



GLOBAL CLIMATE AND ENERGY PROJECT | STANFORD UNIVERSITY



Energy Tutorial: Carbon Capture 101

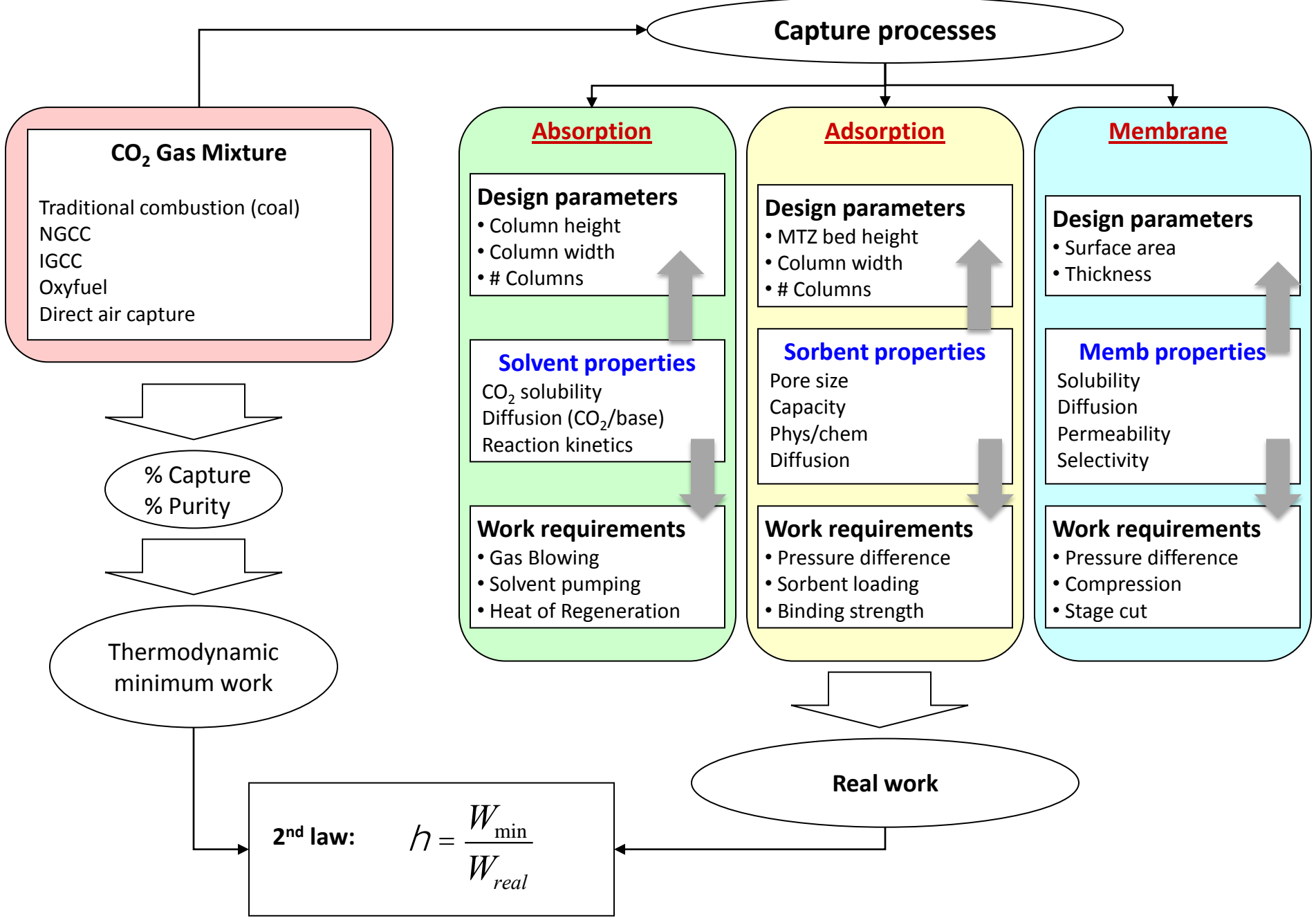
GCEP RESEARCH SYMPOSIUM 2011 | STANFORD, CA

Professor Jennifer Wilcox

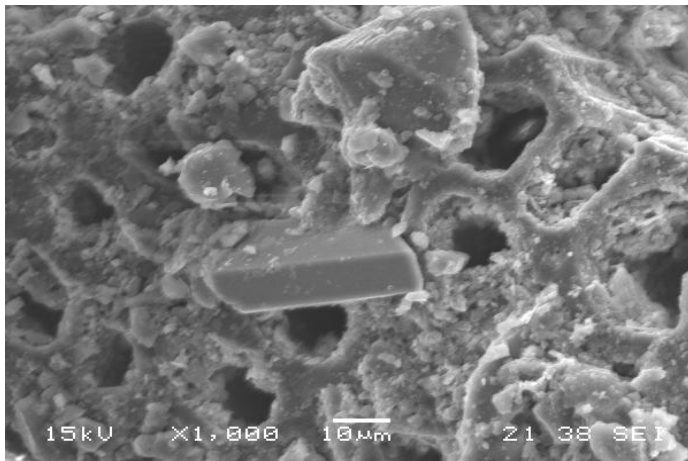
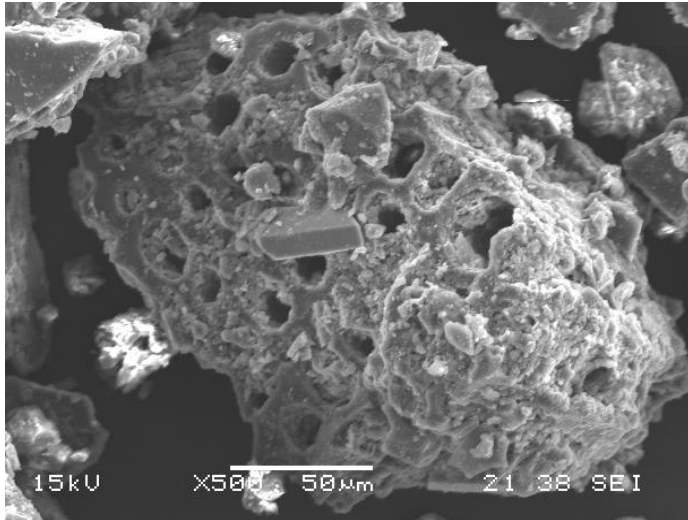
Energy Resources Engineering Department
Global Climate and Energy Project
Stanford University

OCTOBER 5, 2011

GLOBAL CHALLENGES – GLOBAL SOLUTIONS – GLOBAL OPPORTUNITIES

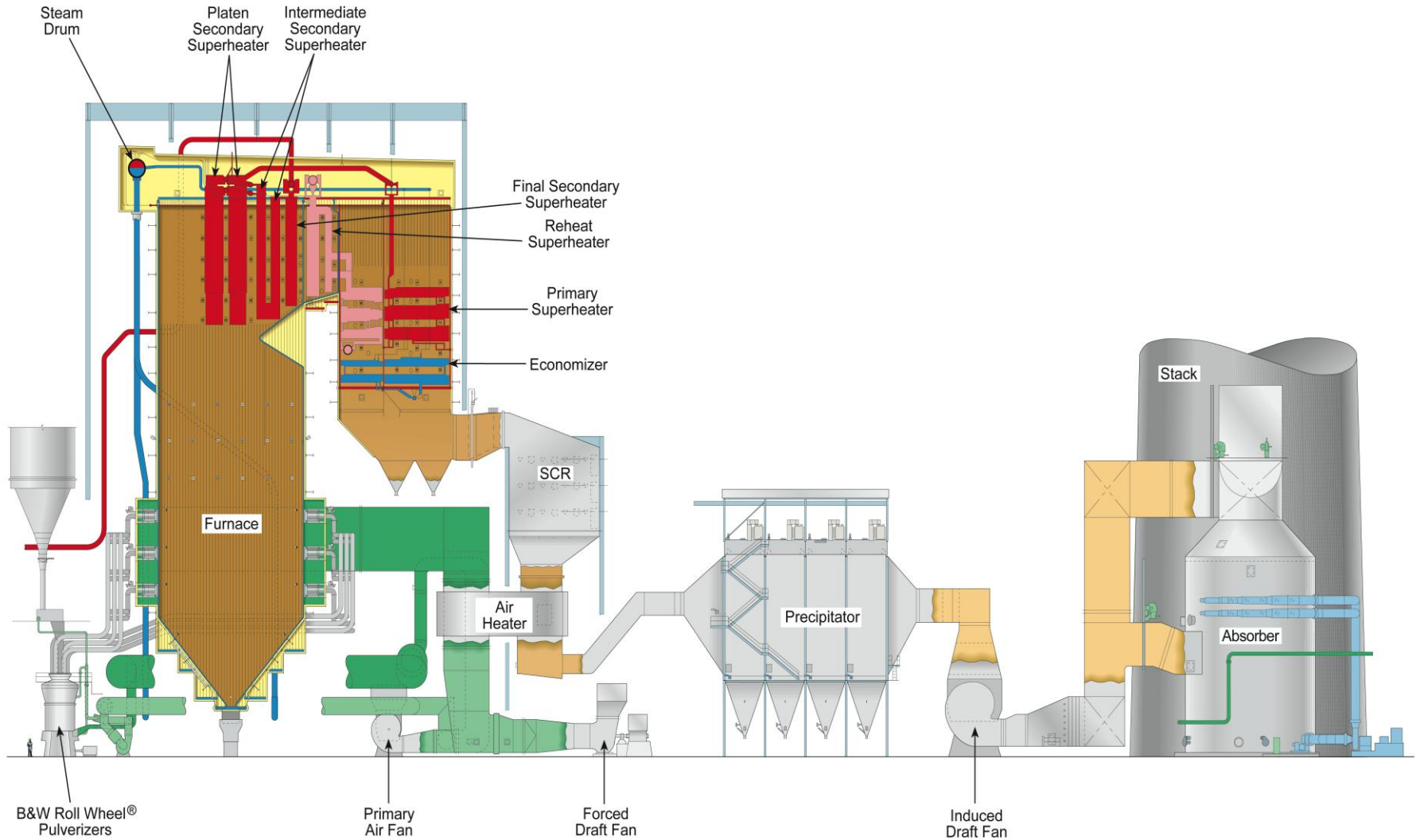


Coal to Electricity



- Furnace is pre-heated by combustion of auxiliary fuel such as natural gas or oil;
- Pulverized coal powder is blown with air into a combustion chamber (boiler or furnace) through a series of nozzles;
- Heat is transferred from hot combustion products to water circulating in tubes along the boiler walls, producing superheated steam, which is the working fluid for the steam turbines;
- Energy from the hot and pressurized steam is extracted in steam turbines that then transmit the energy to electric generators;
- The electric generators convert the shaft work of the turbines into alternating current electricity;
- Pumps are used to return the condensed water to the boiler, where the cycle is then repeated; and
- Pollution control devices are also in place for NO_x, SO_x, PM, and Hg.

Typical Coal-Fired Power Plant



Pulverized Coal Combustion (PCC)

- Oxidizing environment
- Mix of CO_2 and N_2
- ~ 12 mol. % CO_2

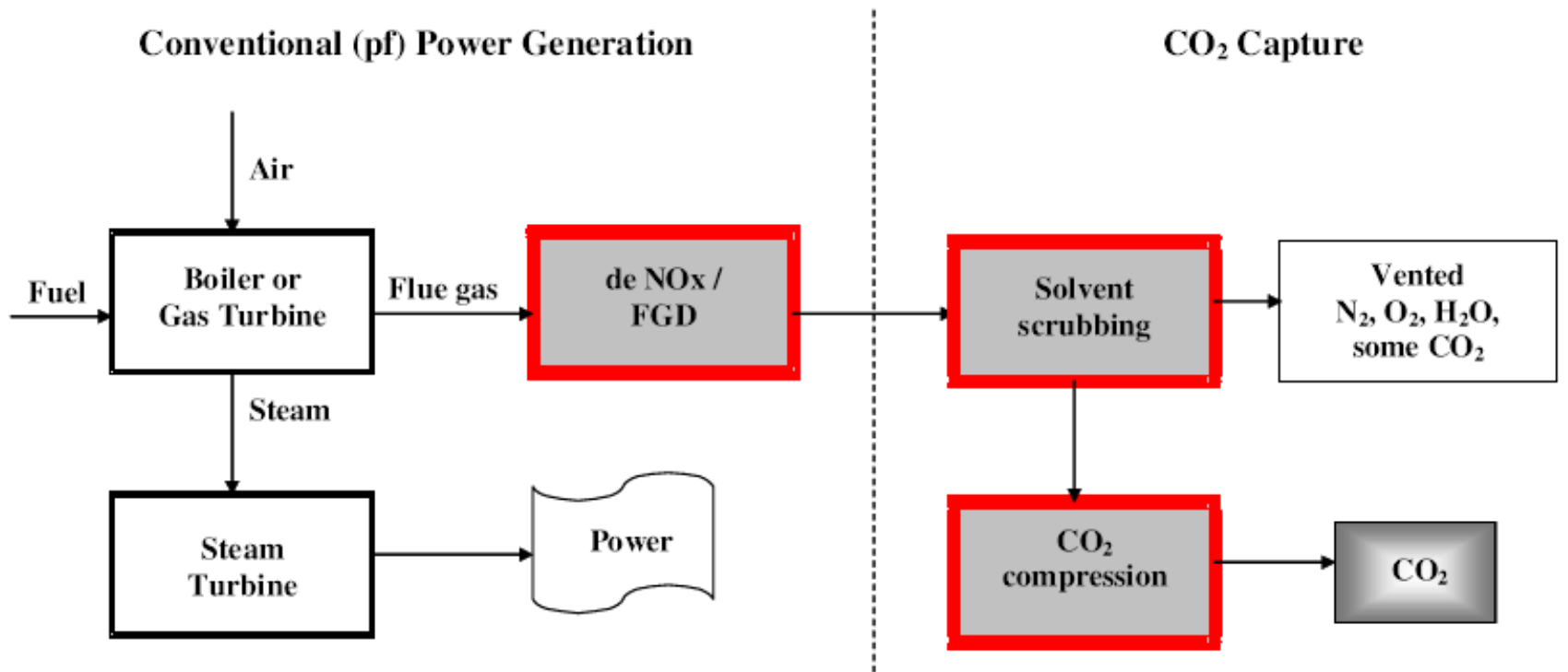


Fig. 1. Illustrative flowsheet for PCC (post-combustion capture) process, with additional unit operations for carbon capture shown bold.

Integrated Gasification Combined Cycle (IGCC)

- Reducing environment
- Mix of CO₂ and H₂
- ~ 40 mol. % CO₂

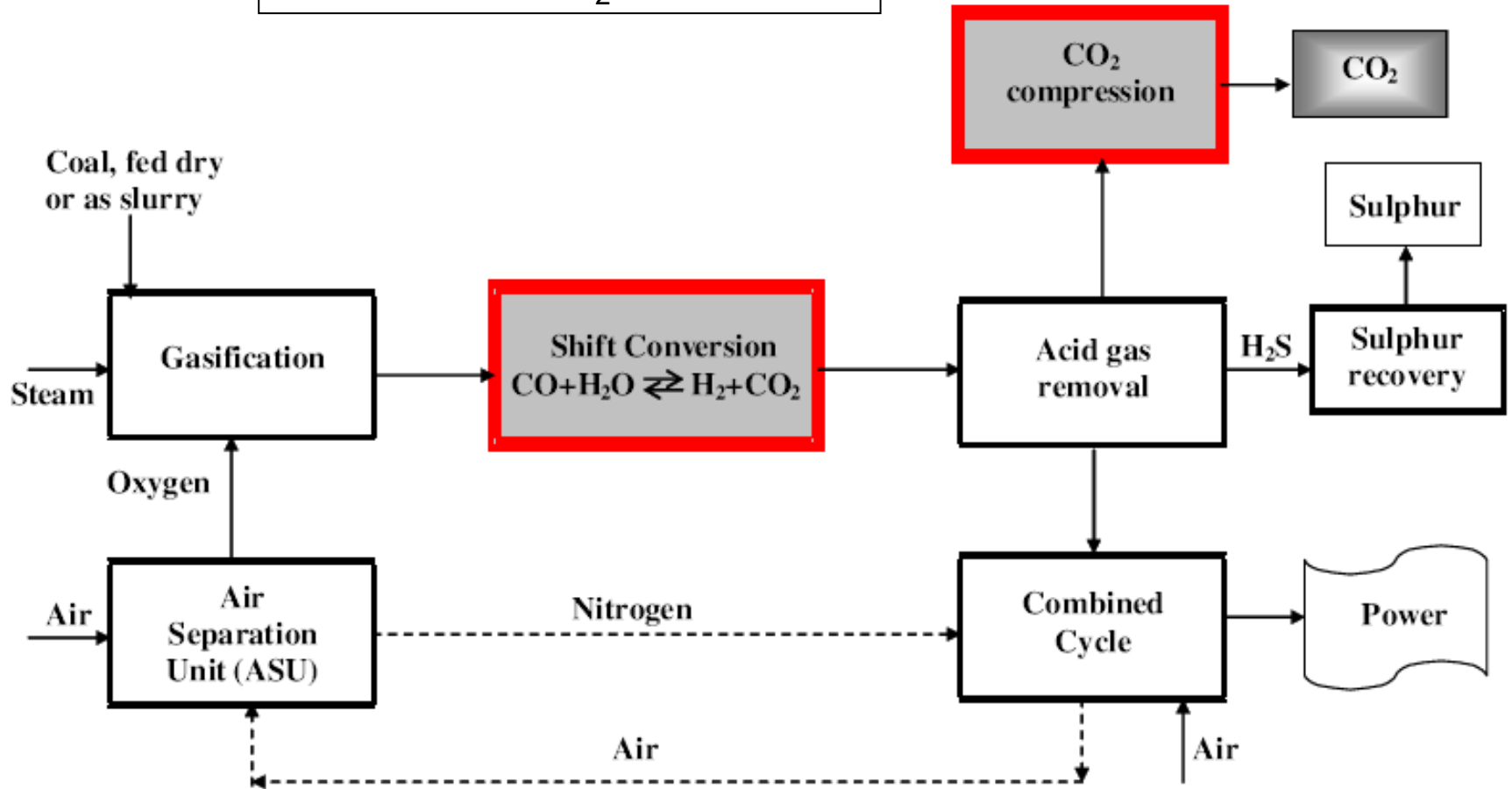


Fig. 2. Illustrative flowsheet for IGCC (pre-combustion capture) process, with additional unit operations for carbon capture shown bold.

Oxy-fuel Combustion

- Oxidizing environment
- Mix of CO_2 and H_2O
- high % CO_2

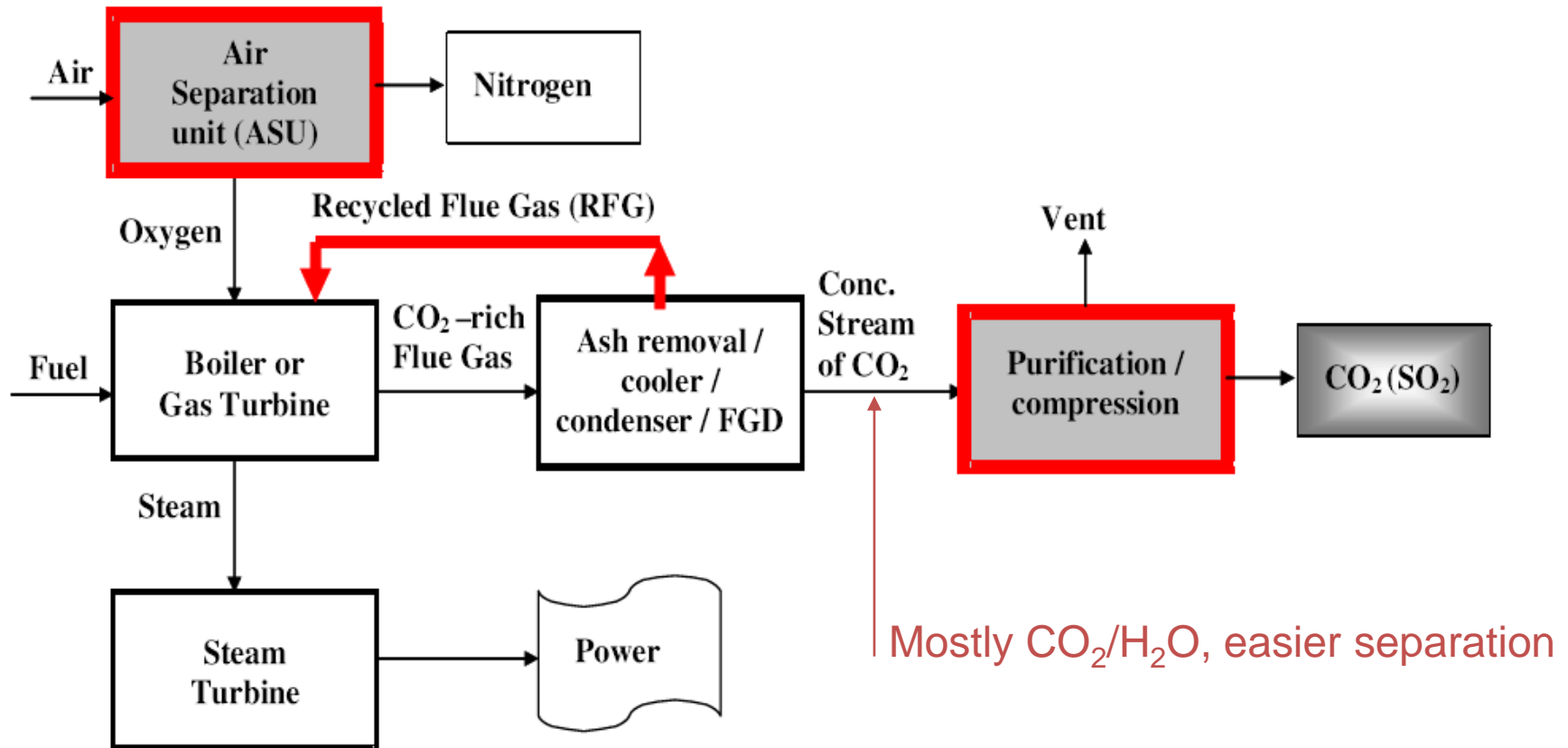
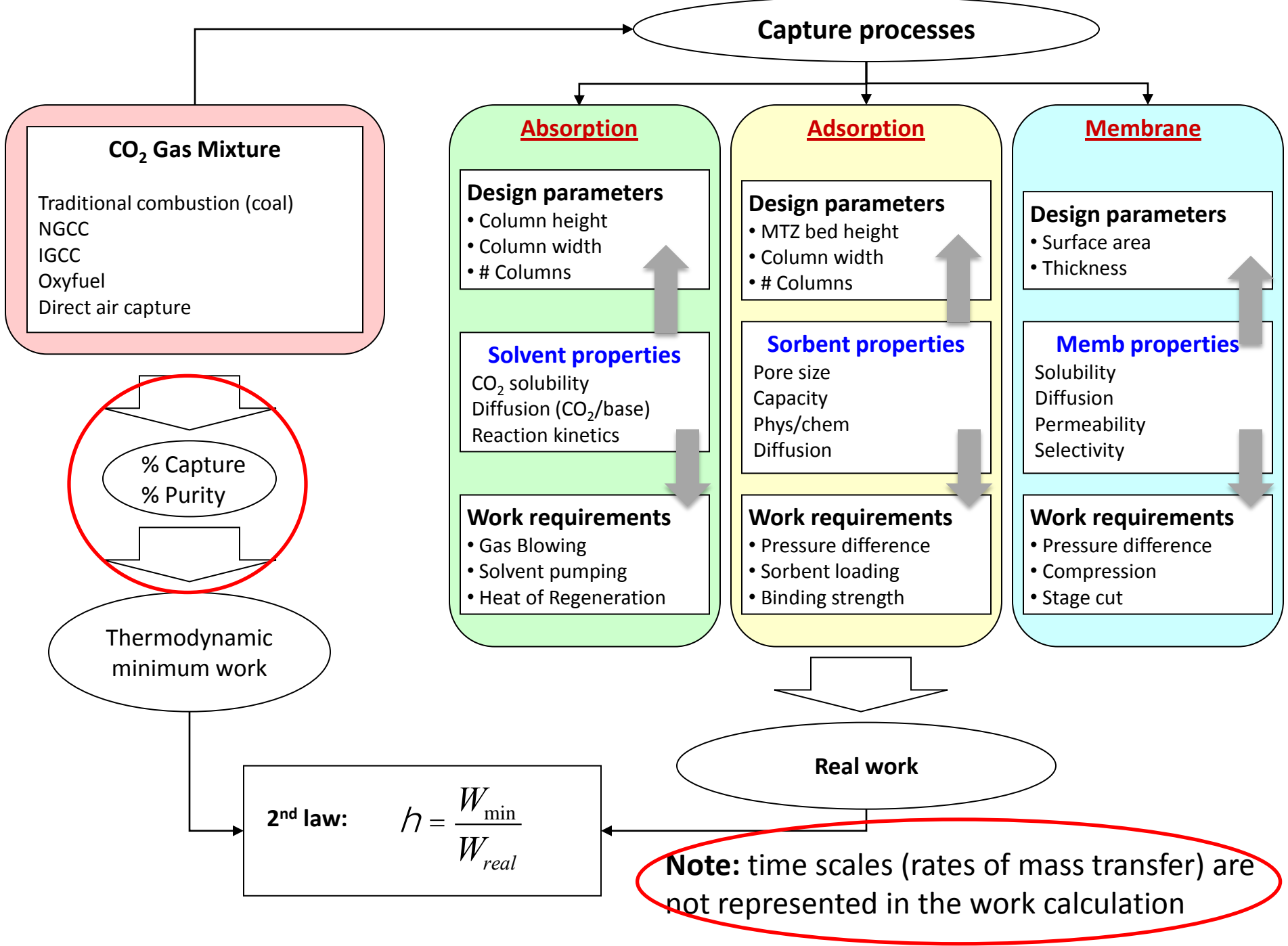


Fig. 3. Illustrative flowsheet for oxy-fuel (Oxyf) process, with additional unit operations for carbon capture shown bold.

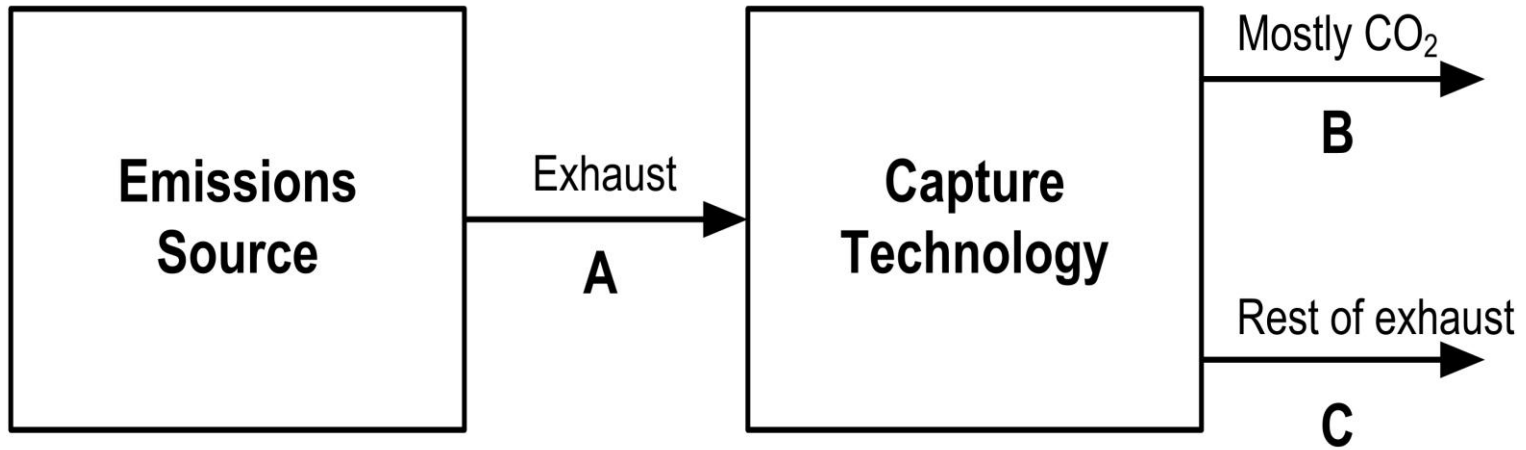
Roadmap

- Concentration of CO₂ in a given gas mixture dictates the energy required for separation
- The energy required for separation only partially dictates the cost and subsequent feasibility of a given separation process



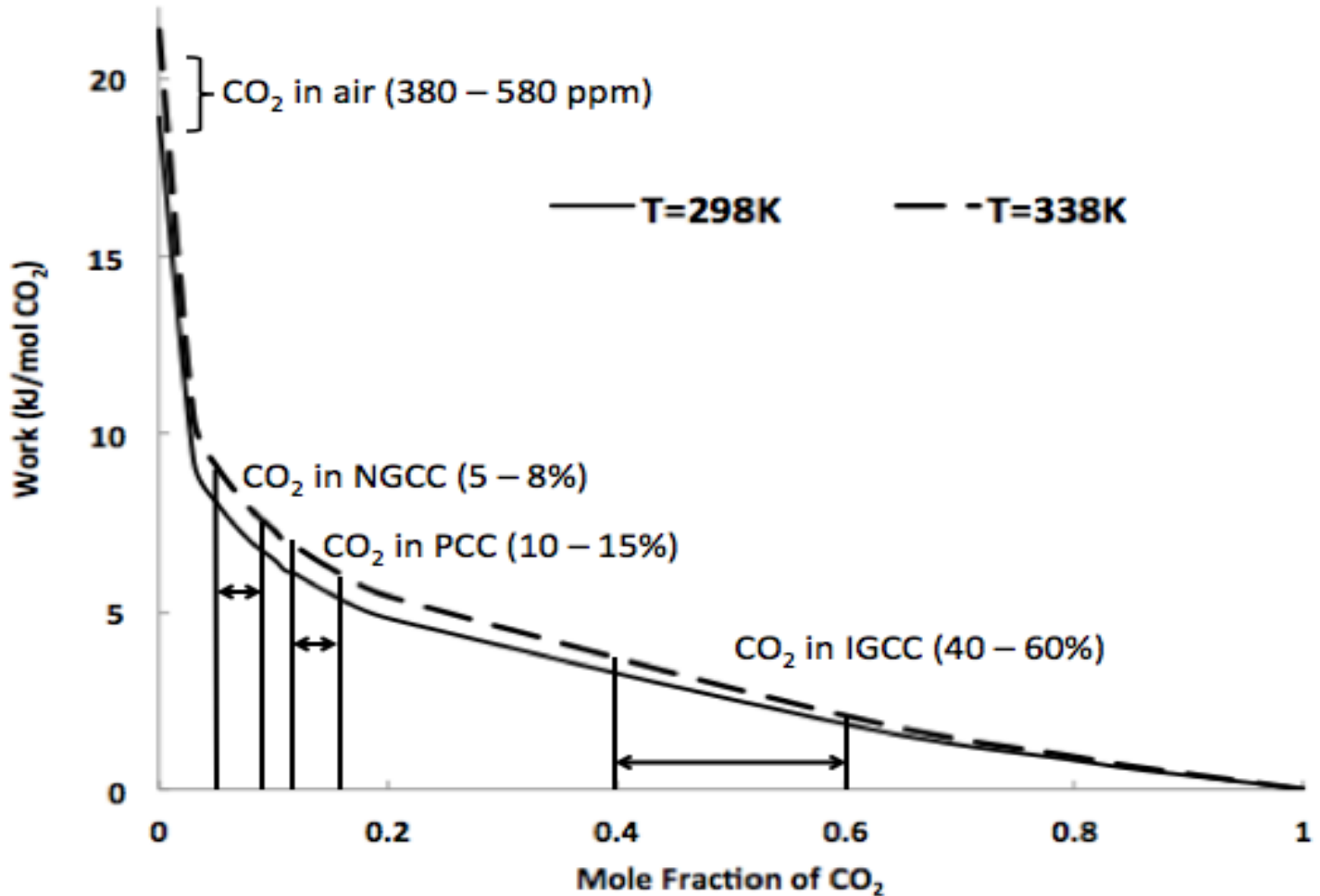
Minimum Work for Separation

combined first and second laws

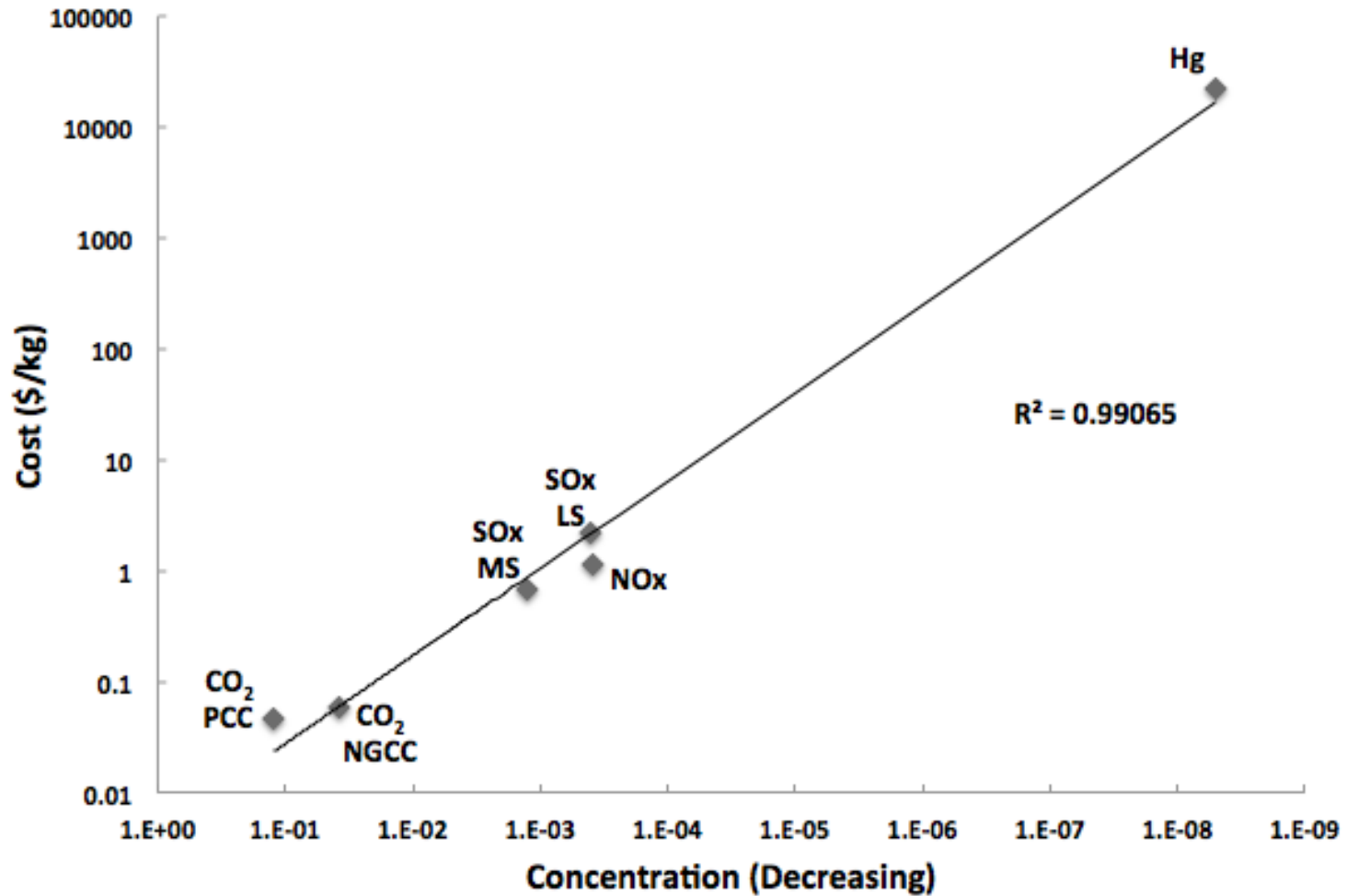


$$W_{\min} = RT \left[n_B^{CO_2} \ln(y_B^{CO_2}) + n_B^{B-CO_2} \ln(y_B^{B-CO_2}) \right] + RT \left[n_C^{CO_2} \ln(y_C^{CO_2}) + n_C^{C-CO_2} \ln(y_C^{C-CO_2}) \right] - RT \left[n_A^{CO_2} \ln(y_A^{CO_2}) + n_A^{A-CO_2} \ln(y_A^{A-CO_2}) \right]$$

Minimum Work for Separation



Sherwood Plot for Flue Gas Scrubbing



*Calculations carried out using IECM, all cases assume 500-MW plant burning Appalachian bituminous, NGCC (477-MW) O&M + annualized capital costs are included in the cost estimates

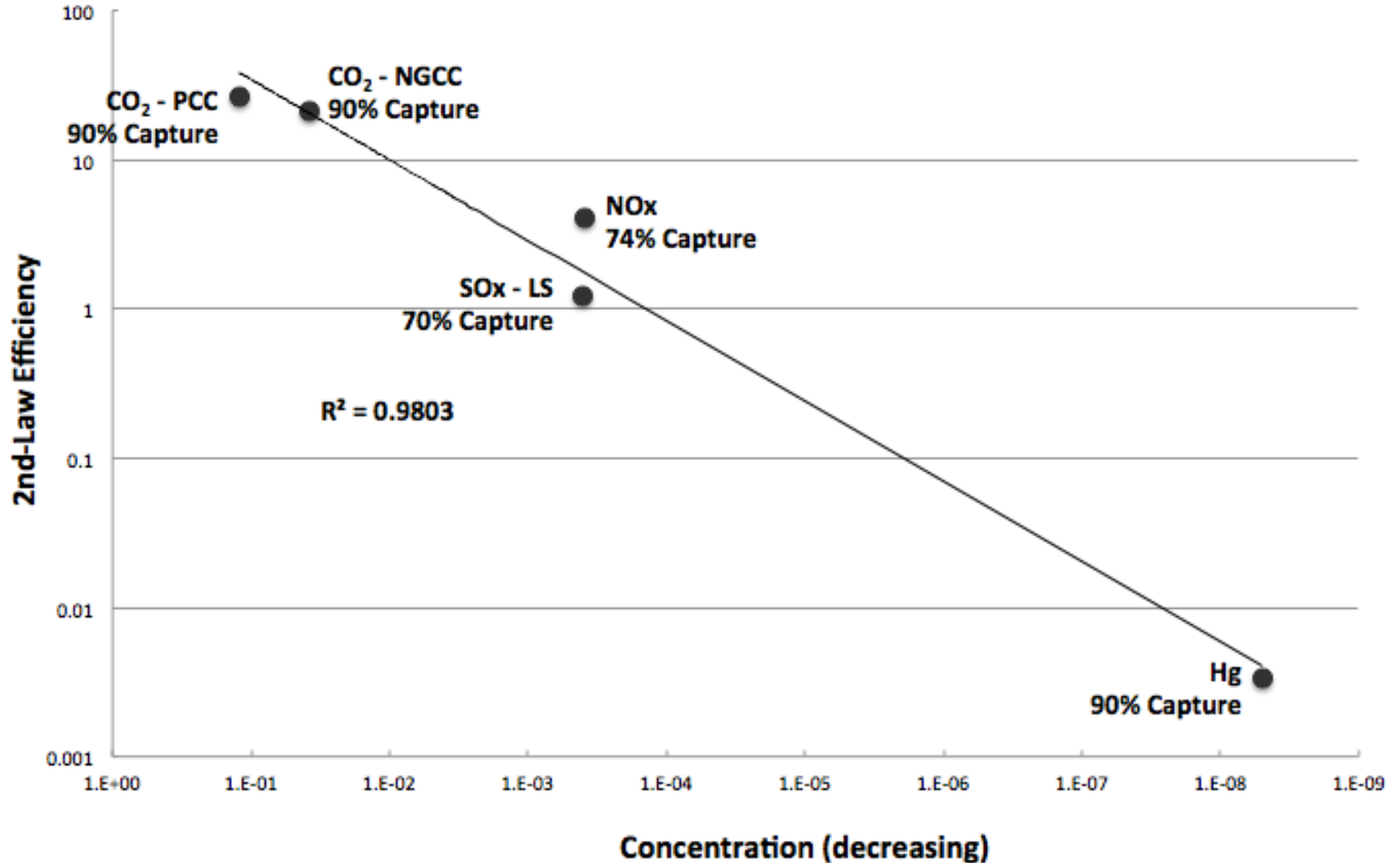
¹Cost and Scale

Process	Price [\$ /kg]	Concentration [mole fraction]	Emissions [kg/day]	Cost [1000s \$/day]
CO ₂ -PCC	0.045	0.121	8.59 x 10 ⁶	392
CO ₂ -NGCC	0.059	0.0373	3.01 x 10 ⁶	178
SO _x (MS)	0.66	0.00127	8.94 x 10 ⁴	59.6
SO _x (LS)	2.1	0.000399 (399 ppm)	2.32 x 10 ⁴	50.4
NO _x	1.1	0.000387 (387 ppm)	1.11 x 10 ⁴	12.5
Hg	22000	5 x 10 ⁻⁹ (ppb)	0.951	21.6

“the recovery of potentially valuable solutes from dilute solution is dominated by the costs of processing large masses of unwanted materials.”² -Edwin Lightfoot

¹These can change based upon coal-type burned and scrubbing methods; ²EN Lightfoot, MCM Cockrem, What Are Dilute Solutions, Sep. Sci. Technol., 22(2), 165, 1987.

2nd-Law Efficiency Drops with Concentration



Second Law Efficiency

- The second law efficiency or the exergy (maximum work possible) efficiency is used to compare the efficiency of a real process to a corresponding ideal process

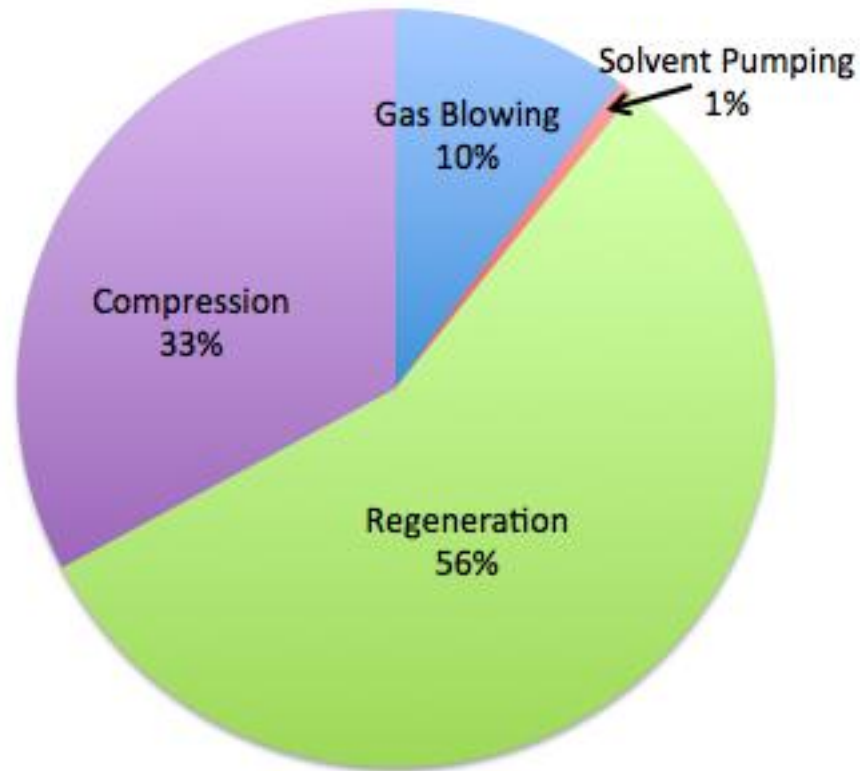
$$\eta_{2nd} = \frac{W_{real}}{W_{ideal}}$$

- The second law efficiency or the exergy efficiency (or effectiveness) is used to compare the efficiency of a cycle to a corresponding ideal cycle

How to Increase the 2nd-Law Efficiency?

Taking a closer look at absorption via MEA as an example:

1. Regeneration
2. Compression
3. Blower/Fan
4. Pumping

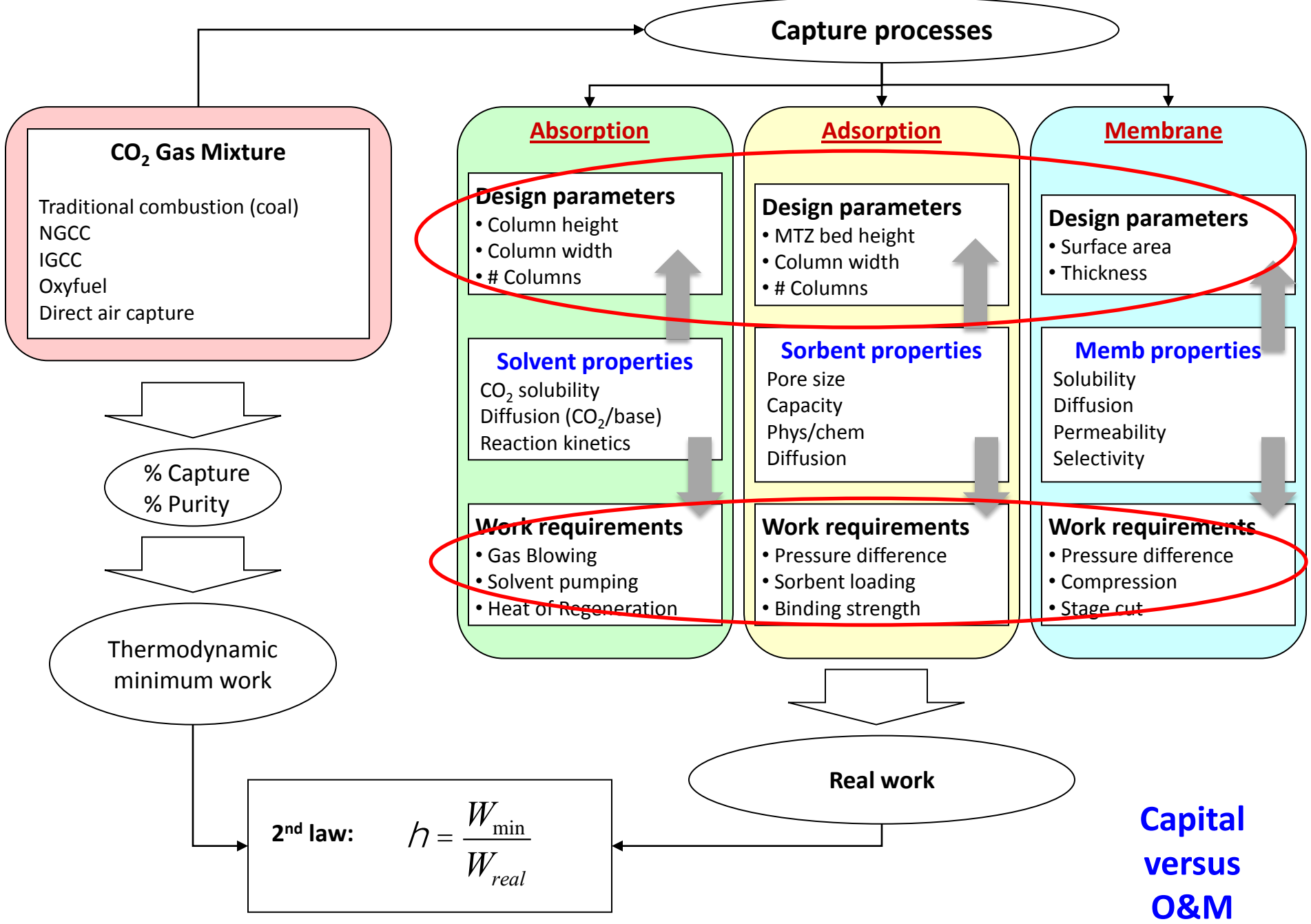


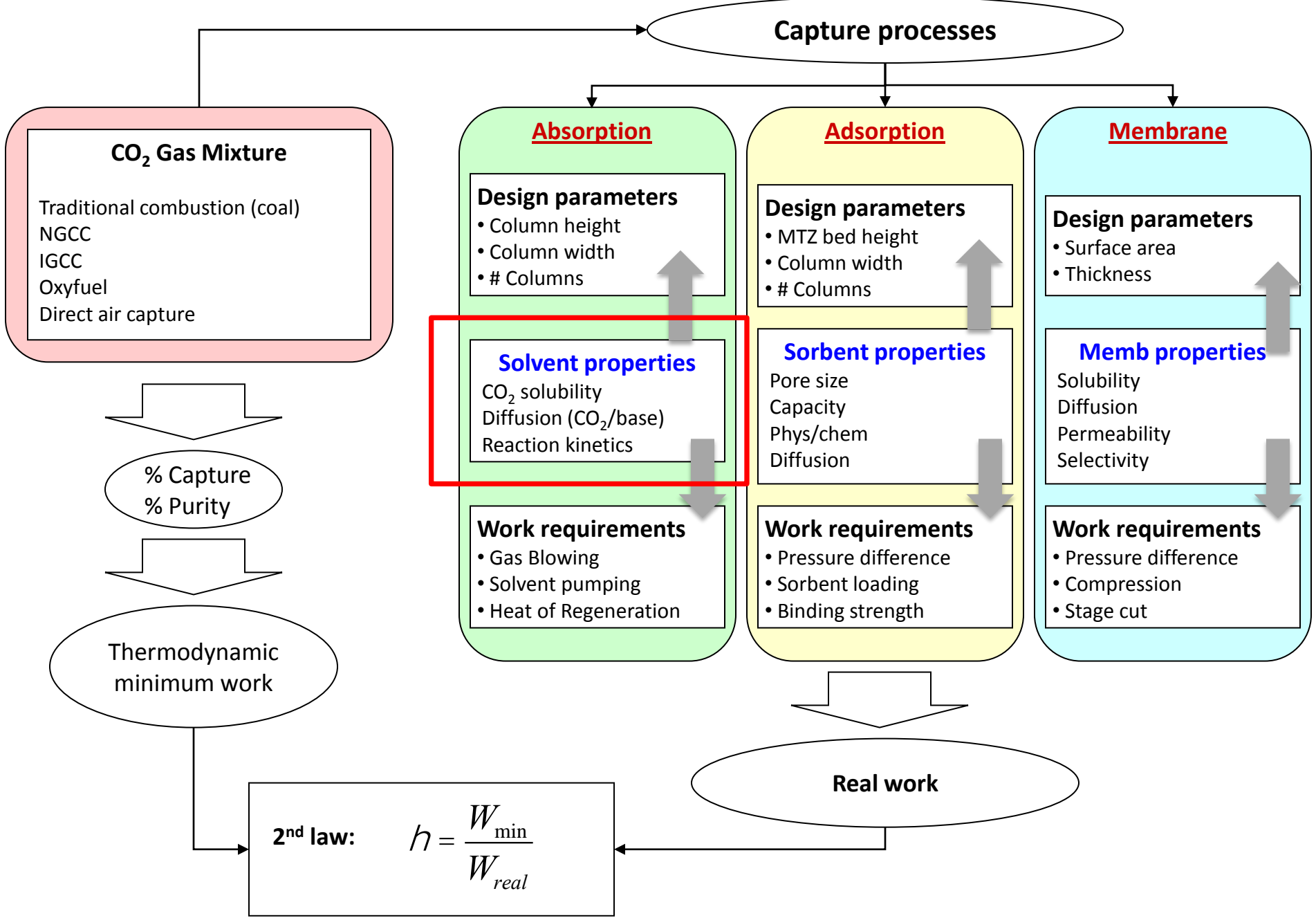
Can we establish targets based upon scientific limits?

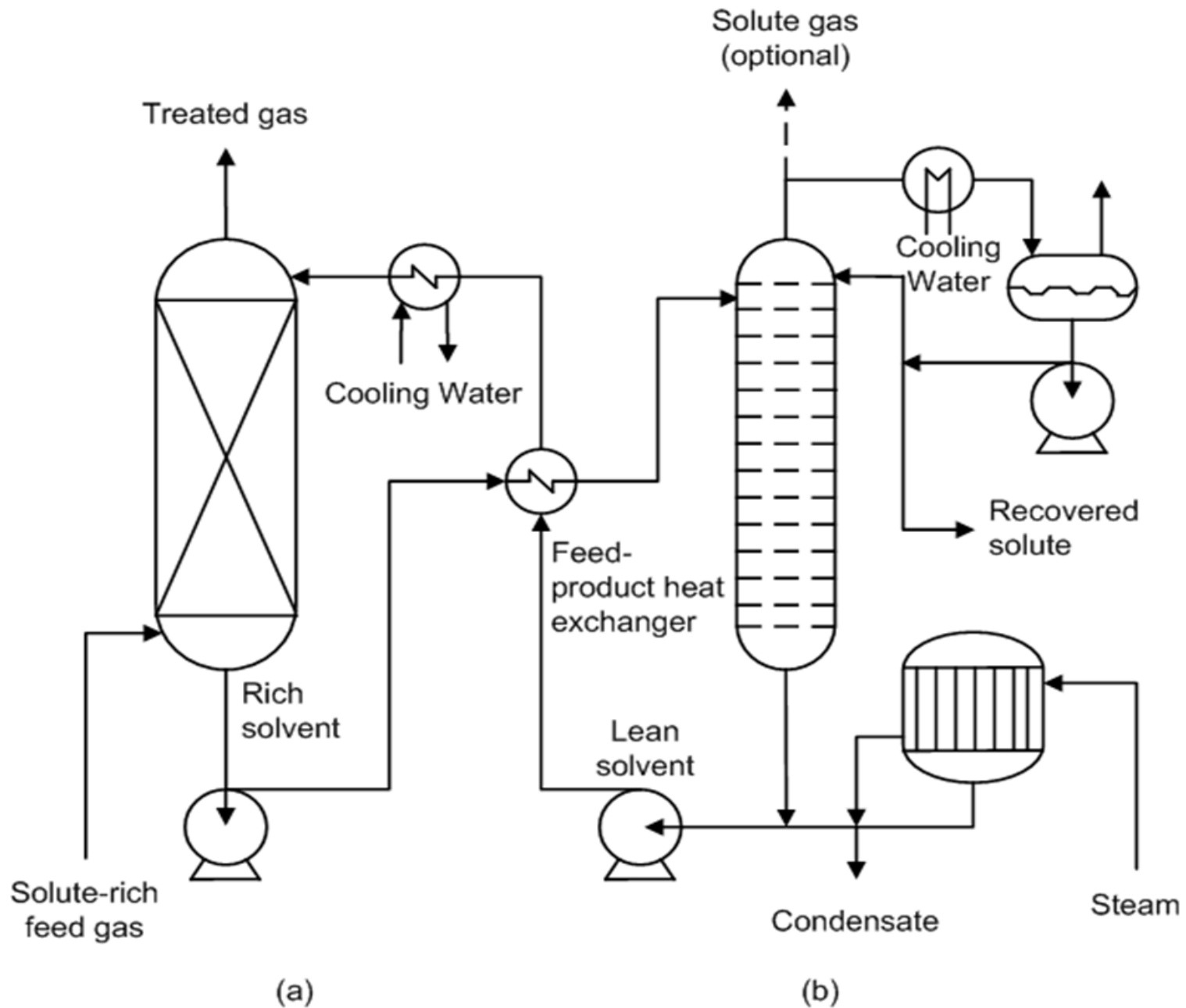
Should we reconsider the way in which we convert coal to energy?

Roadmap

- Operating vs Capital costs
- Where does minimum energy fit in?
- How should cost of CO₂ captured be defined?

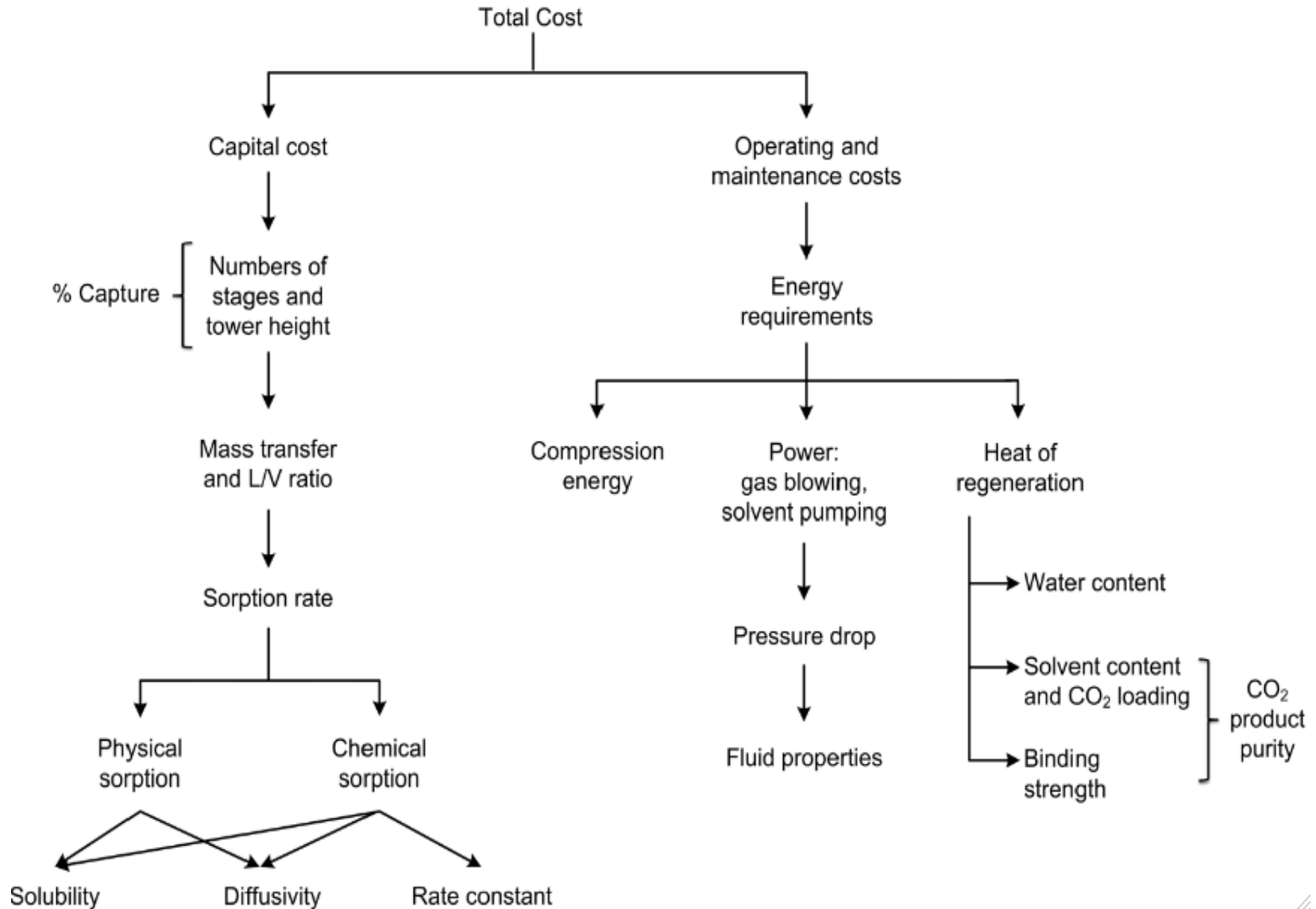






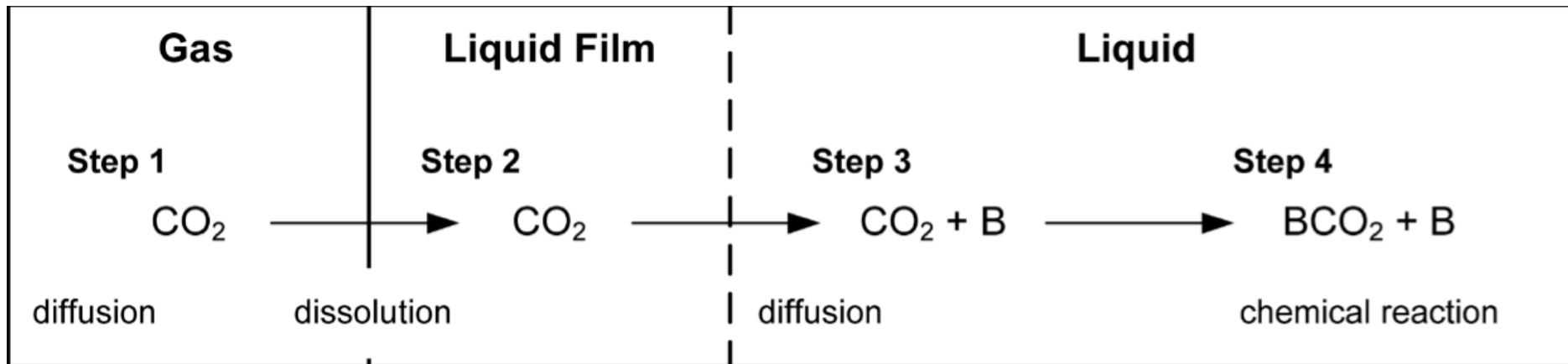
Gas absorber using a solvent regenerated by stripping (a) Absorber, (b) Stripper

Components of Absorption



Mass Transfer of CO₂ in Absorption

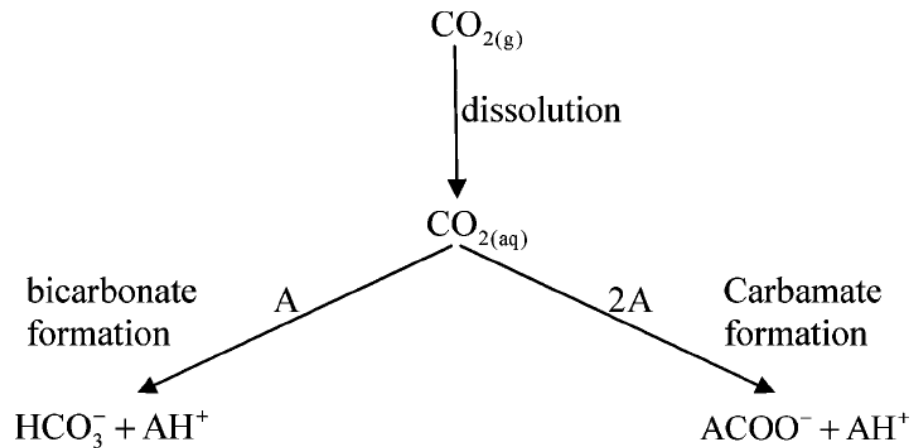
- Gas-phase CO₂ diffusion
- CO₂ concentration in the bulk gas is based upon the CO₂ concentration in the gas mixture
- CO₂ dissolution at the gas-liquid interface
- CO₂ concentration at the interface is determined by Henry's Law
- Liquid-phase CO₂ diffusion
- Simplifying assumption is that bulk liquid-phase CO₂ concentration is zero



Later – Rate of Absorption and what this entails!

Carbonate versus Carbamate

1. Dissolution of CO_2 (physical)
2. Bicarbonate formation
 - CO_2 :amine = 1
 - Low heat of absorption
3. Carbamate formation
 - CO_2 :amine = 0.5 (lower capacity)
 - High heat of absorption

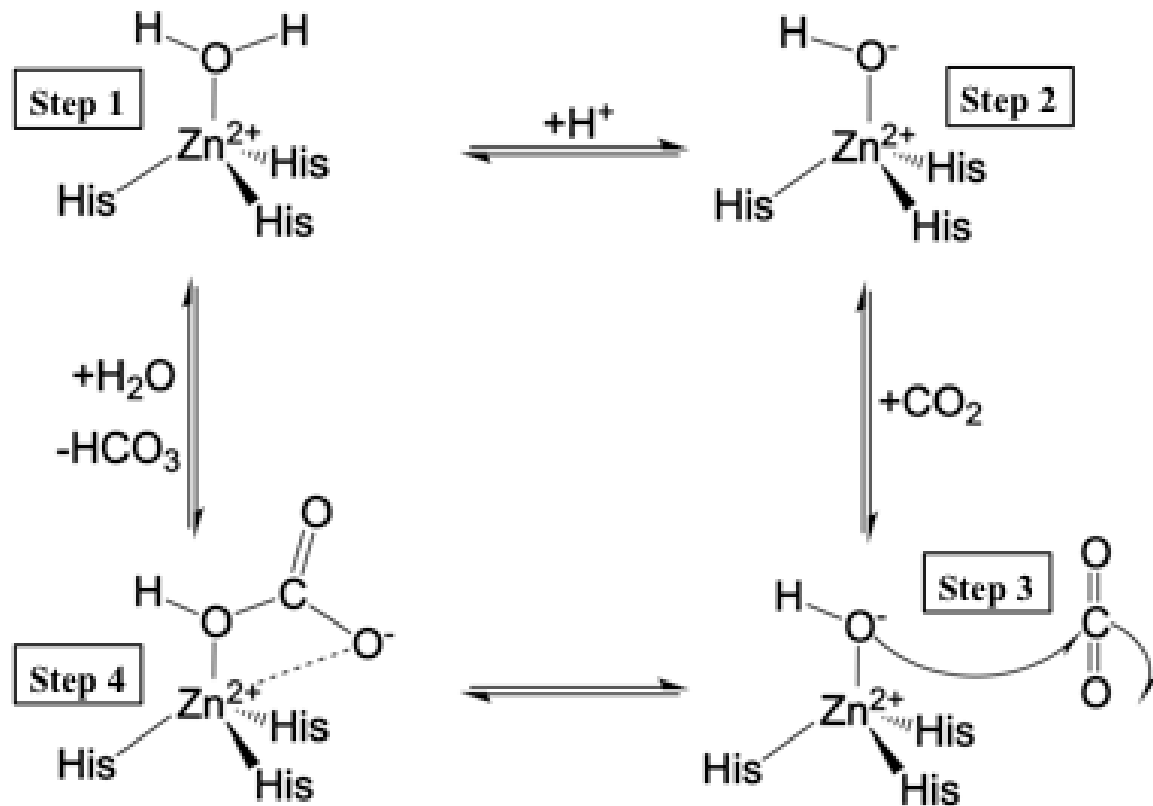


Tertiary amine acts as a base catalyst, forming a H bond with water, weakening the OH bond and allowing for hydration of CO_2 to bicarbonate

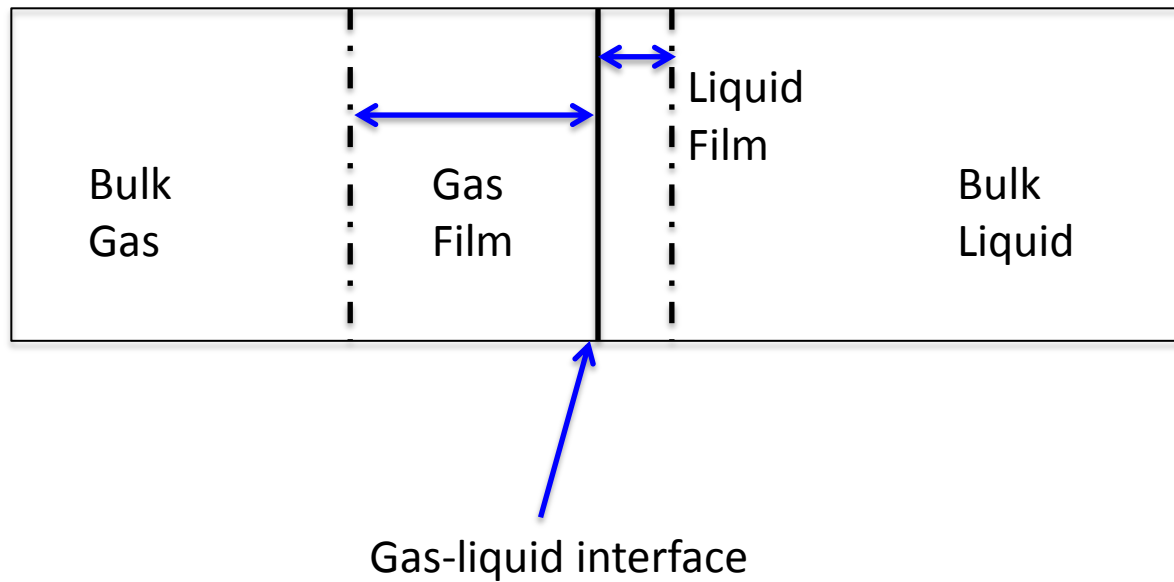


Special Case: Carbonic Anhydrase

- CA is a Zn-containing metalloenzyme
- Facilitates hydration and dehydration of CO_2
- Rate of reaction is up to 8 orders of magnitude faster than CO_2 binding in neutral water w/out catalyst



Gas and Liquid Diffusion Films



Rate of Absorption

- Gas-phase:

$$\begin{aligned} J_{G,CO_2} &= c_{CO_2} G - D_{G,CO_2} \left. \frac{dc_{CO_2}}{dz} \right|_i = c_{CO_2} G - \frac{D_{G,CO_2}}{d} (c_{G\neq,CO_2} - c_{i,CO_2}) \\ &= c_{CO_2} G - k_{G,CO_2} (c_{G\neq,CO_2} - c_{i,CO_2}) \end{aligned}$$

- Liquid-phase:

$$\begin{aligned} J_{L,CO_2} &= c_{CO_2} L - D_{L,CO_2} \left. \frac{dc_{CO_2}}{dz} \right|_i = c_{CO_2} L - \frac{D_{L,CO_2}}{d} (c_{i,CO_2} - c_{L\neq,CO_2}) \\ &= c_{CO_2} L - k_{L,CO_2} (c_{i,CO_2} - c_{L\neq,CO_2}) \end{aligned}$$

J is the overall flux including bulk and diffusive terms, δ is the film thickness (gas or liquid), c_∞ is the concentration of the bulk (gas or liquid), i represents the interface, and k is the mass-transfer coefficient

Absorption (chemical)

- Irreversible 2nd-order Reaction: $CO_2 + B \xrightarrow{k_2} CO_2B$
 - Assume that bulk CO_2 concentration = 0 (i.e., $c_\infty = 0$)
- Rate of Absorption = $k_L c_{i,CO_2} E$
- E = enhancement factor → factor by which absorption rate is increased by rxn
- Enhancement factor is a function of:

$$\sqrt{M} = \frac{\sqrt{D_{CO_2} k_2 c_B}}{k_L} \quad \text{and}$$

$$E_i = 1 + \frac{D_B c_B}{2D_{CO_2} c_{i,CO_2}}$$

- E_i corresponds to instantaneous rxn

Limiting Cases of the Film Model

Limiting Case	Enhancement Factor	Physical explanation
1. $\sqrt{M} > 10E_i$	$E = E_i$	Instantaneous reaction
2. $\sqrt{M} < 1/2 E_i$	$E = \left(\frac{\sqrt{M}}{\tanh \sqrt{M}} \right)$	Pseudo first-order reaction
3. #2 satisfied and $\sqrt{M} > 3$	$E = \sqrt{D_{L,CO_2} k_2 c_B}$	Fast pseudo first-order reaction
4. None of the above	Determine E from Fig. 3.9	

In the case of the diffusion ratio between the base and CO₂ in the liquid deviates from unity, the Higbie Model is preferred

Higbie Model

- E_i is calculated from:

$$E_i = \sqrt{\frac{D_{L,CO_2}}{D_B}} + \frac{c_B}{zC_{i,CO_2}} \sqrt{\frac{D_B}{D_{L,CO_2}}}$$

Comparison of Model Absorption Rate Predictions for ↓HL; DR=2 Case

	Flue	Fuel
<i>Fast Pseudo-first Order</i>	1.1(-4); 1.0(-6)	3.8(-4); 3.5(-6)
<i>Film Model</i>	5.2(-3); 1.0(-6)	7.9(-3); 3.4(-6)
<i>Higbie Model</i>	4.2(-3); 1.0(-6)	8.5(-3); 3.4(-6)

Enhancement Factor Predictions for Various Applications using the Film and Higbie Models

		E_i (Film)			E_i (Higbie)			if $\sqrt{M} > 3$ and $< \frac{1}{2}E_i$	$E = \frac{\sqrt{M \left(\frac{E_i - E}{E_i - 1} \right)}}{\tanh \left(\sqrt{M \left(\frac{E_i - E}{E_i - 1} \right)} \right)}$			
		Air	Flue	Fuel	Air	Flue	Fuel	$E = \sqrt{D_{L,CO_2} k_2 c_B}$	from E_i (Film)		from E_i (Higbie)	
									Flue	Fuel	Flue	Fuel
↓HL	DR=1	4.6(5)	1.5(3)	4.5(2)	-	-	-		2600	520	-	-
	DR=2	9.3(5)	3.0(3)	9.1(2)	6.5(5)	2.1(3)	6.4(2)	34.6 (fast);	1600	720	1300	780
↑HL	DR=1	3.9(7)	2.7(4)	8.2(3)	-	-	-	0.316 (slow)	-	-	-	-
	DR=2	7.9(7)	5.5(4)	1.6(4)	5.5(7)	3.8(4)	1.1(4)		-	-	-	-

Rate of CO₂ Estimates for Various Applications using the Film and Higbie Models

		$J_{L,CO_2} = c_{i,CO_2} k_{L,CO_2} E \left(\frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} \right)$					
		from E_i (Film); [fast:slow]			from E_i (Higbie); [fast:slow]		
		Air	Flue	Fuel	Air	Flue	Fuel
↓HL	DR=1	3.8(-7); 3.0(-9)	8.5(-3); 1.0(-6)	5.7(-3); 3.4(-6)	-	-	-
	DR=2	3.8(-7); 3.0(-9)	5.2(-3); 1.0(-6)	7.9(-3); 3.4(-6)	-	4.2(-3); 1.0(-6)	8.5(-3); 3.4(-6)
↑HL	DR=1	4.0(-9); 3.9(-11)	6.3(-7); 6.0(-9)	2.1(-5); 1.9(-7)	-	-	-
	DR=2	4.0(-9); 3.9(-11)	6.3(-7); 6.0(-9)	2.1(-5); 1.9(-7)	-	-	-

Potentially Tunable Parameters

Parameter	Name	Typical Units	Likely Range
D	Gas diffusivity	cm^2/s	0.1 – 1.0
H_{CO_2}	Henry's law constant	atm	20 – 1700
$D_{\text{L,CO}_2}$	Liquid diffusivity	cm^2/s	$(0.5 - 2.0) \times 10^{-9}$
D_B	Liquid diffusivity of absorbent		
k_2	Reaction rate constant	$\text{L}/\text{mol}\cdot\text{s}$	$6.7 \times 10^{-4} - 1.2 \times 10^8$
c_B	Bulk concentration of absorbent	mol/L	0.1 – 8 [†]
$k_{\text{L,CO}_2}$	Liquid-phase mass-transfer coefficient	cm/s	10^{-2}
c_{i,CO_2}	Concentration of CO_2	mol/L	set by p_{CO_2} and H_{CO_2}
$D_B/D_{\text{L,CO}_2}$	Diffusivity ratio		0.2 – 2.0

[†]depending on the corrosive nature, typically less than 1.0 mol/L

Rate of Absorption

- Gas-phase:

$$\begin{aligned} J_{G,CO_2} &= c_{CO_2} G - D_{G,CO_2} \left. \frac{dc_{CO_2}}{dz} \right|_i = c_{CO_2} G - \frac{D_{G,CO_2}}{d} (c_{G\neq,CO_2} - c_{i,CO_2}) \\ &= c_{CO_2} G - k_{G,CO_2} (c_{G\neq,CO_2} - c_{i,CO_2}) \end{aligned}$$

- Liquid-phase:

$$\begin{aligned} J_{L,CO_2} &= c_{CO_2} L - D_{L,CO_2} \left. \frac{dc_{CO_2}}{dz} \right|_i = c_{CO_2} L - \frac{D_{L,CO_2}}{d} (c_{i,CO_2} - c_{L\neq,CO_2}) \\ &= c_{CO_2} L - k_{L,CO_2} (c_{i,CO_2} - c_{L\neq,CO_2}) \end{aligned}$$

These equations may be used to then determine the number and height of the mass-transfer units to determine the design of the absorption (or stripping tower)

Real Work: Fan and Blower Power

- Fans and blowers:
 - Fans operate near atm P w/ $\Delta P < 15$ kPa
 - Efficiency, ε , gas density, ρ , and pressure drop, ΔP , fan power is:

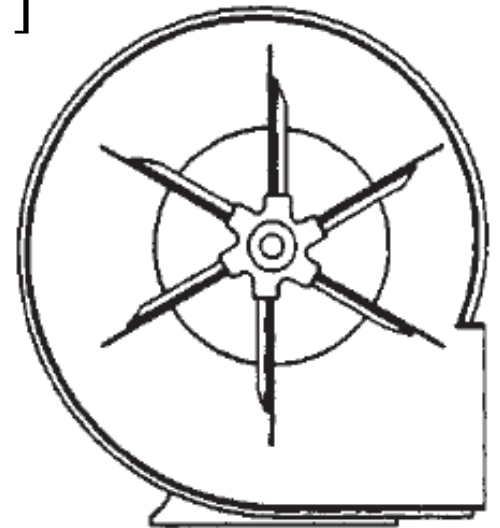
$$Power = \frac{dw_f}{dt} = \frac{\dot{m}\Delta p}{\rho \cdot \varepsilon}$$

- Blowers handle $3 < \Delta P < 500$ kPa
- For adiabatic and reversible compression of an ideal gas, blowing power is:

$$Power = \frac{dw_b}{dt} = \frac{\dot{m}RT_1 k}{M(k-1)\varepsilon} \left[\left(\frac{p_2}{p_1} \right)^{(k-1)/k} - 1 \right]$$

T_1 is the initial gas temperature, p_1 and p_2 are the initial and final gas pressures, and k is the ratio of specific heats (Appendix B of text)

- Efficiencies can range from 65 - 85%

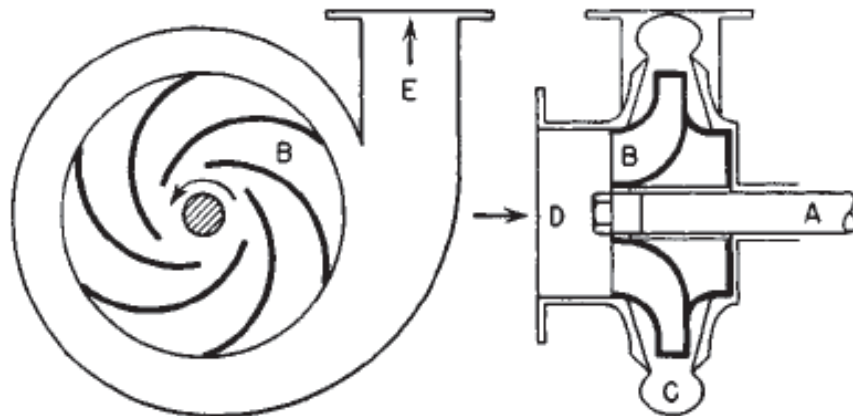


Real Work: Solvent Pumping Power

- Pumps for solvent pumping:
 - To cause liquid to flow work must be expended; a pump can assist in overcoming pressure drop associated with solvent friction in a column and can also assist in raising the solvent to a higher elevation
 - Work is a function of the change in pressure and volumetric flow rate, Q :

$$Power = \frac{dw_p}{dt} = \frac{Q\Delta p}{\varepsilon_i \varepsilon_d}$$

- Intrinsic efficiencies, ε_i range from 40 to 85%, while drive efficiency, ε_d can be approximated as 85%



Real Work: Heat of Regeneration

Heat required for regeneration:

- lean loading: 0.2 mol CO₂/mol MEA
- rich loading: 0.4 mol CO₂/mol MEA
- heat up solvent, e.g., heat capacity of 30 wt.% MEA w/ 0.4 mol bound CO₂ = 3.418 J/g·K
- mass of solution = 0.4 mol CO₂ + 7.9 mol H₂O + 1 mol MEA
- 40 to 120 °C is ~ 60.5 kJ to just heat up the water
- Additional 16.9 kJ/mol MEA to break the CO₂ bond (~ 84 kJ/mol CO₂)
- For regeneration of 0.2 mol CO₂/1 mol MEA:
 - (60.5 + 16.9) kJ/mol MEA x 1.0 mol MEA/0.2 mol CO₂ = 387 kJ/mol CO₂
 - IECM (Rubin et al.) estimates ~ 39 kJ/mol; Rochelle estimates ~ 30 kJ/mol
- Why the gap?
 - Heat exchange from the absorption process (water is an excellent heat transfer fluid)
 - Heat exchange from multiple cycles

Real Work: Compression

- Compression of CO₂ to 10 MPa is recommended for pipeline transport
- Adiabatic single-stage compression power can be calculated for an ideal gas by:

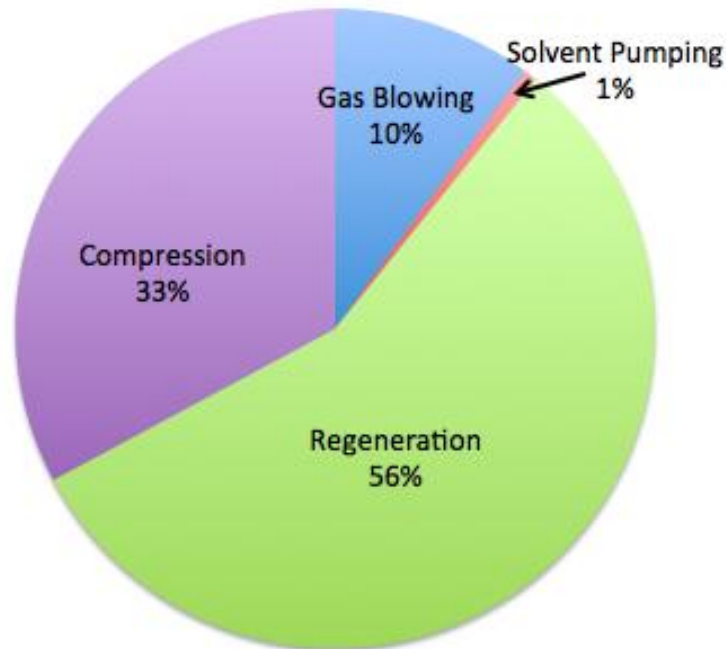
$$P_{ad} = \frac{\dot{m}RT}{M} \frac{k}{k-1} \left(r^{(k-1)/k} - 1 \right)$$

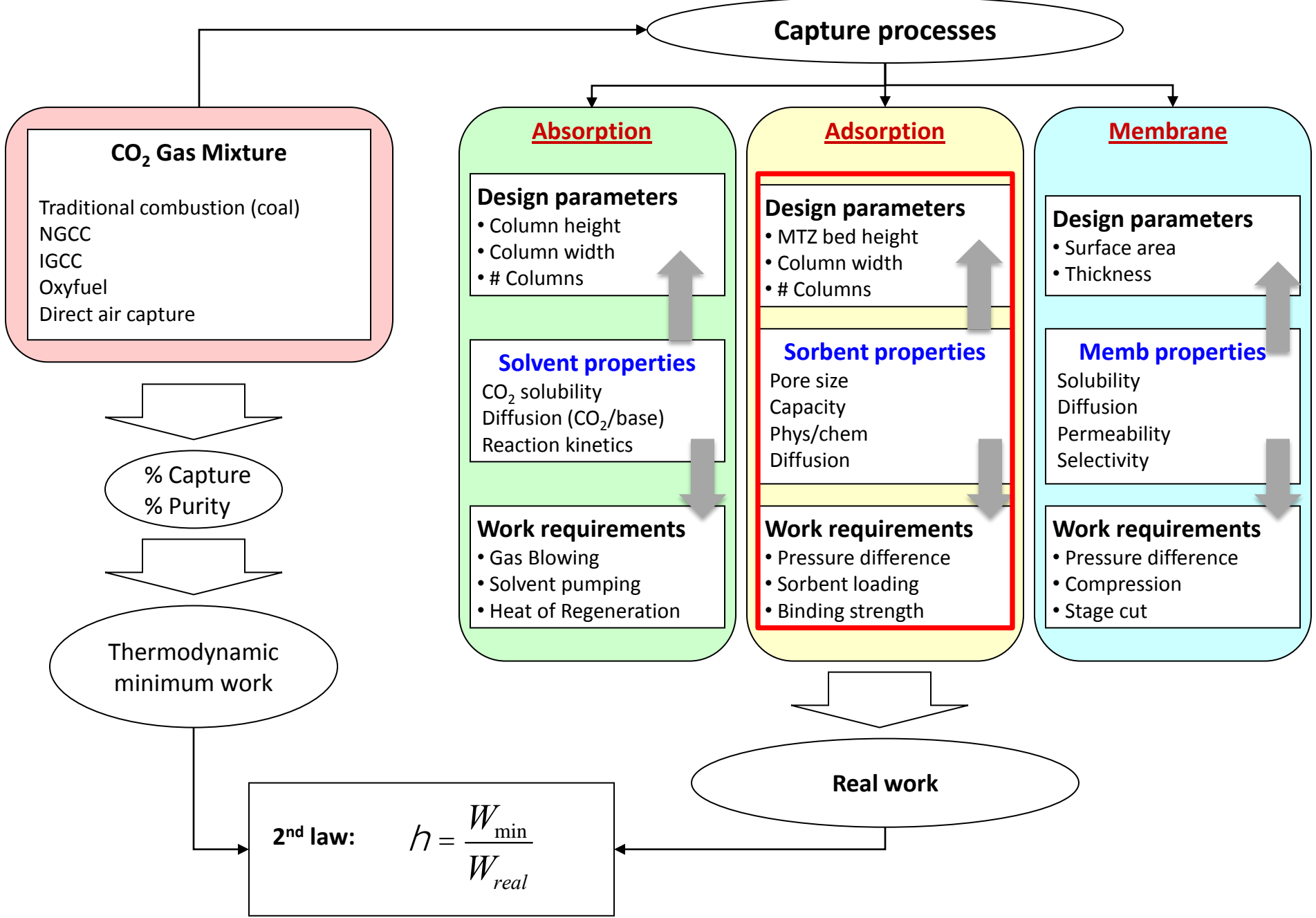
Such that \dot{m} is the mass flow rate, T is the gas temperature, r is the compression ratio, i.e., p_2/p_1 , k is the ratio of heat capacities (i.e., C_v/C_p), and M is the molecular weight of the gas

- Compression of CO₂ from 1 atm (0.101 MPa) to 10 Mpa ~ 20 kJ/mol CO₂
- Rochelle et al. report significantly lower compression (~ 10 kJ/mol CO₂) requirements due to novel stripping schemes that incorporate gas compression within the process
- IECM (Rubin et al.) report compression work ~ 23 kJ/mol CO₂

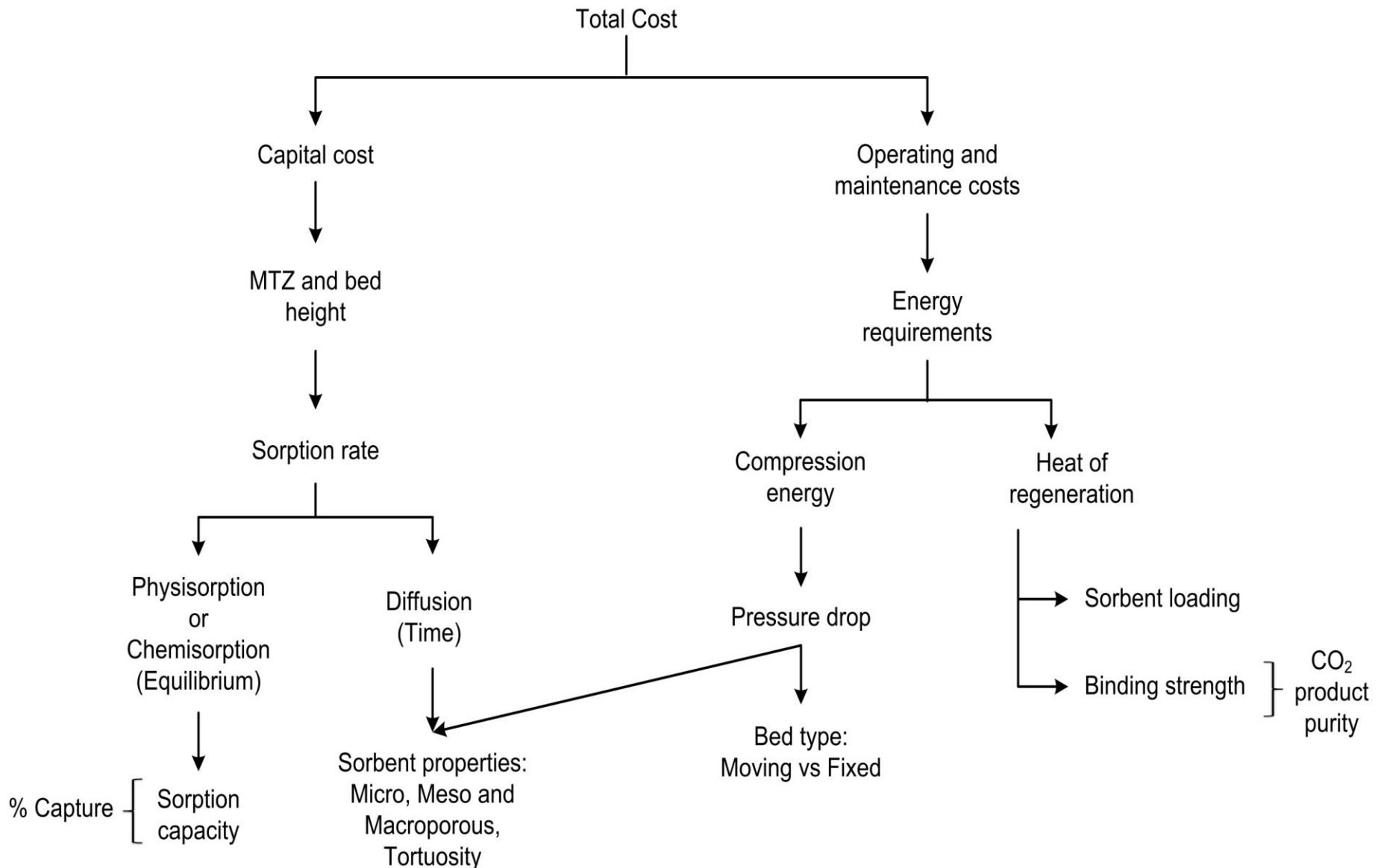
Real Work – Total

- Total real work required for CO₂ capture includes:
 - $W_{\text{fan}} + W_{\text{pump}} + W_{\text{regen}} + W_{\text{comp}}$
- On average, estimates for an amine-based absorption process (from IECM)
 - $W_{\text{fan}} \sim 7 \text{ kJ/mol CO}_2$
 - $W_{\text{pump}} \sim 0.5 \text{ kJ/mol CO}_2$
 - $W_{\text{regen}} \sim 39 \text{ kJ/mol CO}_2$
 - $W_{\text{comp}} \sim 23 \text{ kJ/mol CO}_2$ [1 atm → 10 MPa]





Outline of Adsorption Processes



Physisorption versus Chemisorption

- When CO₂ is held loosely via weak intermolecular forces it's termed physisorption, heat of adsorption ~ 10 – 15 kcal/mol
- When CO₂ is held via covalent bonds it's termed chemisorption
- Most CO₂ adsorption mechanisms are physisorption due to the need for low heats of adsorption
- Heats of adsorption of zeolites and MOFs can actually be quite high (e.g., ~ 50 kcal/mol)
- Common sorbents: activated carbon, zeolites, MOFs, etc.

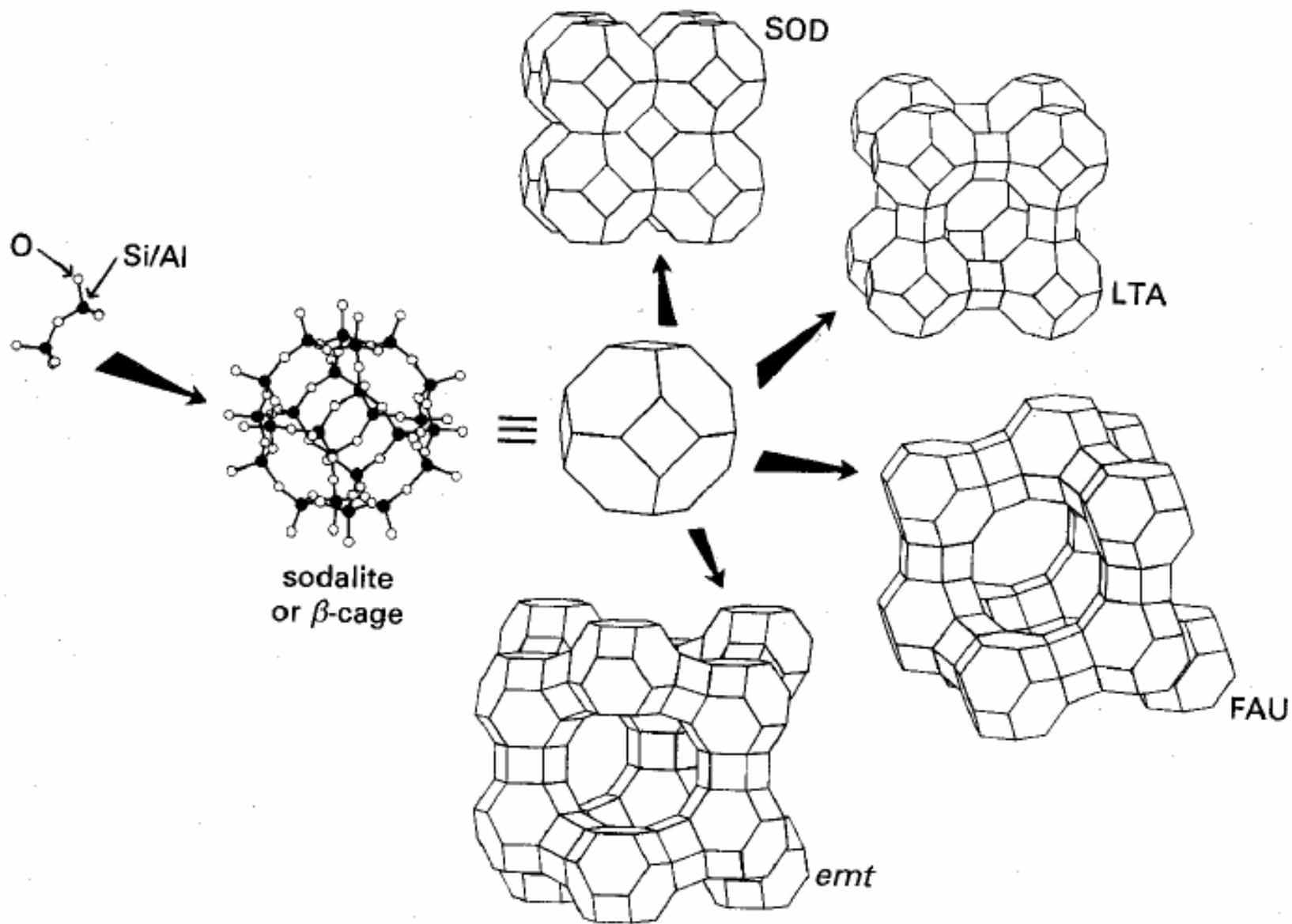
Zeolite Properties

- Silicon and aluminum atom structures tetrahedrally bonded with oxygen
- Aluminum typically exists in a 3+ oxidation state, so will have a charge of -1 when tetrahedrally bonded
- Cations (positive charges) are used to stabilize these charges, distributing themselves in a way to minimize the free energy of the system
- How do zeolites work to separate N_2 from O_2 or CO_2 from N_2 ?
 - They actually prefer to adsorb N_2
 - The interaction energy bet/ ions and N_2 are much stronger than ions and O_2
 - O_2 - Na^+ (20 kJ/mol); N_2 - Na^+ (36 kJ/mol)
 - O_2 - Li^+ (32 kJ/mol); N_2 - Li^+ (51 kJ/mol)
 - N_2 has a higher quadrupole moment than O_2
 - Adsorption is dependent upon the interaction energy bet/ an adsorbate and a cation of a zeolite and includes contributions from van der waals and electrostatic interactions; electrostatic energies include induced dipoles, permanent dipoles and quadrupoles

Kinetic and Electrostatic Properties of Gases

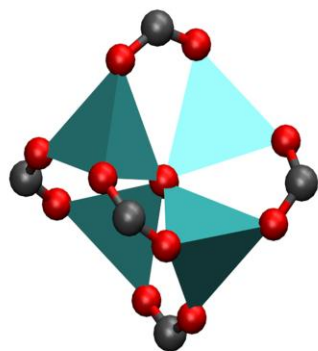
Molecule	¹⁵ Kinetic Diameter (nm)	¹⁶ Dipole Moment (Debye)	¹⁷ Quadrupole Moment (10^{-40} Coulomb·m ²)	^{16-17, 17d} Polarizability (10^{-24} cm ³)
CO ₂	0.33	0	-13.71, -10.0	2.64, 2.91, 3.02
N ₂	0.346	0	-4.91	0.78, 1.74
O ₂	0.346	0	-1.33	1.57, 1.77
H ₂ O	0.280	1.85	6.67	1.45, 1.48
SO ₂	0.360	1.63	-14.6	3.72, 3.89, 4.28
NO	0.317	0.16	-6.00	1.7
NO ₂	0.340	0.316	unknown	3.02
NH ₃	0.260	1.47, 5.10	-7.39	2.22, 2.67, 2.81
HCl	0.346	1.11, 3.57	13.28	2.63, 2.94
CO	0.376	0.11, 0.37	-8.33, -6.92	1.95, 2.19
N ₂ O	0.317	0.16, 0.54	-12.02, -10.0	3.03, 3.32
Ar	0.340	0	0	1.64, 1.83
H ₂	0.289	0	2.09, 2.2	0.81, 0.90
CH ₄	0.380	0	0	2.6

Zeolite Framework



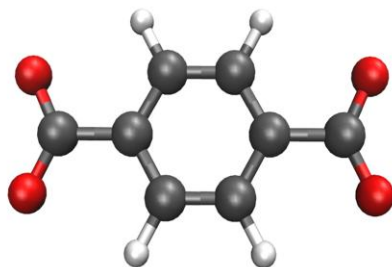
MOF Framework

(a)



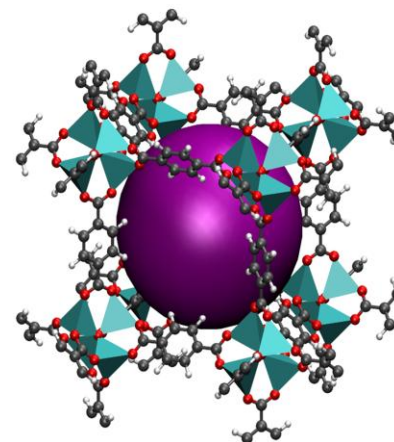
$Zn_4(O)O_{12}C_6$ cluster

+



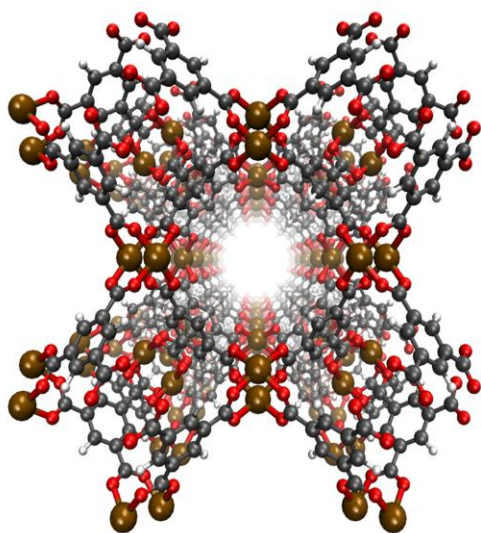
organic linker

→



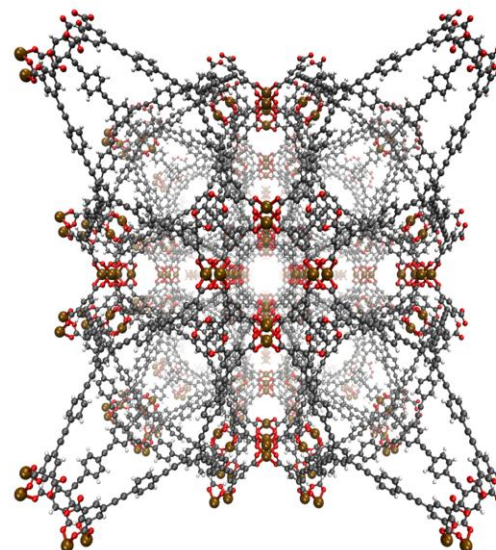
8 clusters comprise the
18.5 Å diameter

(b)

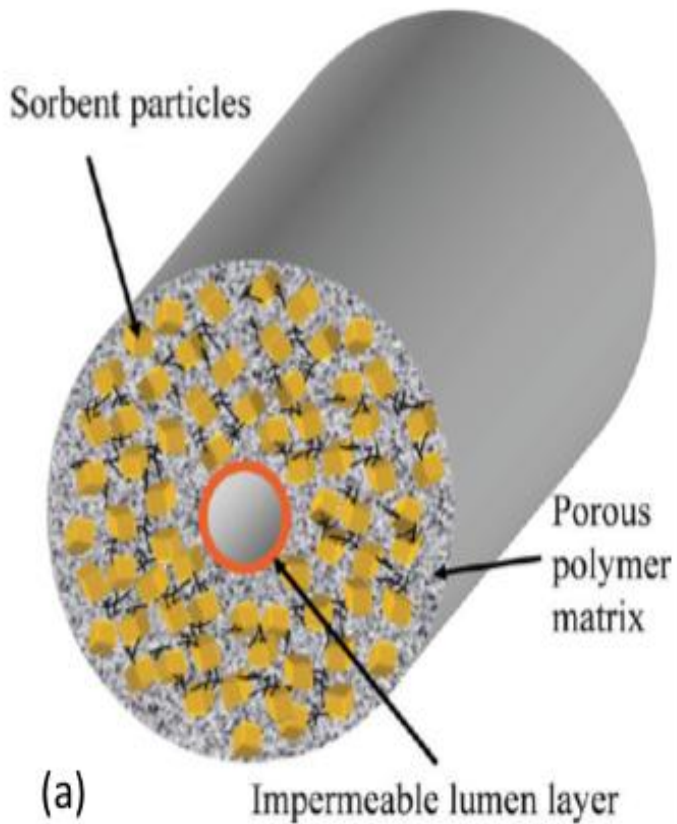


(b) And (c)
show MOF
structural
features

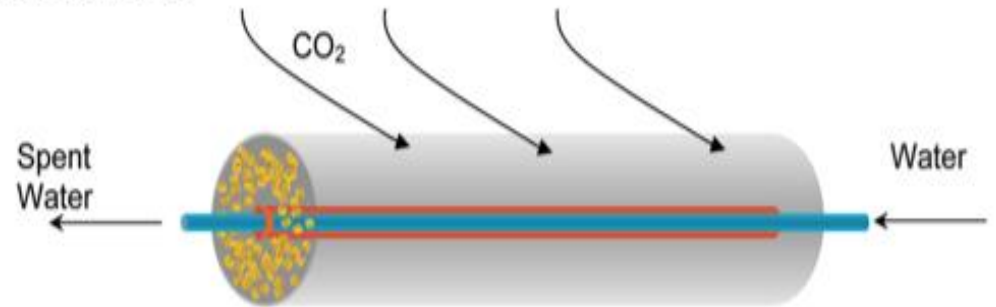
(c)



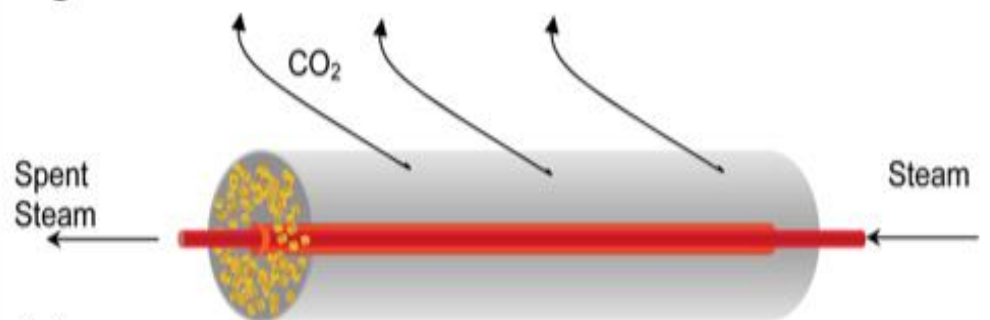
Hollow-fiber Sorbents



Adsorption



Regeneration



(b)

Adsorption Cycles

Process condition	Temperature Swing	Displacement Purge	PSA
Adsorbate concentration in feed, < 3%	yes	unlikely	unlikely
Adsorbate concentration in feed, 3-10%	yes	yes	yes
Adsorbate concentration in feed, > 10%	no	yes	yes
High product purity required	yes	yes	possible
Thermal regeneration required	yes	no	no
Difficult adsorbate separation	possible	unlikely	NA

Pressure Drop

- Ergun verified this eqn. for a variety of different shapes of packing material with varying packing densities; the first void space term accounts for the viscous loss component and the second for the KE loss component

$$\frac{\Delta P}{L} = \frac{150\bar{V}_0\mu}{\Phi_s^2 D_p^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} + \frac{1.75\rho\bar{V}_0^2}{\Phi_s D_p} \frac{1-\varepsilon}{\varepsilon^3}$$

- It is important to note that a small change in ε results in a large change in ΔP
- Typical numbers for calculations:
 - Void fractions for spheres, cylinders, and granular packings typically range from 0.3-0.6
 - Sphericity ranges from 0.6-0.95

Real Work: Overcoming Pressure Drop

- How much blower power is required to overcome the pressure drop in an adsorption system of a packed tower?

$$Power = P_1 V_1 \left(\frac{k}{k-1} \right) \left[\left(\frac{P_2}{P_1} \right)^{(k-1)/k} - 1 \right]$$

- P is power in kilowatts, P_1 is the inlet pressure, P_2 is outlet pressure, V_1 is the flow rate of gas, k is the ratio of specific heat ($k=C_p/C_v$, where C_p and C_v are the heat capacity at constant pressure and volume, respectively)
 - Typical values for $k = 1.4$ for air

Capture processes

CO₂ Gas Mixture

Traditional combustion (coal)
NGCC
IGCC
Oxyfuel
Direct air capture

% Capture
% Purity

Thermodynamic
minimum work

2nd law:

$$h = \frac{W_{\min}}{W_{\text{real}}}$$

Absorption

Design parameters

- Column height
- Column width
- # Columns

Solvent properties

CO₂ solubility
Diffusion (CO₂/base)
Reaction kinetics

Work requirements

- Gas Blowing
- Solvent pumping
- Heat of Regeneration

Adsorption

Design parameters

- MTZ bed height
- Column width
- # Columns

Sorbent properties

Pore size
Capacity
Phys/chem
Diffusion

Work requirements

- Pressure difference
- Sorbent loading
- Binding strength

Membrane

Design parameters

- Surface area
- Thickness

Memb properties

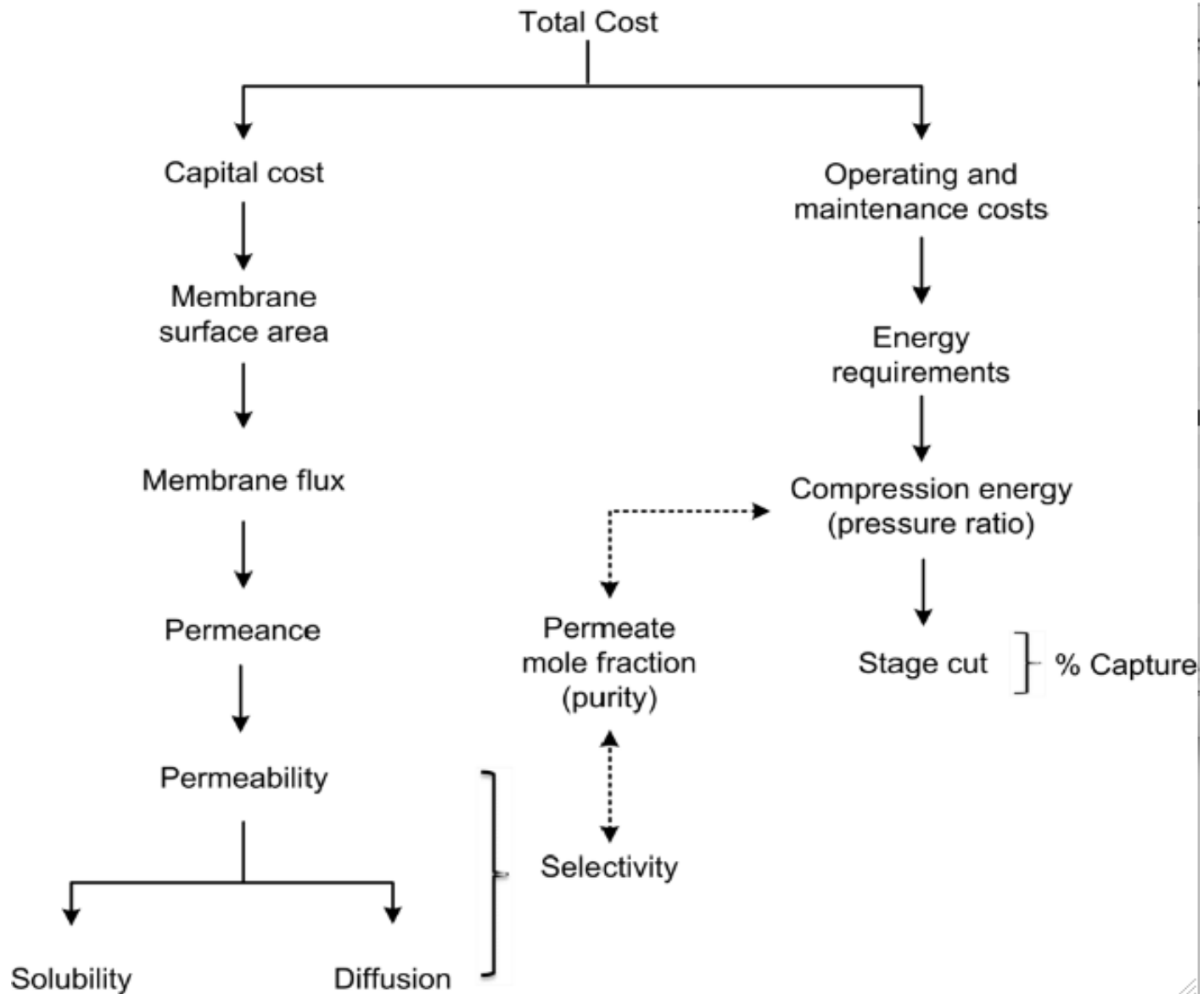
Solubility
Diffusion
Permeability
Selectivity

Work requirements

- Pressure difference
- Compression
- Stage cut

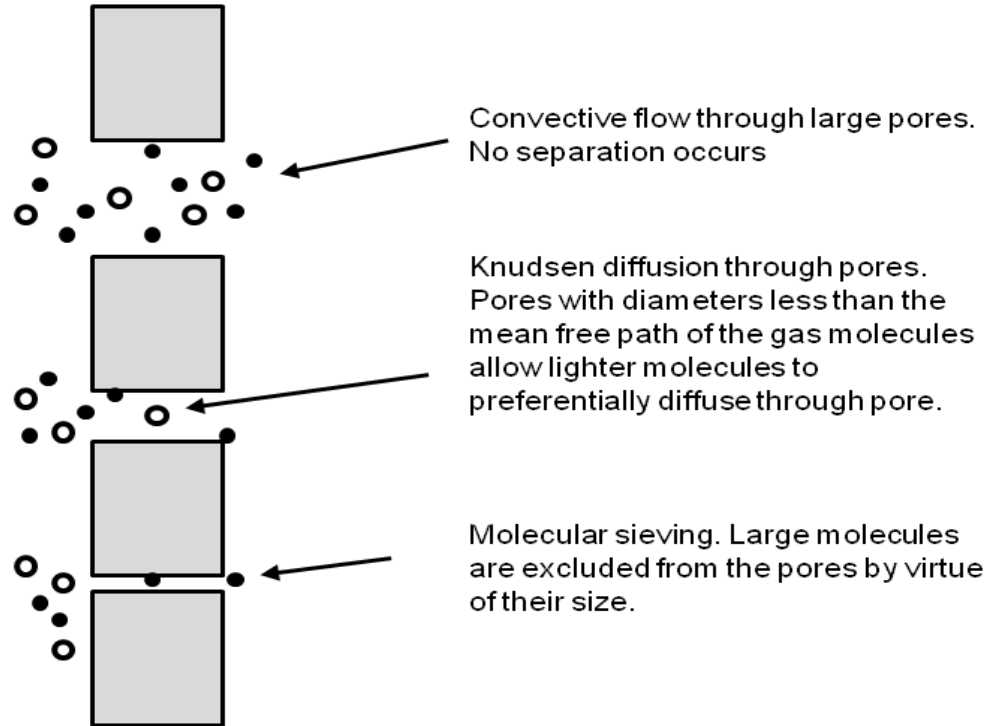
Real work

Outline of Membrane Processes

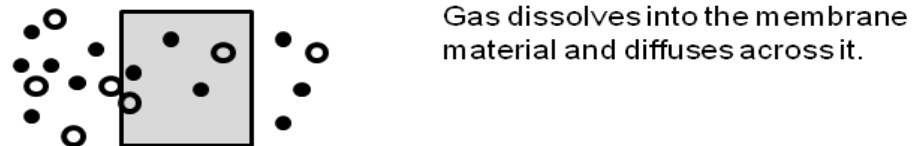


Membrane Separation Mechanisms

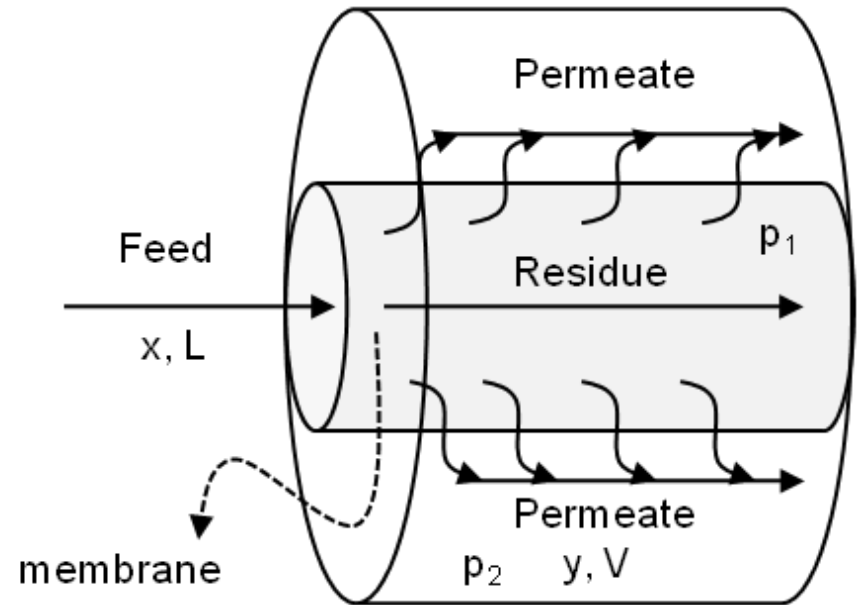
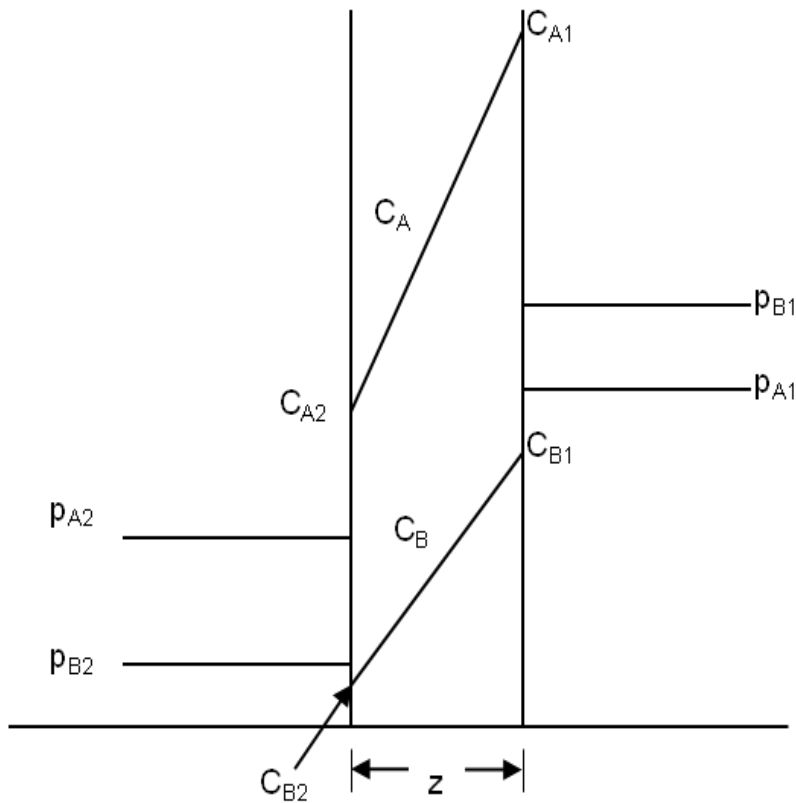
A. Porous Membranes



B. Solution-Diffusion Membranes



Gradients and Terminology



Important Terms:

Stage cut = permeate flow rate/feed flow rate

Permeate/Residue Concentrations

Pressure Ratio = permeate pressure/feed pressure

Permeability vs. Permeance

- Permeability vs Permeance

$$J_A = \frac{D_A S_A (p_{A1} - p_{A2})}{z} = \bar{P}_A (p_{A1} - p_{A2})$$

- J = flux; D = diffusivity, S = solubility, z = membrane thickness, and coefficient of pressure difference is the permeance
- Permeability is the product of diffusivity and solubility and is a property of the material
- Typical units of permeance are GPUs or standard ft³/ft² h atm
- Permeance is a property of a particular membrane
- Typical units of permeability are Barrers

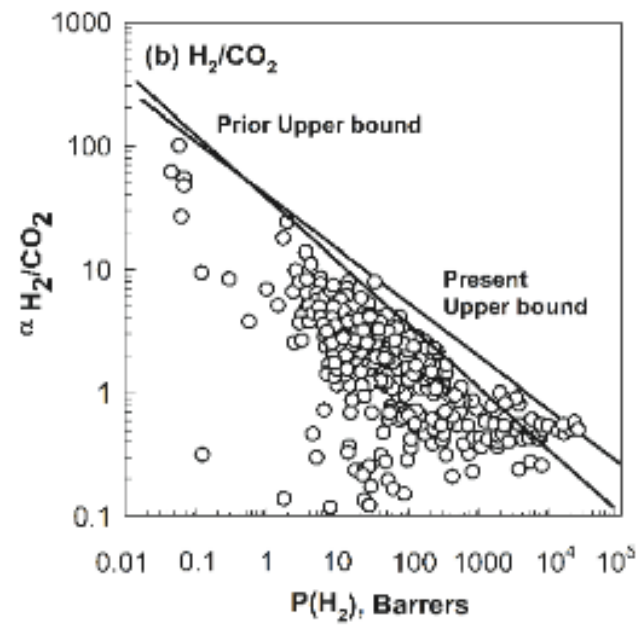
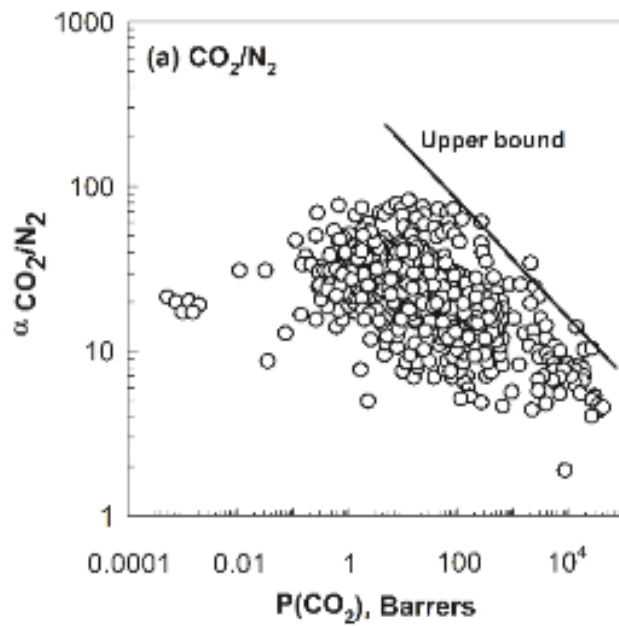
$$1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3(\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$$

Selectivity

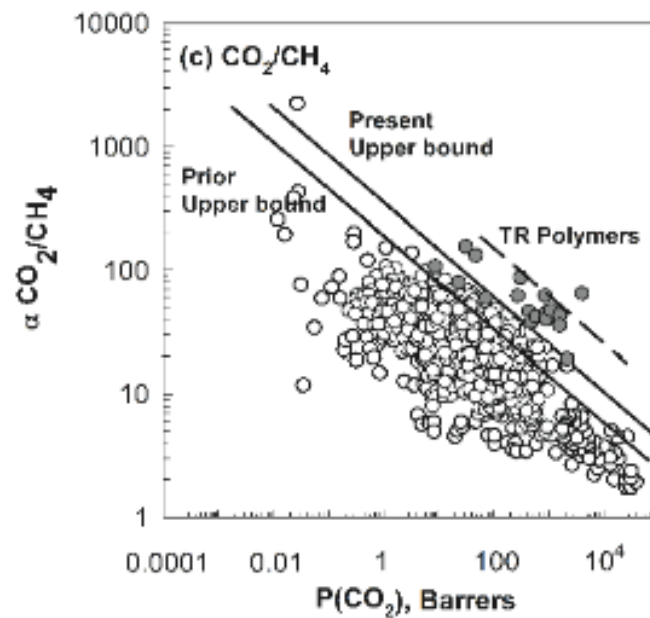
- Selectivity may be in terms of permeability, diffusivity, or solubility

$$\alpha = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right)$$

- In 1991, Lloyd M. Robeson quantified the trade-off between permeability and selectivity; displayed in terms of Robeson plots

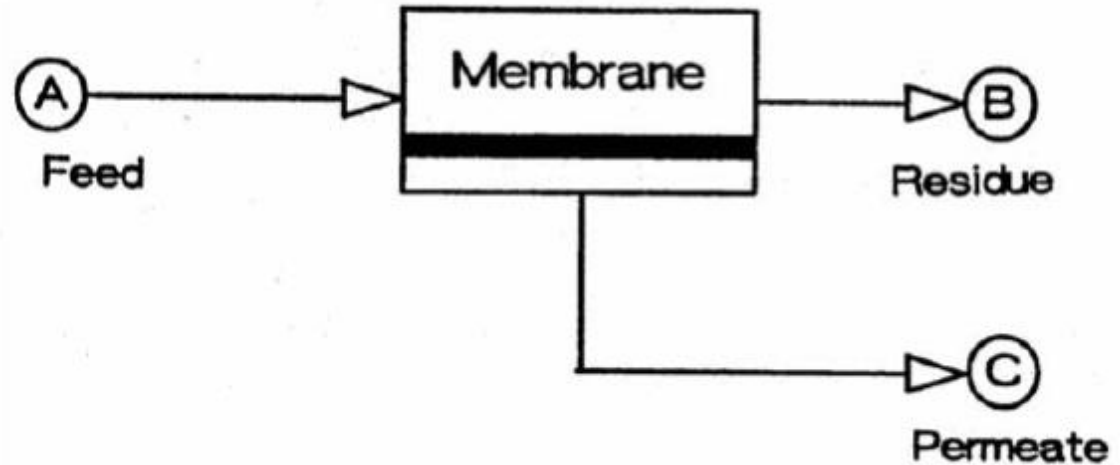


Robeson Plots



Gas Separation Process Design

- CO₂ capture from natural gas
- Residue is purified CH₄ w/ permeate stream enriched in CO₂
- Note high feed and residue streams



	Stream		
	A	B	C
Composition (mole %)			
CH ₄	93.0	98.0	63.4
CO ₂	7.0	2.0	36.6
Flow Rate (MMscfd)	20.00	17.11	2.89
Pressure (psig)	850	835	10
Methane Recovery = 90.2%			
Flow Rate (SCFM)	13890	11880	2007

Figure 5. Single-stage membrane process for natural gas treating.

Short-Cut Design Calculation

- Short-cut area calculation described by Hogsett and Mazur, Hydrocarbon Processing, 62, 52 (1983)

$$Area = \frac{x_{1perm} Q_{perm}}{\frac{P_1}{l} (p_{feed} x_{\log-mean} - p_{perm} x_{1perm})} @ \frac{\text{permeate flow rate of 1}}{\text{flux of species 1}}$$

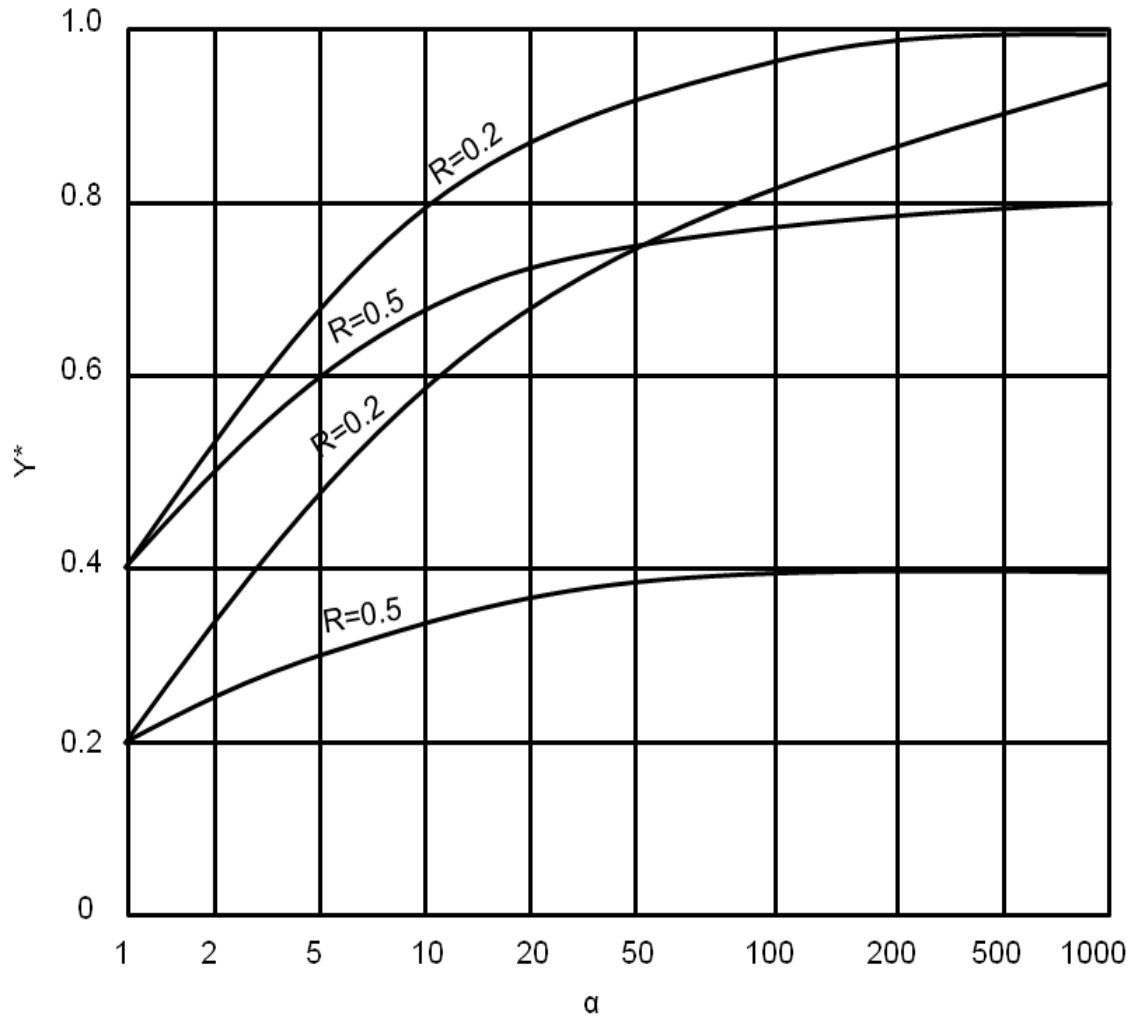
where Q is volumetric flowrate, x is mole fraction, p is pressure

$\frac{P_1}{l}$ is permeance of species 1

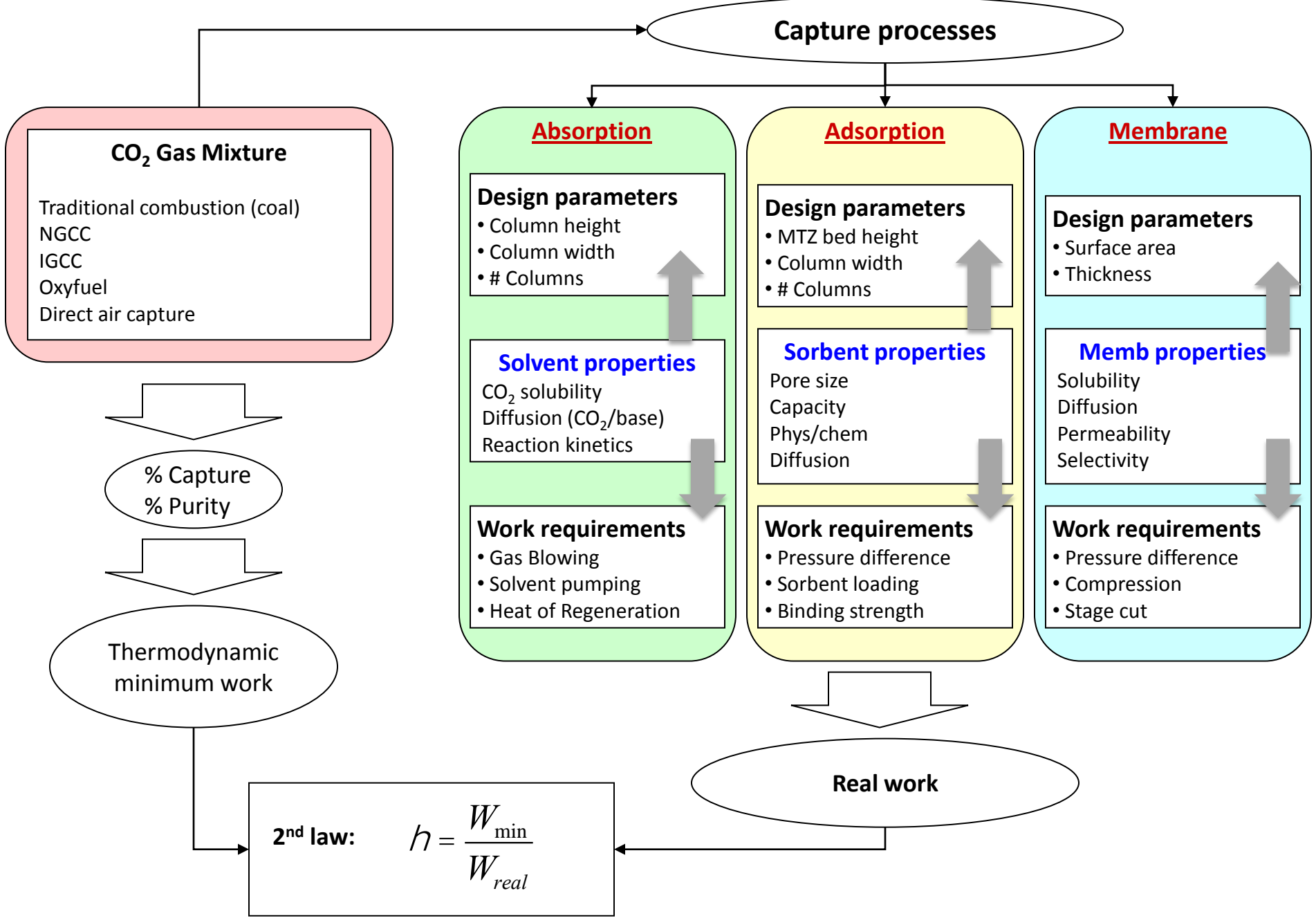
$$x_{\log-mean} = \frac{x_{1feed} - x_{1residue}}{\ln \frac{x_{1feed}}{x_{1residue}}}$$

- Using values from the previous slide and a CO₂ permeance of 5.5 ft³ (STP)/(ft² 100 psi hr), results in a membrane area of 31,500 ft²

Local Permeate Concentration



Selectivity and pressure ratio effects on the local permeate concentration



Additional Slides

Absorption-Related Mass-Transfer Correlations

Scenario	Correlation	Remarks
Liquid in packed-bed	$k \left(\frac{1}{vg} \right)^{1/3} = 0.0051 \left(\frac{u}{va} \right)^{0.67} \left(\frac{D}{v} \right)^{0.5} (ad)^{0.4}$ $\frac{kl}{D} = 25 \left(\frac{lu}{v} \right)^{0.45} \left(\frac{v}{D} \right)^{0.5}$	Known as best available correlation for liquids Classical result and widely referenced
Gas bubbles in stirred tank	$\frac{kl}{D} = 0.13 \left(\frac{(P/V)l^4}{\rho v^3} \right)^{1/4} \left(\frac{v}{D} \right)^{1/3}$	k is not dependent on bubble size
Gas bubbles in unstirred tank	$\frac{kl}{D} = 0.31 \left(\frac{l^3 g \Delta\rho / \rho}{v^2} \right) \left(\frac{v}{D} \right)^{1/3}$	$\Delta\rho$ = density difference between bubble and fluid
Falling films	$\frac{kz}{D} = 0.69 \left(\frac{zu}{D} \right)^{0.5}$	z = position along film

Notes: a = packing area per bed volume; l = characteristic length (or bubble or drop diameter); ε = bed voidage; P/V = stirrer power per volume; u = superficial velocity (or drop velocity)

Choosing an Appropriate Solvent

- high CO₂ capacity
- fast kinetics with CO₂
- low volatility
- low viscosity
- nontoxic, nonflammable, and noncorrosive
- high thermal stability
- resistance to oxidation
- Examples include amines, carbonates, and ammonia

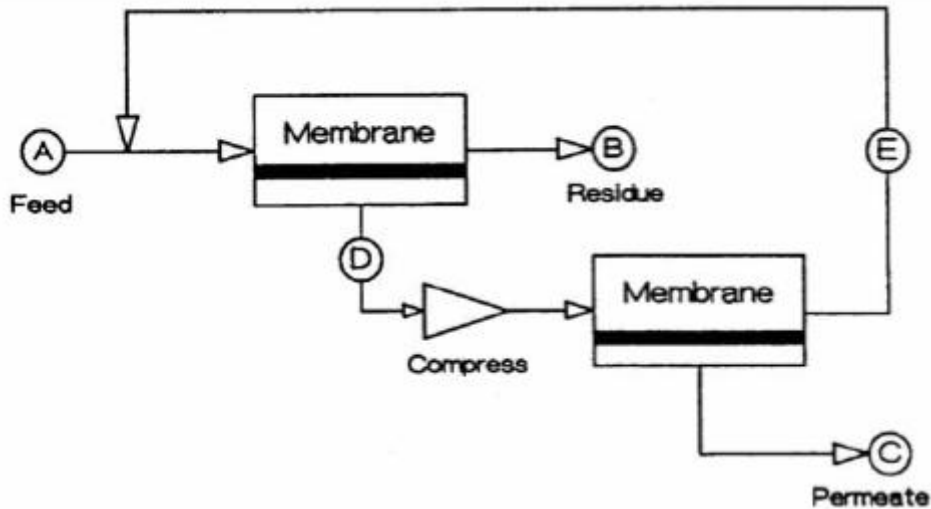
Common Types of Sorbents

Sorbent	Pore Diameter (nm)	Sorbent Density (kg/m ³)	Sorbent Porosity	BET Surface Area (m ² /g)	H ₂ O cap. Wt. %, 25 °C, 4.6 mmHg	CO ₂ cap. Wt. %, 25 °C, 250 mmHg	Regeneration Temp, °C
^{17a} Activated carbon							
Small pore	1-2.5	500-900	0.4-0.6	400-1200	1	5	-
Large pore	> 3	600-800	-	200-600	-	7	-
^{17a} Zeolites							
3A	0.3	670-740	0.2	700	20	-	> 350
4A	0.4	660-720	0.3	700	23	13	120-350
5A	0.5	670-720	0.4	650	21	15	120-350
13X	0.8	610-710	0.5	600	25	16	120-350
Mordenite	0.3-0.4	720-800	0.25	700	9	6	-
Chabazite	0.4-0.5	640-720	0.35	650	16	12	-
^{17a} Silica gel							
Small pore	2.2-2.6	1000	0.47	800	11	3	130-280
Large pore	10-15	620	0.71	320	-	-	130-280
^a Activated alumina	1-7.5	800	0.50	320	7	2	150-315
^{14a, 28} MOFs	0.4-2.4	200-1000	0.79-0.90	150-6200	9	^f 4-14, 15	25-80
Ion exchange resins	<1-12	^a 1100, ^b 1270	0.2-0.5	15-120	-	-	60
²⁹ Hollow fibers	2.5-11	1250	0.3-0.8	450-1100	-	-	100-150
^{29a, 30} CMS	0.3-0.9	640-1000	0.5	400	>20	1.2-2.5	100-200
³¹ Amine-based	8-40	1000-1500		5-500	-	5-14	80-120
³² Hydrotalcites	2-20	150-550	0.15-0.5	16-290	-	-	120-400
^{32c, 33} Chemisorbents	0.2-20	2000		250-1250	-	-	^c 700-920 ^d 150-500 ^e 350

Influence of Pressure Ratio

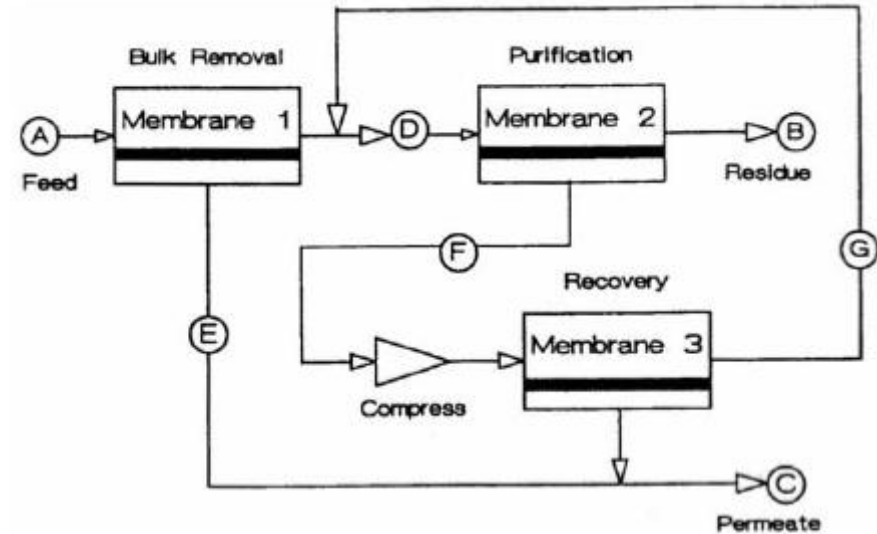
- Original Case:
 - 100 MSCFH natural gas
 - Feed pressure = 480 psia
 - Permeate pressure = 20 psia
 - $\Delta P = 460$ psia
 - Pressure ratio, $\gamma = 0.042$
 - Feed $\text{CO}_2 = 12\%$
 - Product $\text{CO}_2 = 2\%$
 - Area required = 1,700 ft²
- New Case:
 - 100 MSCFH natural gas
 - Feed pressure = 1200 psia
 - Permeate pressure = 200 psia
 - $\Delta P = 1000$ psia
 - Pressure ratio, $\gamma = 0.17$
 - Feed $\text{CO}_2 = 12\%$
 - Product $\text{CO}_2 = 2\%$
 - Area required = 7,800 ft²

Multi-Stage Processes



	Stream				
	A	B	C	D	E
Composition (mole %)					
CH ₄	93.0	98.0	18.9	63.4	93.0
CO ₂	7.0	2.0	81.1	36.6	7.0
Flow Rate (MMscfd)	20.00	18.74	1.26	3.16	1.90
Pressure (psig)	850	835	10	10	850
Methane Recovery = 98.7%					

Figure 8. Two-stage gas separation membrane process for natural gas treating.



	Stream						
	A	B	C	D	E	F	G
Composition (mole %)							
CH ₄	93.0	98.0	49.2	96.1	56.1	72.1	93.0
CO ₂	7.0	2.0	50.8	3.9	43.9	27.9	7.0
Flow Rate (MMscfd)	20.00	17.95	2.05	19.39	1.62	1.44	1.01
Pressure (psig)	850	835	10	840	10	10	850
Methane Recovery = 94.6%							

Figure 9. Multi-stage gas separation membrane process for natural gas treating.