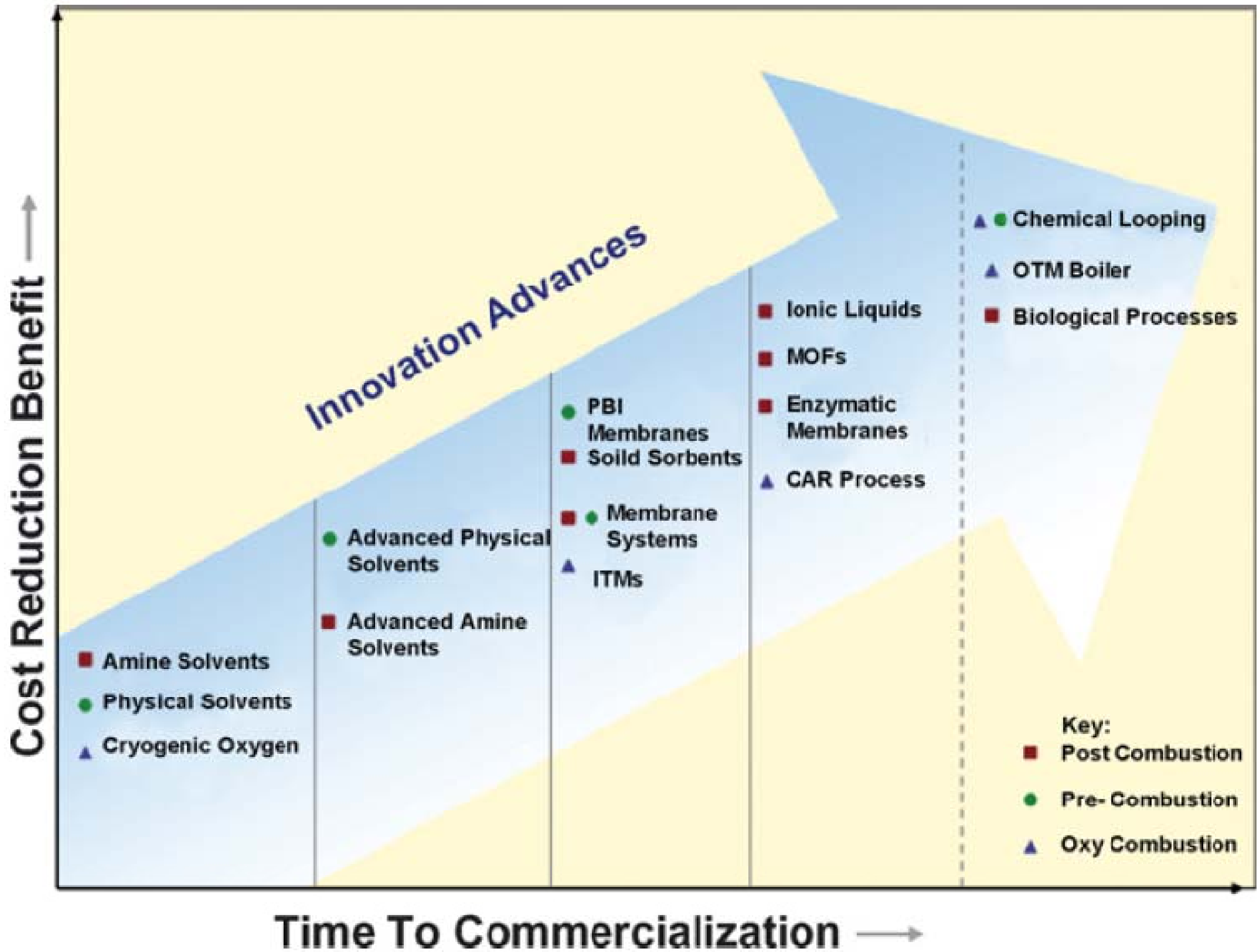
Pleasant Prairie (US) – Coal	5 MWt	EPRI, We	ALSTOM
Mountainer (US) – Coal Northeastern (US) – Coal	30 MWt >200 MWe	AEP	ALSTOM
Karlshamm (Sweden) – Oil/Gas	5 MWt	e-on	ALSTOM
TCM Mongstad (Norway) – Gas	40 MWt	StatoilHydro	ALSTOM

Hurdles: cooling flue gas & maintaining absorber temps, mitigating NH_3 loss, achieving 90% removal efficiency in single stage, fouling of equipment

If overcome, potential for significant increase in energy efficiency over amines.

Post-combustion capture

Cost Benefit of Emerging Technologies



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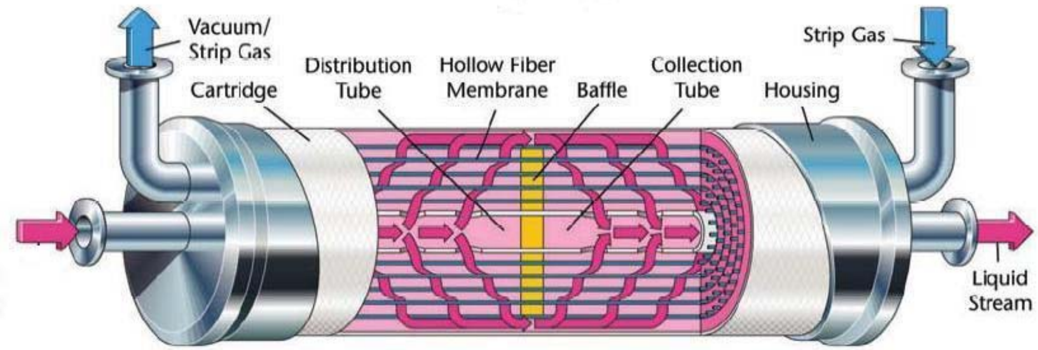
Membranes

Variety of options



Examples:

- Flue gas flows through membrane tubes, amine solution around shell, protects amine from impurities
- Using functionalized membranes (e.g. amine groups) or shape-selective membranes (e.g. zeolites) to increase selectivity

R&D opportunities: membrane materials, configuration design, need to ↑ selectivity, ↑ permeability, ↓ cost

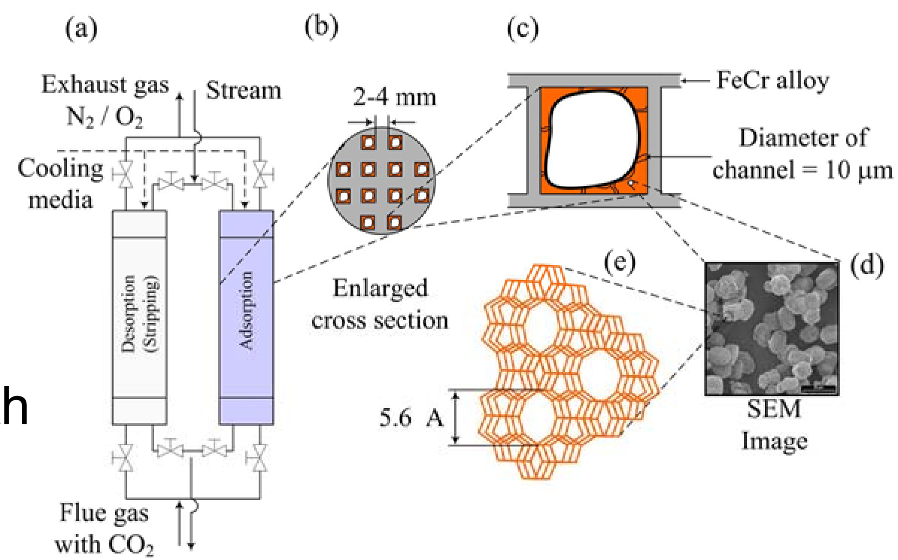
Post-combustion capture

CO_2 Capture Sorbents

- Physical or chemical interactions at the solid surface cause CO_2 to “stick” to the surface at one set of conditions release at another
- Use porous materials with high surface area
- Selectivity improved with shape-selective pores or functionalizing the surface
- No risk of cross-contamination of the gas stream
- Not commercialized for large scale CO_2 removal, but zeolites are used for removing impurities

Hurdles: System design using solids such as mass transfer, pressure drop, and heat transfer

R&D Opportunities: new materials with increased capacity, process design



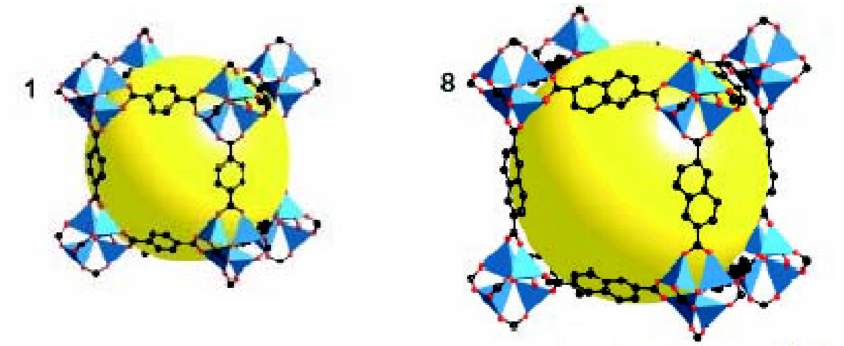
Post-combustion capture

Amine-grafted zeolites (S. Chuang at U. Akron)

Metal-Organic Frameworks (MOFS)

- Crystalline, organic-inorganic hybrid porous materials
- Very open structures, some of highest known surface areas (> 4500 m^2/g)
- Can be tailor-designed for specific system
- Great potential for adsorption separations
- **Hurdles**: cost, scale-up, unknown long-term stability and/or sensitivity to other pollutants

Post-combustion capture



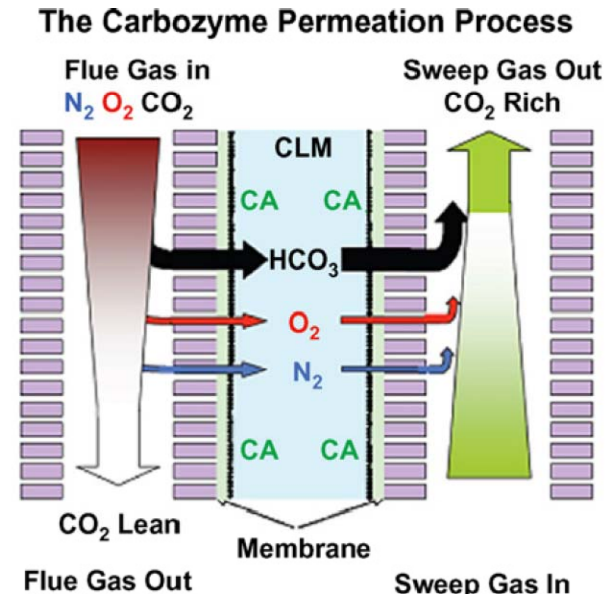
MOF Examples (K. Walton at GATech)

Enzyme-Based Systems

- Based on naturally occurring reactions with CO_2 in living organisms
- Use enzyme to mimic mammalian respiratory process
- Lab-scale tests show significant decrease in energy requirement
- Solution method limited by rate of CO_2 dissolution & life of enzyme (6 mo.)
- Potential by immobilizing enzyme on membrane

Hurdles: scale-up, membrane fouling & wetting, boundary layers, enzyme activity loss, long term operation and stability

CA= Carbonic Anhydrase

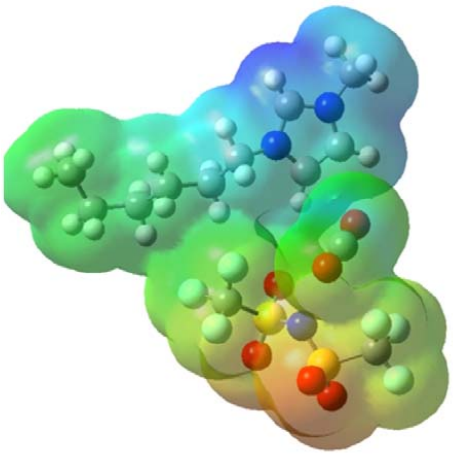


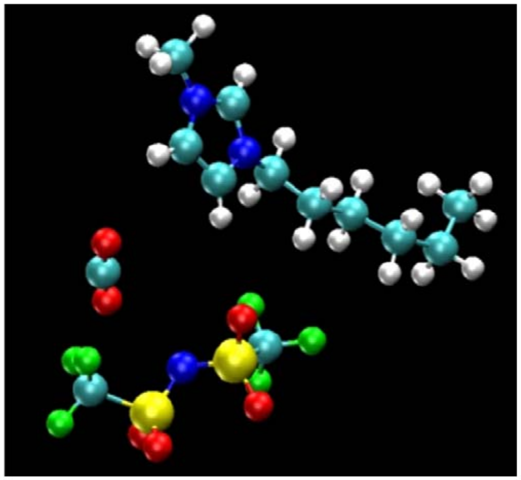
Post-combustion capture

Ionic Liquids

- Organic/inorganic salts that are liquid at ambient conditions
- Capture CO_2 through physical or chemical absorption (or combination)
- Essentially no volatility
- Relatively easy to design task-specific ionic liquids (U. Notre Dame)
- Possible to combine with amine additives (U. Colorado)

Hurdles: viscosity/capacity trade-off, cost, scale-up, unknown long-term stability and/or sensitivity to other pollutants

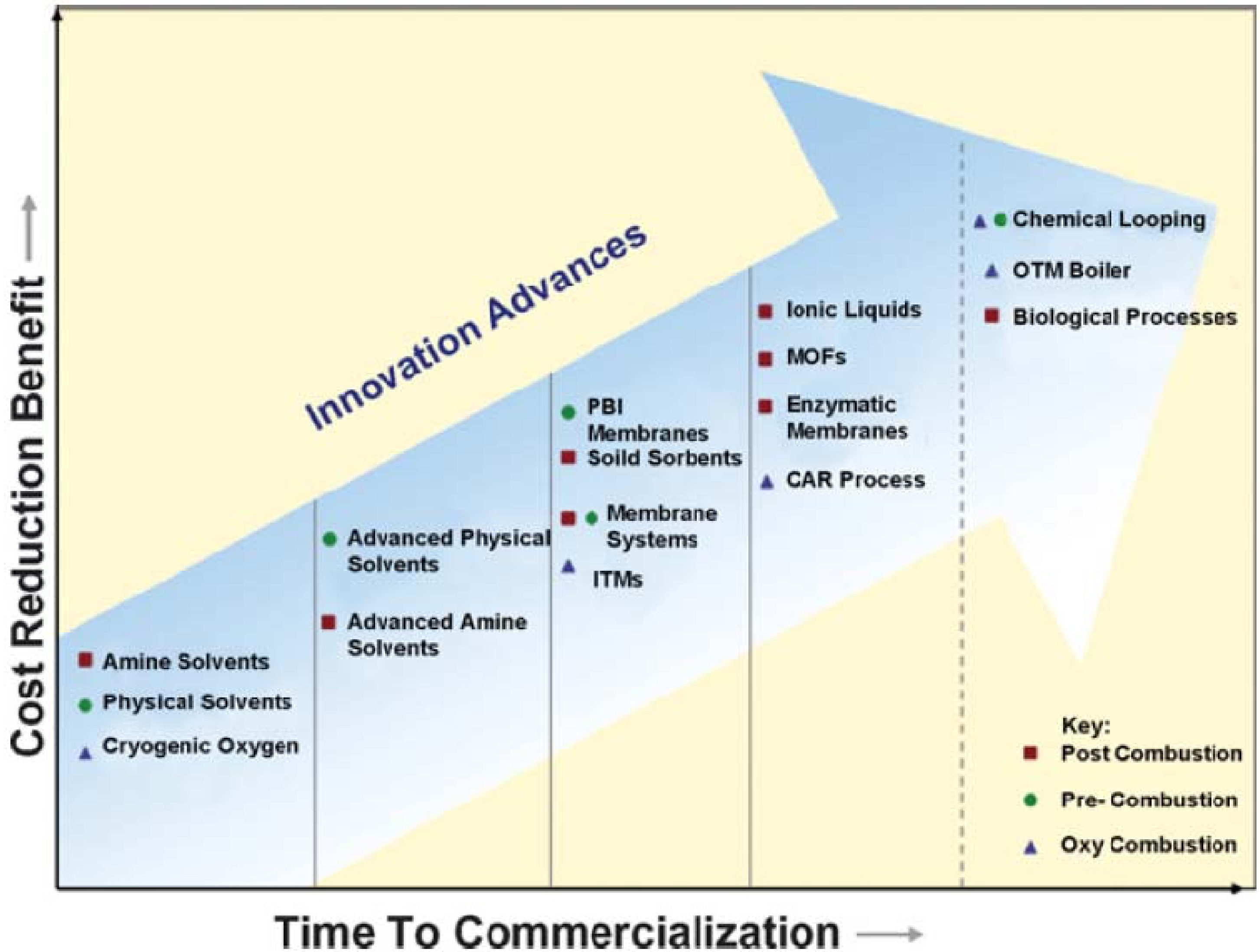




Post-combustion capture

CO_2 interacting with [hmim][Tf_2N]

Cost Benefit of Emerging Technologies



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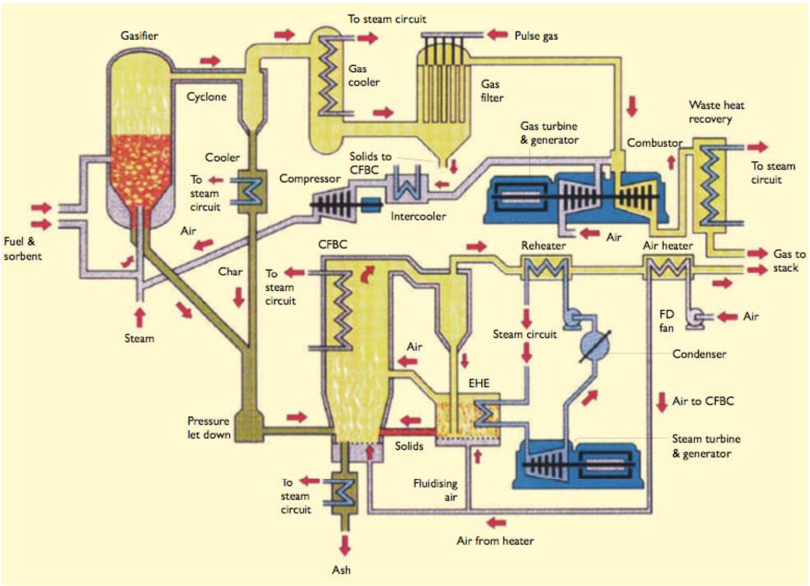
Integrated Gasification Combine Cycle

- Promising approach to pre-combustion
  - Gasify coal with oxygen to produce syngas (CO & H_2)
  - Add steam for water gas shift reaction ($CO+H_2O \rightarrow CO_2+H_2$)
  - Separate CO_2 from H_2
  - H_2 mixed with steam or nitrogen and sent to combustion turbine

High CO_2 concentration → efficient capture with state of the art Rectisol or Selexol processes

Not yet operated on power generation scale



Pre-combustion capture

Physical Solvent Processes

- Absorbs CO_2 without chemical reaction, just physical solubility
- Limited by thermodynamic equilibrium
- Absorption capacity directly correlates to CO_2 concentration so only works for high concentration
- Capacity generally decreases with increase temperature

State of the art:

- Rectisol: uses refrigerated methanol
- Selexol: uses dimethyl ethers of polyethylene glycol
- Fluor: uses propylene carbonate

- R&D opportunity: solvent with high capacity at higher temperatures

Pre-combustion capture

Other Emerging Technologies

- Membranes
  - Polymer-based membranes exhibit potential
  - Limited by selectivity/permeability, cost, fouling challenges

- Pre-combustion sorbents
  - Li_4SiO_4 is capable of high temperature removal of CO_2 from syngas
  - May promote syngas reaction as well

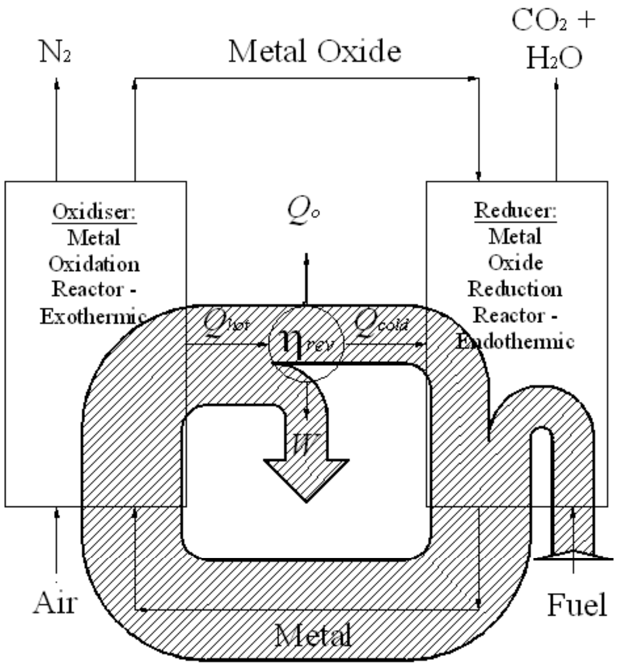
Pre-combustion capture

Chemical Looping Combustion

- Enables production of concentrated CO_2 stream without a separate (expensive) air separation unit
- Oxygen supplied by solid oxygen-carrier rather than air stream (e.g. a fluidized bed containing metal-oxide solid)
- Can then reoxidize solid for reuse

- Early stages of development

Hurdles: multiple solid streams, development of adequate oxygen carriers



Pre-combustion capture

Oxy-Combustion

- Modifying oxidation process so flue gas has high concentration of CO_2
- Fuel is burned with nearly pure O_2 (>95%) mixed with recycled flue gas
- Produces flue gas of primarily CO_2 and H_2O
  - Easily separated by condensing water
- Current promising version uses cryogenic air separation unit for high purity O_2
- Recycled flue gas necessary to keep reaction conditions compatible with reactor materials

- Early stages of development

Summary

- No single cost-effective solution for carbon capture currently exists
- Many emerging technologies have definite potential
- Opportunities for retrofit through post-combustion capture
- Opportunities for new power generation processes that will allow for pre-combustion or oxy-combustion capture