CO_2 capture by solvents; challenges and possibilities

Post-Combustion CO_2 Capture Workshop
Talloires, July 11-13, 2010

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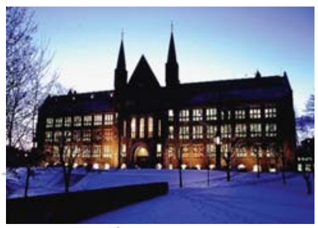
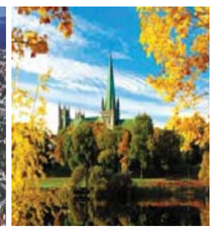




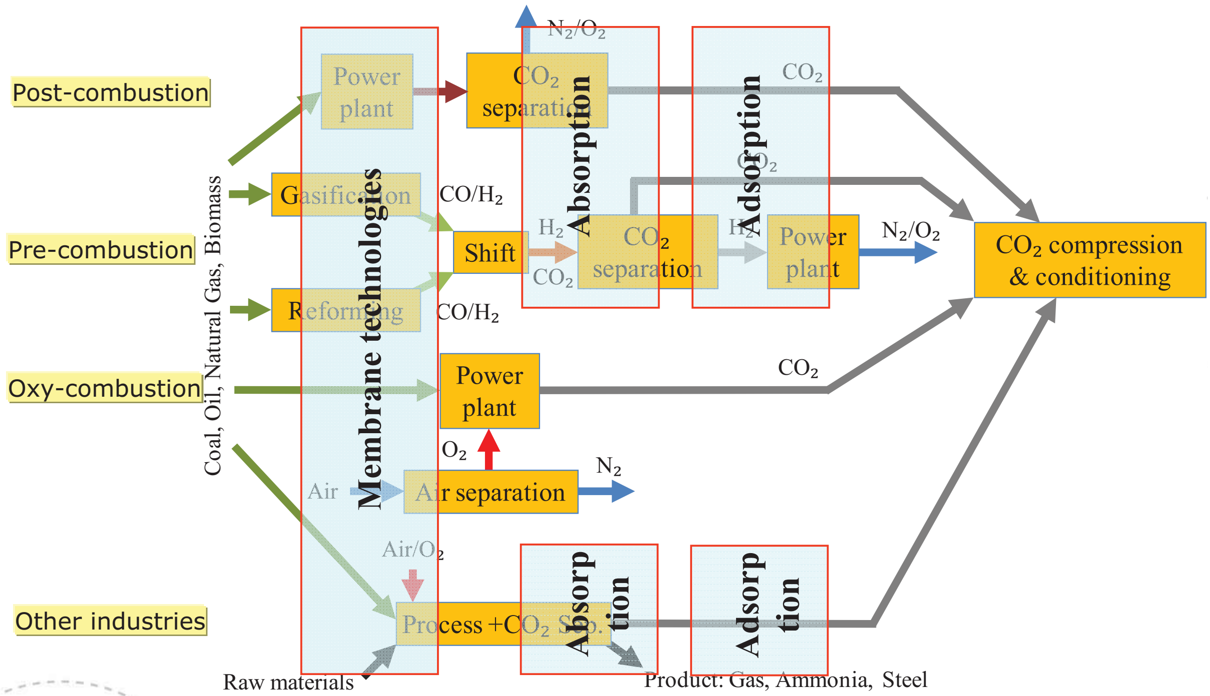

Outline

Introduction

Post combustion CO_2 capture by reactive absorption

- Energy requirements
  - Heat
  - Electricity
- Equipment size
- Degradation
- Environmental issues

Pathways to CO_2 capture and Separation technologies



Challenges

- High requirements of thermal and electrical energy
- Costly process and large space requirements
- Production of waste products
- Possible emissions of volatile amines and degradation products

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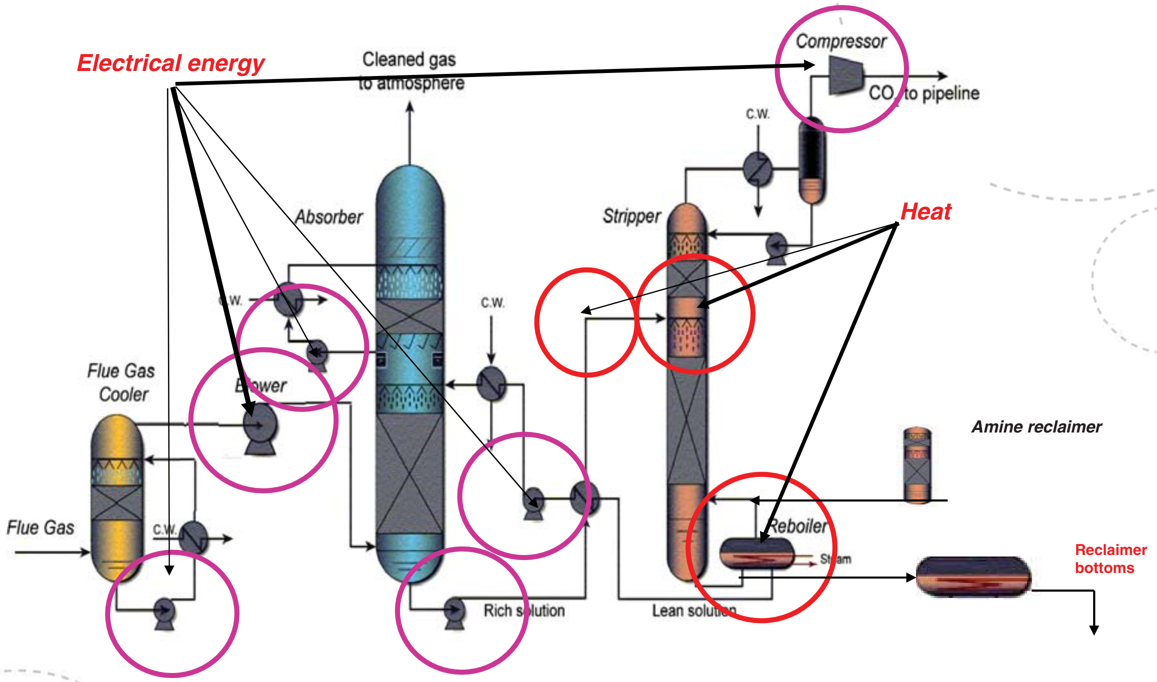
Energy considerations



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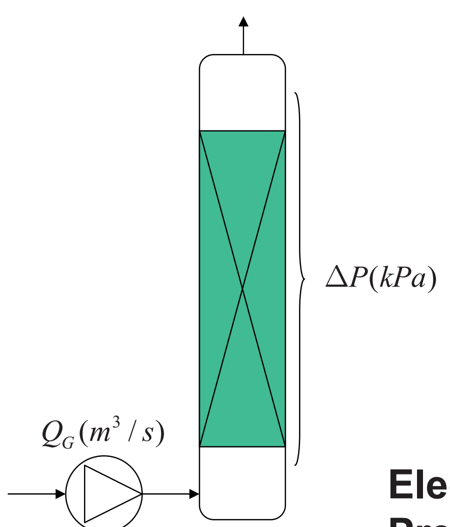
Energy requirements



$$W \approx Q_G \cdot \Delta P$$

400 MW NG fired power station

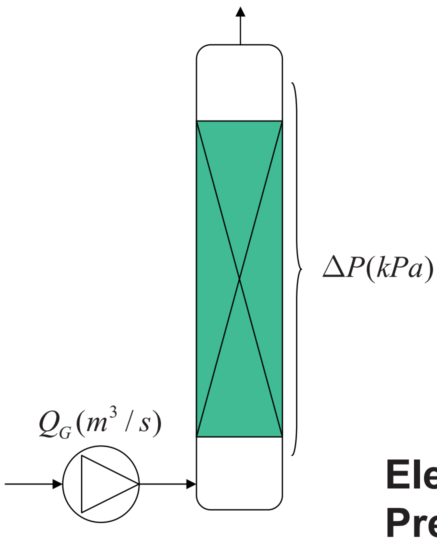
Exhaust gas rate:

2000000 m^3/h flue gas
3,5 % CO_2
1000000 tons CO_2/year

Heat required for CO_2 capture:
90-140 MW_{steam} ~ 22,5-35 MW_{el}

Electricity required
Pressure drop in absorber: ~ 6 MW_{el}
Recompression: ~ 12 MW_{el}
Miscellaneous: ~ 1 MW_{el}

Energy requirements



$$W \approx Q_G \cdot \Delta P$$

Coal example:

400 MW pulverized coal fired power station

Exhaust gas rate:

1000000 m^3/h flue gas
12 % CO_2
2200000 tons CO_2/year

Heat required for CO_2 capture:
200-310 MW_{steam} ~ 50-77.5 MW_{el}

Electricity required
Pressure drop in absorber: ~ 3.5 MW_{el}
Recompression: ~ 27 MW_{el}
Miscellaneous: ~ 2 MW_{el}

How can solvents influence these factors

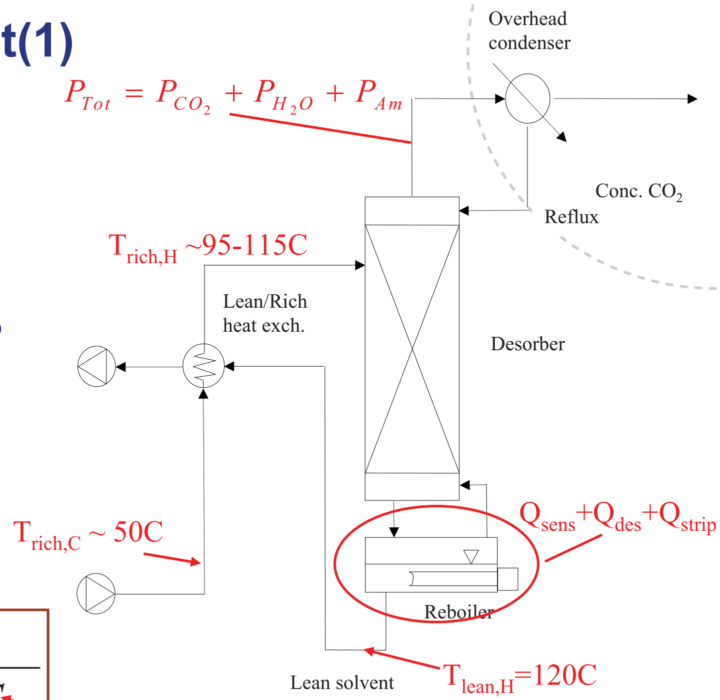
- **High requirements of thermal and electrical energy**
  - Heat of reaction
  - Equilibrium temperature sensitivity
  - Equilibrium approcah
  - Cyclic capacity
  - Water solubility
- **Costly process and large space requirements**
  - Rate of reaction/Mass transfer rates
  - Cyclic capacity
  - Foaming properties
  - Corrosion
- **Production of waste products**
  - Chemical stability
- **Possible emissions of volatile products**
  - Ecotoxicity
  - Biodegradability
  - Volatility

Heat requirement(1)

Total heat required,
(J/mol CO_2 captured)

$= Q_{sens} + Q_{des} + Q_{strip}$

$\Delta T = T_{lean,H} - T_{rich,H}$



$$Q_{sens} = \frac{\rho C p \Delta T}{(\alpha_{rich} - \alpha_{lean}) C_{Ab}}$$

Absorbent concentration mol/l

CO_2 loading, molCO_2/mol absorbent

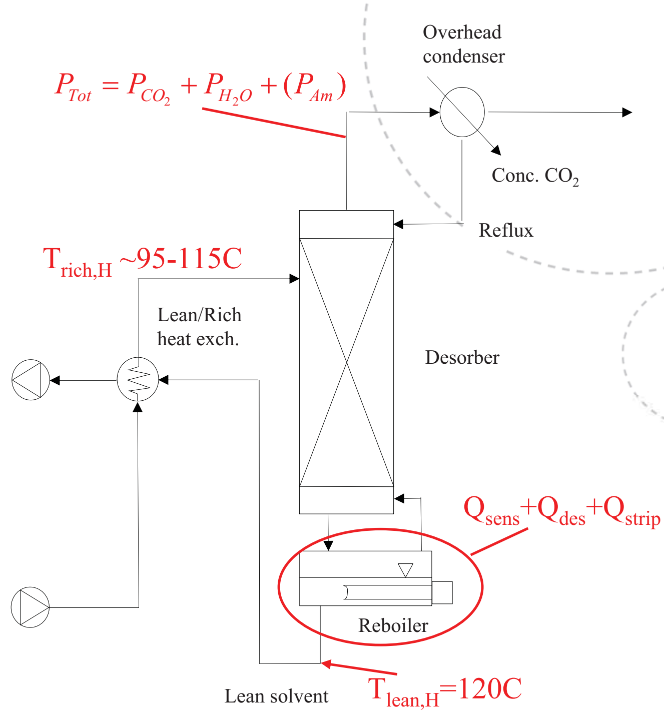
Heat requirement(2)

Reversion of the reaction:

$$Q_{des} = \Delta H_{absCO_2}$$

Water reflux(stripping steam):

$$Q_{strip} = \frac{P_{H_2O}\left(T_{rich,H}, \alpha_{rich}\right)}{P^*_{CO_2}\left(T_{rich,H}, \alpha_{rich}\right)} \Delta H^{vap}_{H_2O}$$



How reduce the heat requirement?

1) Sensible heat loss:

$$Q_{sens} = \frac{\rho Cp \Delta T}{(\alpha_{rich} - \alpha_{lean}) C_{Ab}}$$

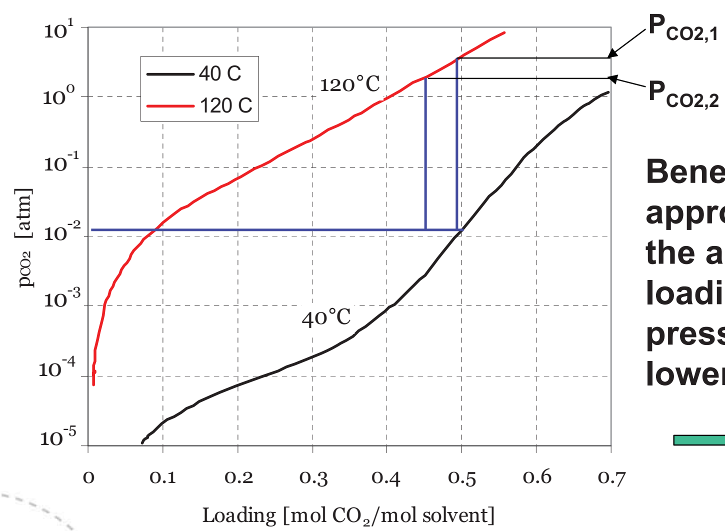
Reduce cross flow heat exchanger temperature approach: ΔT

Increase cyclic capacity: $CC = (\alpha_{rich} - \alpha_{lean}) C_{Ab} = C_{CO_2,rich} - C_{CO_2,lean}$

- High rich loading
  - Amine class
  - Polyamines
  - Fast amines
- Low lean loading
  - Close to intersection between steam and heat limited regimes

2) Stripping steam requirement(1):

$$Q_{strip} = \frac{P_{H_2O}\left(T_{rich,H}, \alpha_{rich}\right)}{P^*_{CO_2}\left(T_{rich,H}, \alpha_{rich}\right)} \Delta H^{vap}_{H_2O}$$

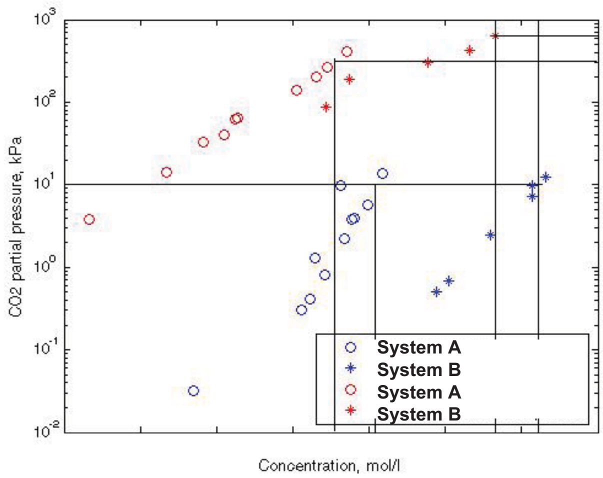


Beneficial with close approach to equilibrium at the absorber bottom: high loading gives high CO_2 pressure in desorber, and lower Q_{strip}

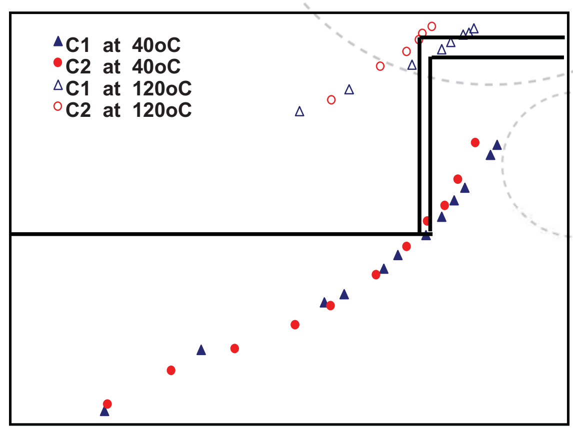
→ **Fast absorbent**

2) Stripping steam requirement(2):

Effect of amine system and concentration



Component A



Left side: Two systems with different temperature sensitivity
Right side: Also amine concentration may affect temperature sensitivity

2) Stripping steam requirement(3):

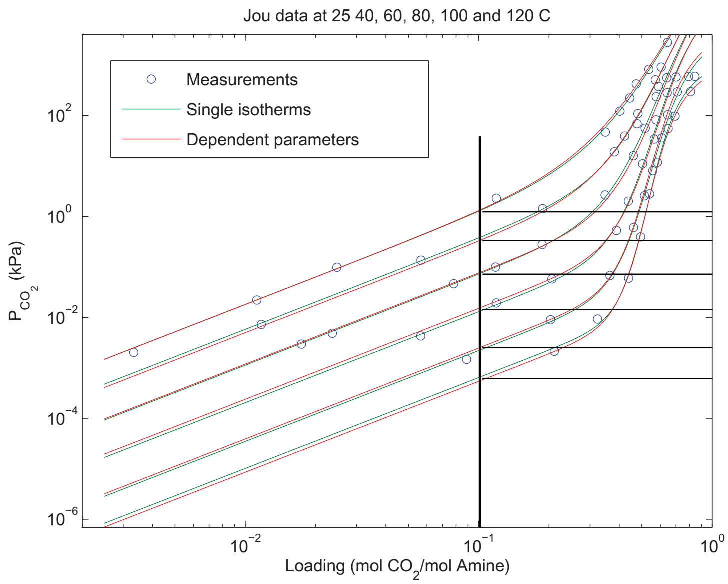
How to take advantage of the increased CO_2 pressure?

a) **Reduce reboiler temperature: Little or no saving in energy but in exergy**

b) **Increase pressure in stripper and maintain reboiler temperature: Improves CO_2/H_2O ratio in vapour leaving stripper, thereby reducing stripping steam requirement**

3) Heat of desorption(1)

$$Q_{des} = \Delta H_{absCO_2}$$



From Gibbs-Helmholtz equation:

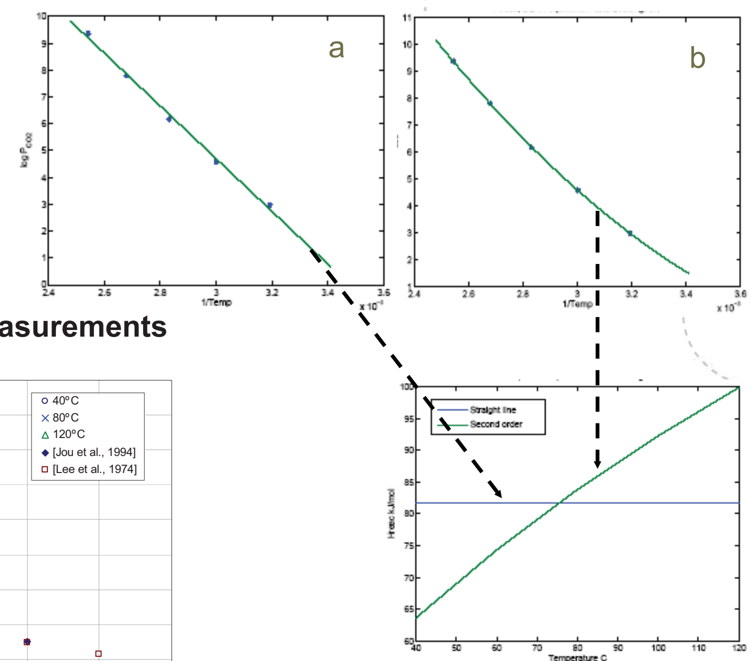
$$\frac{\partial \ln p_{CO_2}}{\partial(1/T)} = \frac{\Delta H_{abs}}{R}$$

High temperature sensitivity of p_{CO2} gives high heat of reaction.

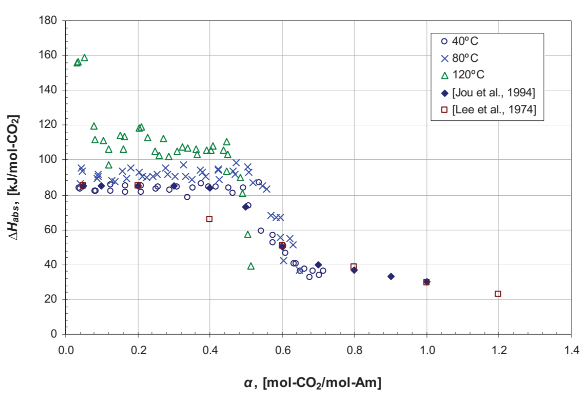
3) Heat of desorption(2)

From equilibrium function with the Gibbs-Helmholtz equation:

$$\frac{\partial \ln p_{CO_2}}{\partial(1/T)} = \frac{\Delta H_{abs}}{R}$$



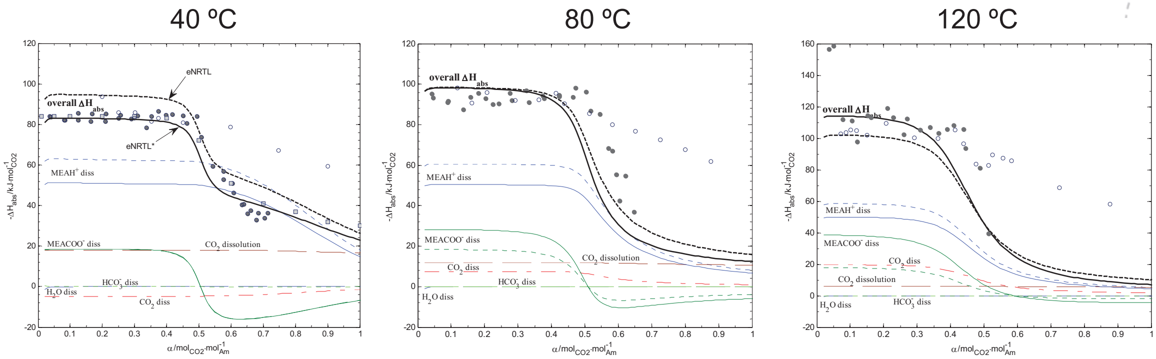
Compared to calorimetric measurements



3) Heat of desorption(3)

Effect of different reactions

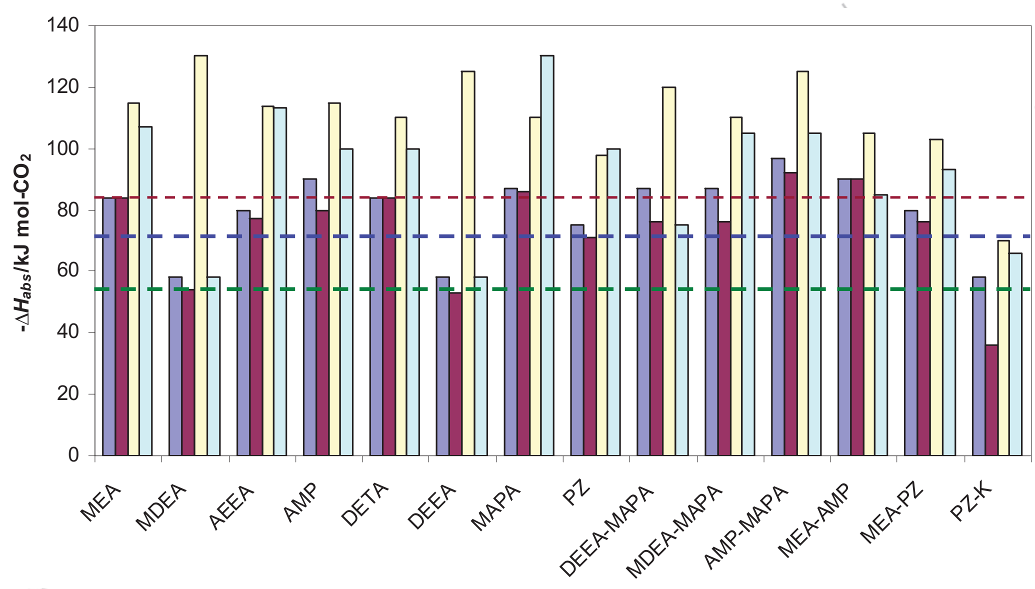
- Heats of each of the key reaction and overall heat of absorption of CO_2 with 30 wt % MEA solution (different sets of correlations for K-values)



●, Kim (2009); ○, Mathonat (1995); ■, Jou et al. (1994).
Lines: —, eNRTL*; ---, eNRTL model (as in ASPEN)

3) Heat of desorption(4)

ΔH_abs for CO_2 with different amine systems at 40 and 120 °C (α~0.1/0.4)

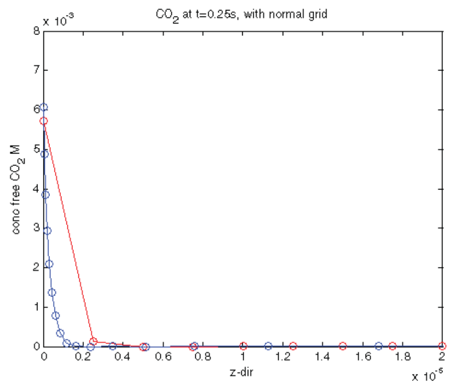


■/■, 40 °C, α=0.1/0.4 mol-CO_2/mol-Am; ■/■ 120 °C, α=0.1/0.4 mol-CO_2/mol-Am

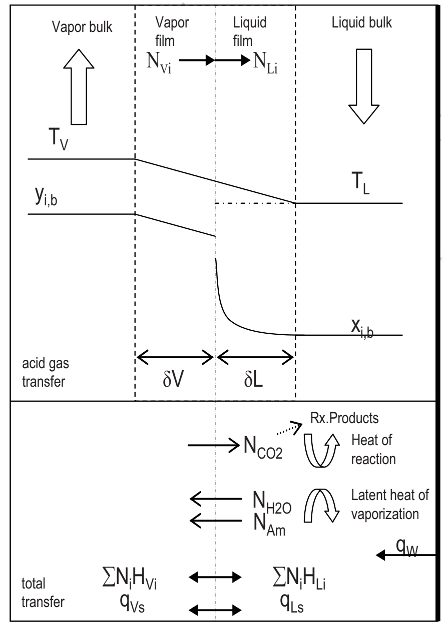
Mass Transfer

Reduce approach to equilibrium

- Kinetic rate constants
- Solubility
- Diffusivity



CO_2 gradients



Rate constants

Termolecular mechanism

$$r_{CO_2} = k_{obs}\left[CO_2\right], \frac{kmol}{m^3 s}$$

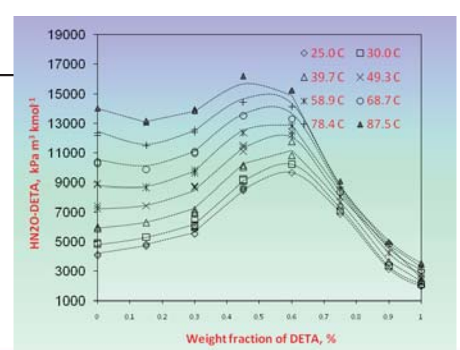
$$k_{obs} = \left\{k_{AmH}\left[AmH\right] + k_{H_2O}\left[H_2O\right] + k_{OH^-}\left[OH^-\right]\right\}\left[AmH\right]$$

$[R_1R_2NH]$	$10^{-3}.k^T_{DETA}$ $(m^3.kmol^{-1}s^{-1})$	$k^T_{H_2O}$ $(m^3.kmol^{-1}s^{-1})$	$[R_1R_2NH]$ $(kmol.m^3)$	Source(s)
MEA	1.7	73.7	0.19 - 5.50	Aboudheir, et al., (2003)
	1.1	140.8	0.5-5.0	Hartono et al. (2009)
AEEA	2.35	161	1.19 - 3.46	Ma'mun, et al. (2007)
EDA	2.79*	17.72*	0.026-0.068	Li, et al. (2007)
DETA	17.5	179.7	1.0-2.9	Hartono et al. (2009)
Pz	70.1	550	0.45 - 1.5	Cullinane & Rochelle (2002)

Large variations, correlated with the water activity

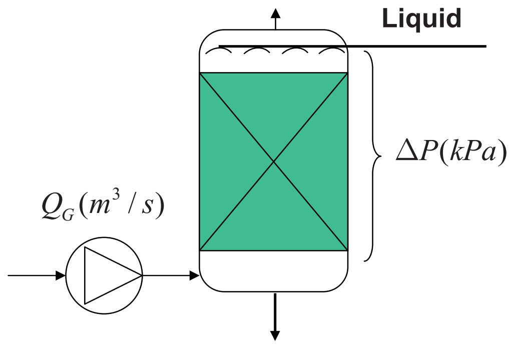
String of discs apparatus

Solubility of CO_2 in amine solutions



Electrical energy requirement

Pressure drop in absorber



Why not:

Reduce packing height
Increase diameter
Maintain area

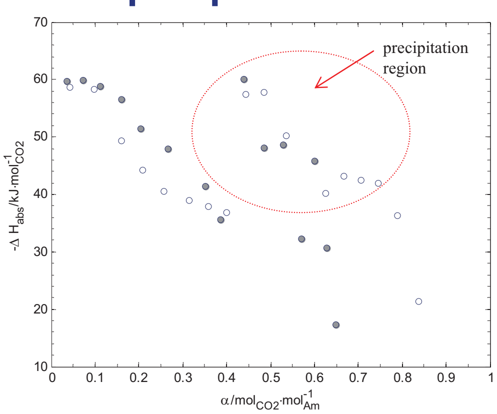
Limitations as effective area can go down. Low liquid load can give partial wetting

$$W \approx Q_G \cdot \Delta P$$

NG fired power stations are worst case Because of low CO_2 content

Desorption at elevated pressure:
Phase change systems

Precipitation/two liquid phases



○ 6 m K⁺ + 1.2 m Pz; ● 5 m K⁺ + 3.5 m Pz

K^+ + Pz system

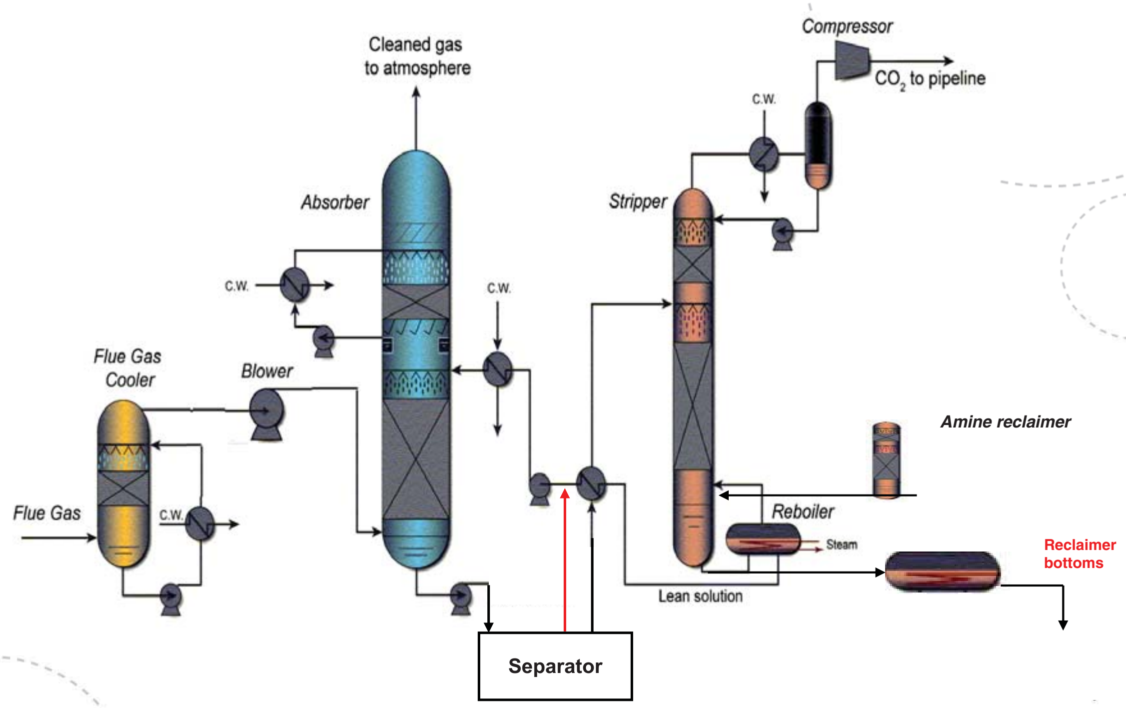
Advantages

- High cyclic capacity
- Improved equilibrium curves
- High pressure desorption
- Retain good liquid load in absorber

Disadvantages

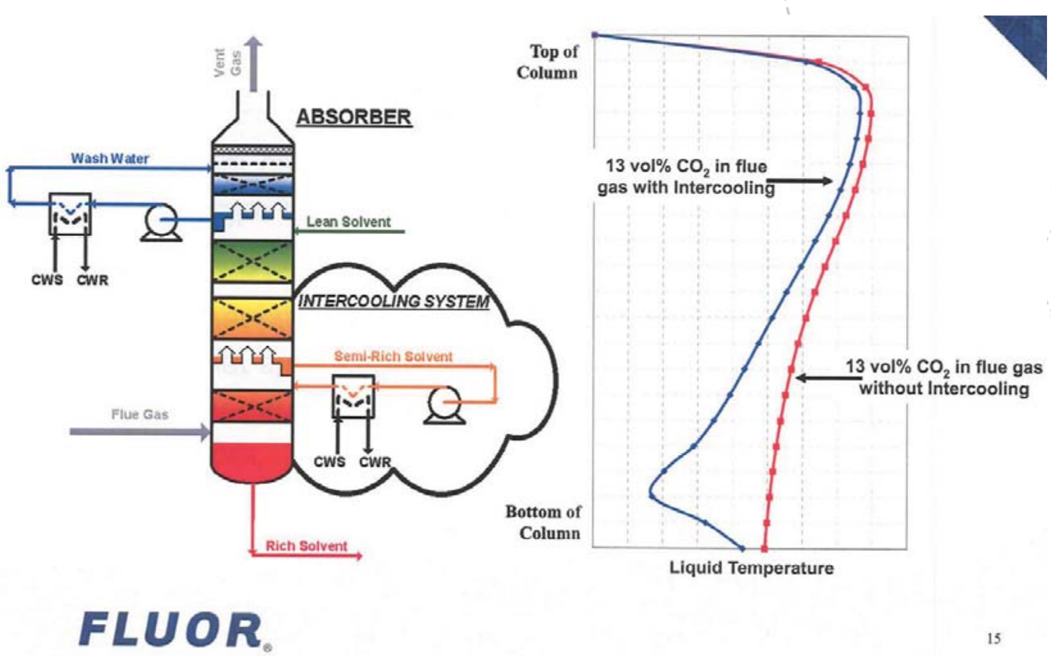
- Possibly higher heat of reaction
- Increased complexity

Phase change processes(liquid/liquid systems)



Process modifications

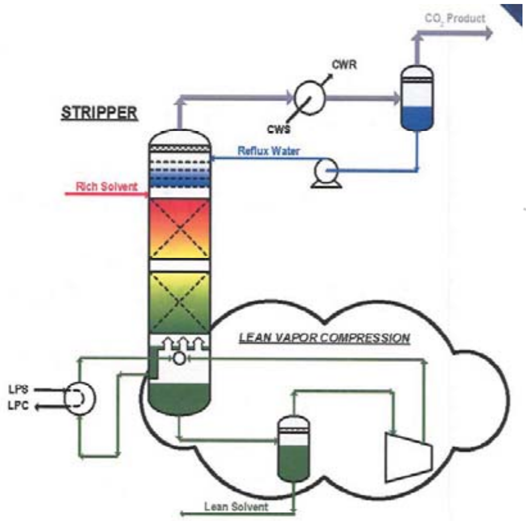
Absorber intercooling



Reddy S., " Econamine FG Plus[SG] Technology for Post Combustion CO_2 Capture", 11th Meeting of IEA GHG International CO2 Capture Network Meeting, Vienna, May 2008

Lean vapour recompression

- Lower steam consumption
- Lower cooling water requirement
- Increases electrical energy input
- Effect depends on solvent



Desorber interheating

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Reddy S., " Econamine FG Plus[SG] Technology for Post Combustion CO_2 Capture", 11th Meeting of IEA GHG International CO2 Capture Network Meeting, Vienna, May 2008

Summing up on energy requirement:

Heat

- High rich loading:
  - Close to equilibrium in absorber
  - Fast absorbent, high heat of absorption
- High absorbent concentration
- Low heat of reaction
- High equilibrium temperature sensitivity
  - High heat of reaction
- Plant design modifications
  - Intercooling
  - Interheating
  - Vapour recompression

Electricity

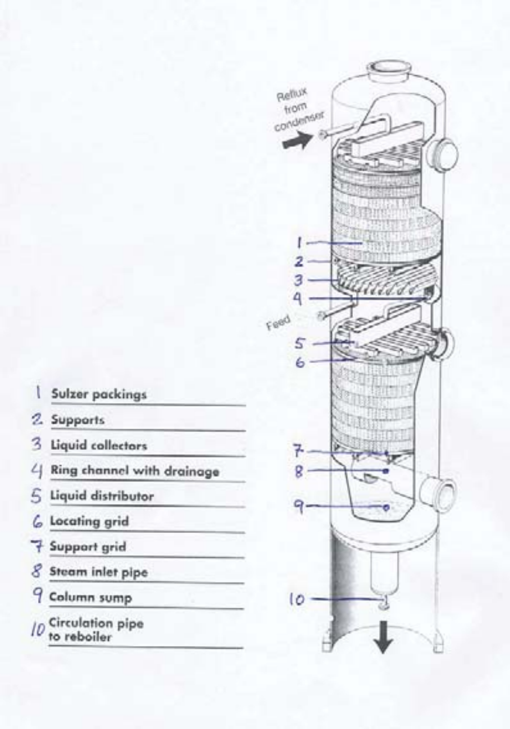
- More effective packing materials
- Solvents that desorb at high pressure

Challenges

- High requirements of thermal and electrical energy
- Costly process and large space requirements
- Possible emissions of volatile amines and degradation products
- Production of waste products

Equipment size

Absorption tower



Example:

400 MW NG fired power station

Exhaust gas rate:
2000000 m^3/h flue gas

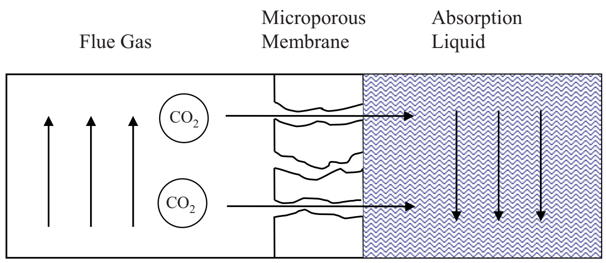
Typical gas velocity: 2 m/s

Tower cross sectional area:
280 m^2

Diameter: 19 m

Height: 35 m

An alternative: Membrane contactors

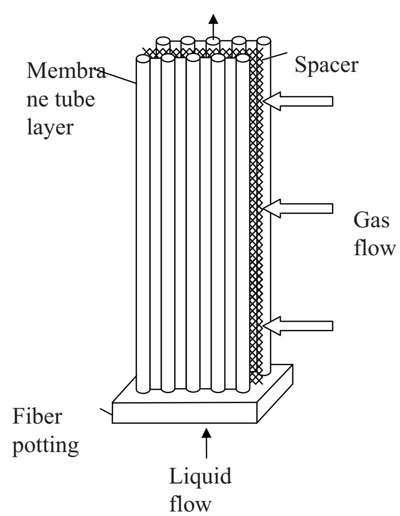


- Membrane not selective, only separates the phases
- CO_2 affinity and selectivity provided by the alkanol-amine solution, e.g. 30 wt% Monoethanolamine (MEA)
- Diffusion through pores followed by reaction in liquid
- Membrane material must not be wetted by liquid (for liquid side controlled absorption)

Membrane properties

High contact angle facilitated by low surface energy:

POLYMER	SURFACE ENERGY
polytetrafluorethylene (PTFE)	**19.1**
polypropylene (PP)	30.0
polyethylene (PE)	33.2
polyvinylchloride (PVC)	36.7



Advantages compared to packed towers:

- No foaming, channeling, entrainment or flooding
- Higher contact area, 500 - 1500 (m^2/m^3)
- Insensitive to motion
- Reduced solvent degradation problems
- Reduced corrosion problems
- Footprint requirement reduced by 40%
- 60 - 75% reduction of size and weight for an offshore application

Disadvantages:

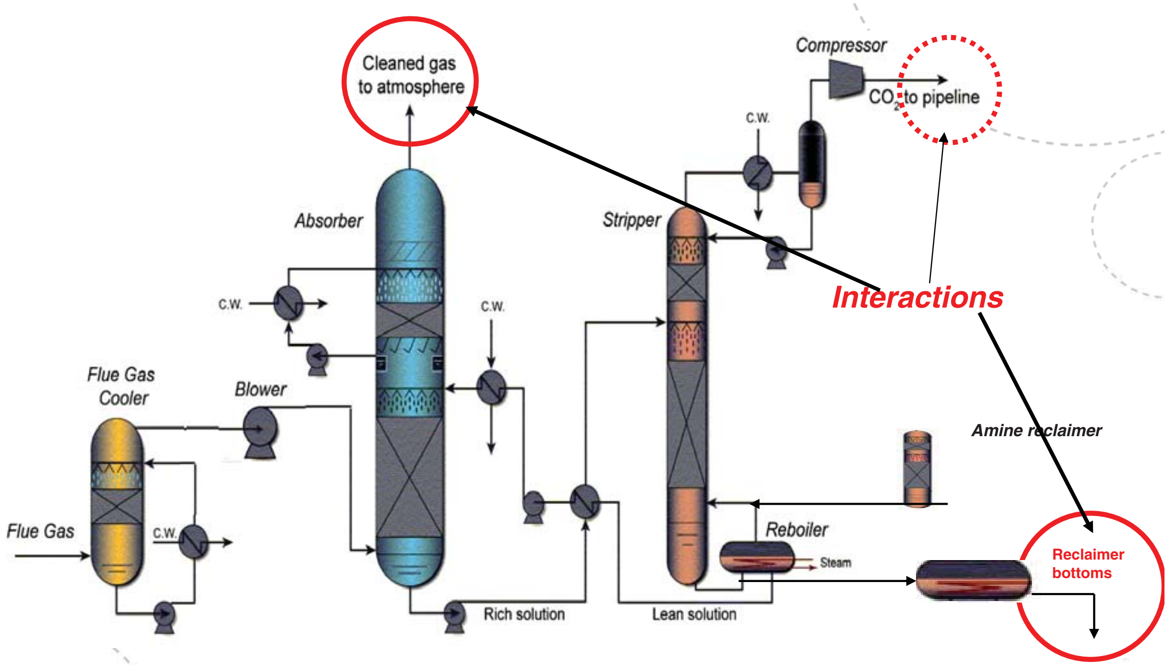
- Possible mass transfer resistance in the membrane
- Liquid is bound to laminar flow (can be improved)

Challenges

- High requirements of thermal and electrical energy
- Costly process and large space requirements
- Production of waste products
- Possible emissions of volatile amines and degradation products

Degradation

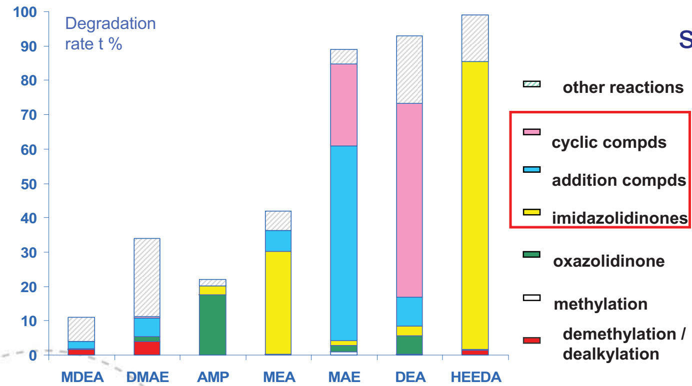
Process interaction with surroundings



Absorbent degradation process conditions.

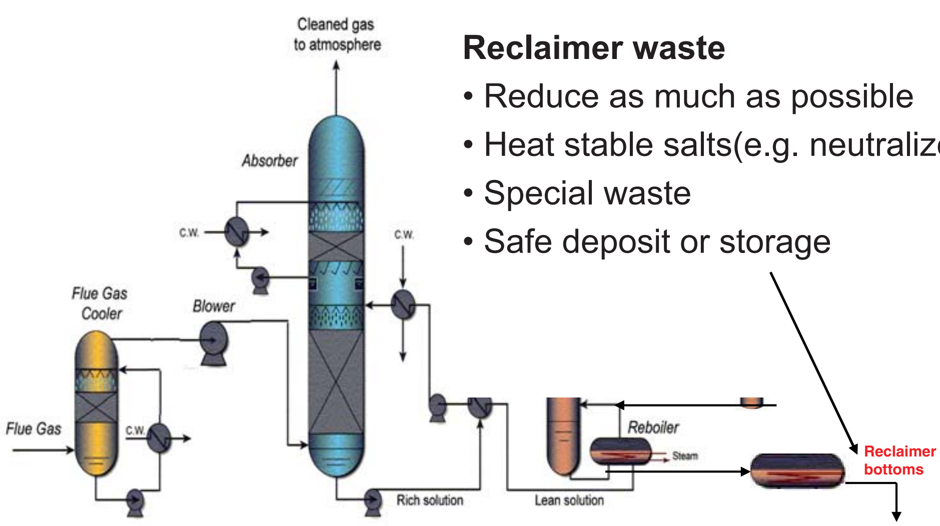
All absorbent degrade. The degradation products vary with:
Type of absorbent,
Process conditions, temperature, O_2 and CO_2 levels

Degradation products are
- Volatile (Ammonia, aldehydes etc.
- Low volatility(Volatility lower than Ethanolamine(MEA))
- Non-volatile(Typically heat stable salts, organic acids, etc.)



Non-volatile degradation products

Reclaimer waste
- Reduce as much as possible
- Heat stable salts(e.g. neutralized acids)
- Special waste
- Safe deposit or storage

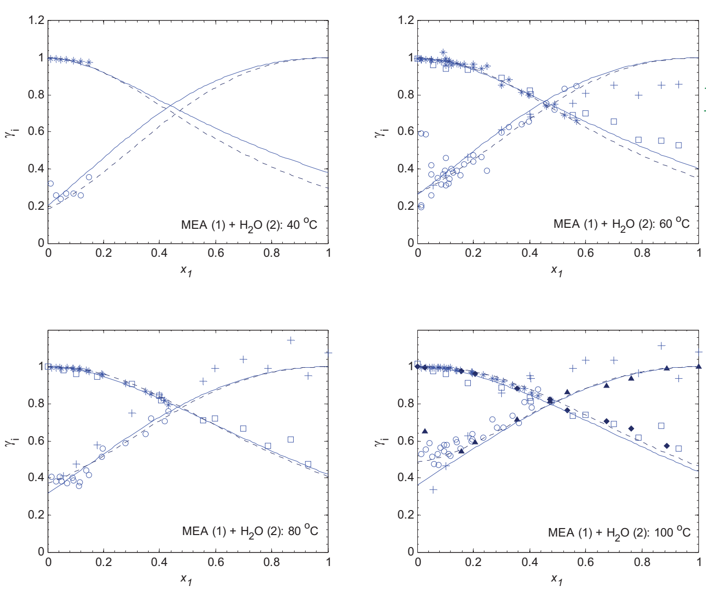


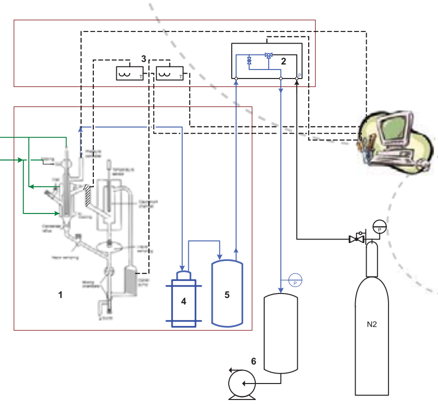
Challenges

- High requirements of thermal and electrical energy
- Costly process and large space requirements
- Production of waste products
- Possible emissions of volatile amines and degradation products

Volatility

Experimental activity coefficients of MEA and H_2O at 40, 60, 80, and 100 °C





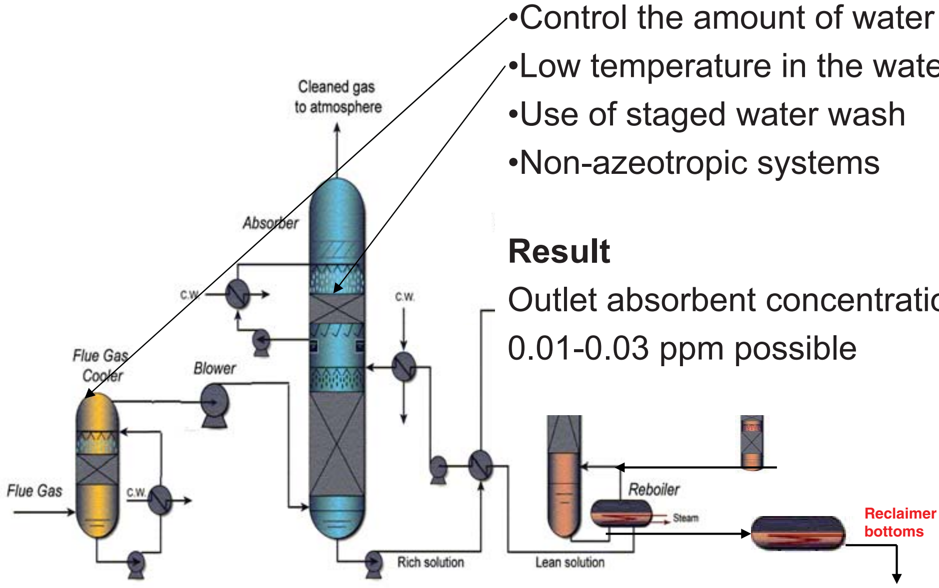
○ /*, Kim(2009) at 40, 60, 80 and 100 °C,

+/□, Nath and Bender (1983) at 60, 78 and 92 °C;

▲/♦, Tochigi et al. (1999) at 90 °C.

Lines: —, Wilson; ---, NRTL

Water wash to reduce absorbent losses



Important features

- Control the amount of water in inlet flue gas
- Low temperature in the water wash section
- Use of staged water wash
- Non-azeotropic systems

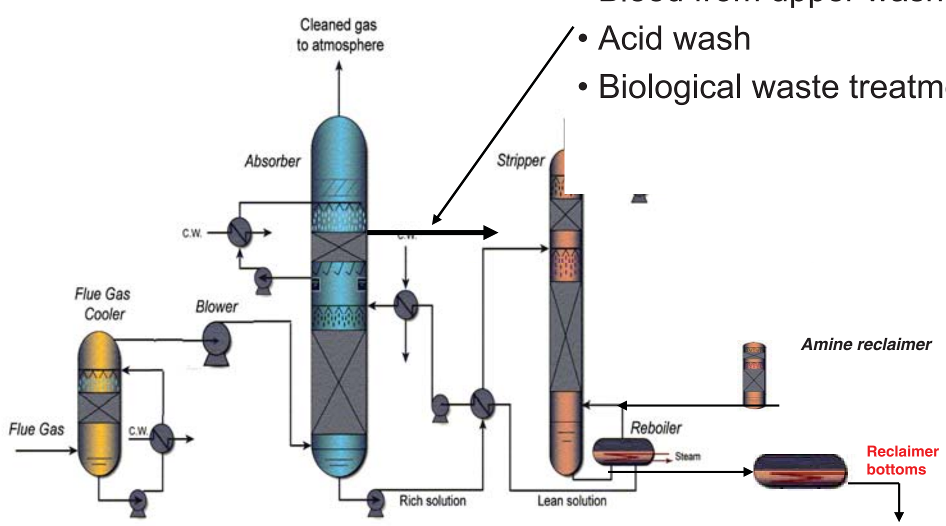
Result

Outlet absorbent concentrations below 0.01-0.03 ppm possible

Outlet for volatile degradation products

Possibilities

- Bleed from upper wash stages
- Acid wash
- Biological waste treatment



Ecotoxicity and bio-degradability(1)

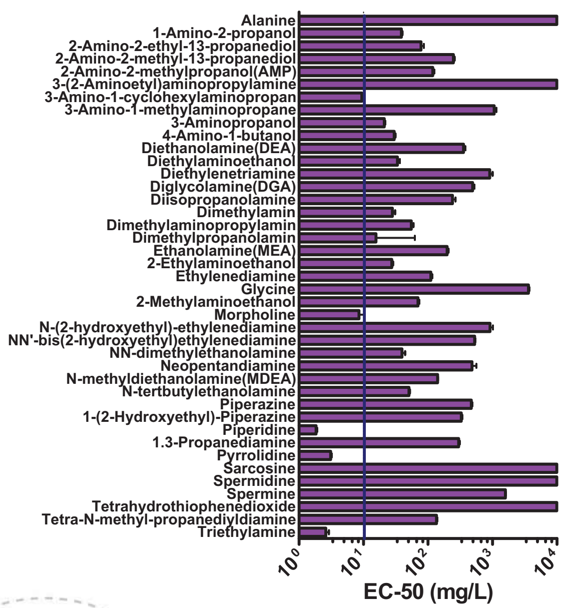
Norwegian offshore oil industry Categorization of chemicals

Category	*Criteria – Ecotoxicity tests*	*Actions*
Black	•Priority list (Stortingsmelding Nr. 25) •OSPAR List of Chemicals for Priority Action •Both low biodegradability and high bioaccumulation (BOD28 < 20 %, and Log $P_{OW} \geq 5$) •Low biodegradability and toxic (BOD28 < 20 %, and EC50 or LC50 ≤ 10 mg/L) •Compounds expected to be carcinogenic/mutagenic or harmful to reproduction	Not discharged
Red	•Inorganic chemicals with high toxicity (EC50 or LC50 ≤ 1 mg/L) •Organic chemicals with low biodegradability (BOD28 < 20 %) •Organic chemicals or mixtures which meet 2 of the 3 following criteria: Biodegradability < 60 %, bioaccumulation potential (Log $P_{OW} \geq 5$), or toxicity of EC50 or LC50 ≤ 10 mg/L	Phased out or replaced
Yellow	•Include compounds which based on their characteristics are not defined as RED or BLACK, and •NOT included in the PLONOR list	Accepted
Green	•Chemicals expected to have NO environmental effects •PLONOR list	Testing not required

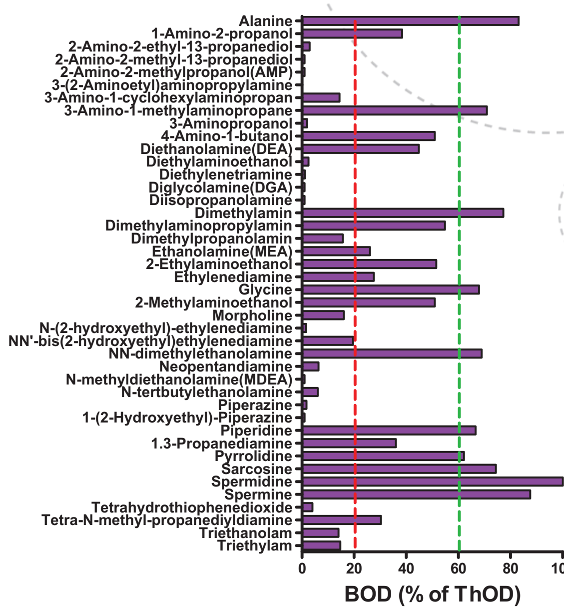
Ecotoxicity and bio-degradability(2)

Assessment of solvents

Ecotoxicity



Biodegradability



Environmental status

- Environmentally benign solvents are available
- Emissions of absorbent(amines) can be brought down to less than 0.01-0.03 ppm
- Volatile degradation products can be handeled by acid wash and biological treatment
- Methods for reducing degradation and corrosion rates are continuously being developed
- The final special waste must be safely deposited
- Alternative uses for this waste are being studied

Summing up

Energy considerations

- Significant variations in equilibrium
- Close approach to equilibrium
- High temperature sensitivity is positive
- Phase change solvents promising
- Run desorber at elevated pressure

Mass transfer

Fast reactions
Watch solubility and viscosity

Volatility

Can be controlled at a cost

Degradation, biodegradation and ecotoxicity

Complex mechanisms
Some trends visible
Some similarities between process and bio-degradation
Toxicity normally not a problem

Thank you