

# INTERACTION BETWEEN PROCESS ARCHITECTURE AND SOLVENT PROPERTIES FOR AMINE-BASED CO<sub>2</sub> CAPTURE

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# CONTEXT & OBJECTIVE

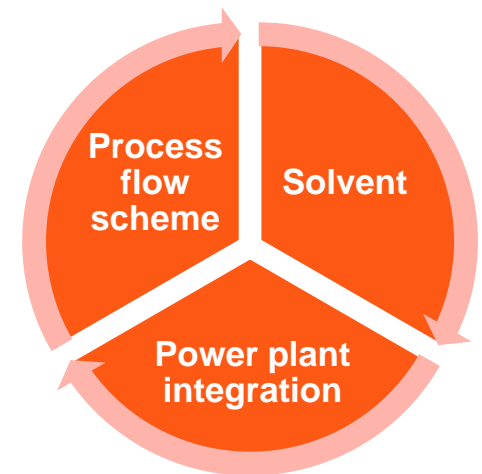
**A challenge for post-combustion CO<sub>2</sub> capture :**  
reduce both energy penalty and cost of avoided CO<sub>2</sub>

## ■ Literature focus individually on

- Solvent development and characterization
- Modifications of the process flow scheme
- Heat integration with power plant

## ■ In this study

- The three aspects are considered together
- An automatic methodology is developed, based on
  - Rigorous calculation of process performance
  - Use of an non-linear optimization algorithm, with LCOE as objective function
  - Simultaneous optimization of design and operating parameters



# TYPE OF AMINE SOLVENTS

## ■ Type of solvent according to physicochemical properties

- Reaction kinetic
- Heat of absorption
- Resistance to degradation
- Cyclic capacity
- Transport properties
- Environmental aspects
- ....

### KEY MESSAGE

Process performance strongly depends on the specific physicochemical properties of the solvent

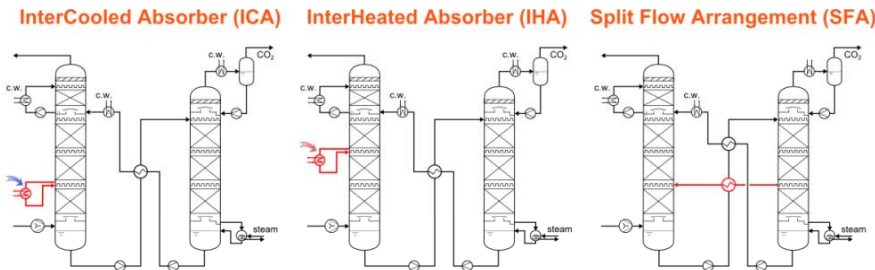
### Example of popular solvents and approximate values of most influent properties for a standard process

Solvent	MEA 30 wt%	AMP 30 wt%	MDEA 30 wt%	AMP+PZ 15+15 wt%	MDEA+PZ 15+15 wt%
Kinetic constant, $\log(k_{App}) [s^{-1}]$	4.6	3.3	1.3	5.1	5.1
Heat of absorption $\Delta_{abs}H [kJ.mol^{-1}]$	80-85	50-90	45-60	60-90	60-80
Cyclic capacity $\Delta\alpha [mol_{CO_2}.mol_{Am}^{-1}]$	0.25	0.5	0.2	0.4	0.35
Thermal degradation at 140°C [% per week]	5.3	0	1.7	0 + 0.25	1.7 + 0.25

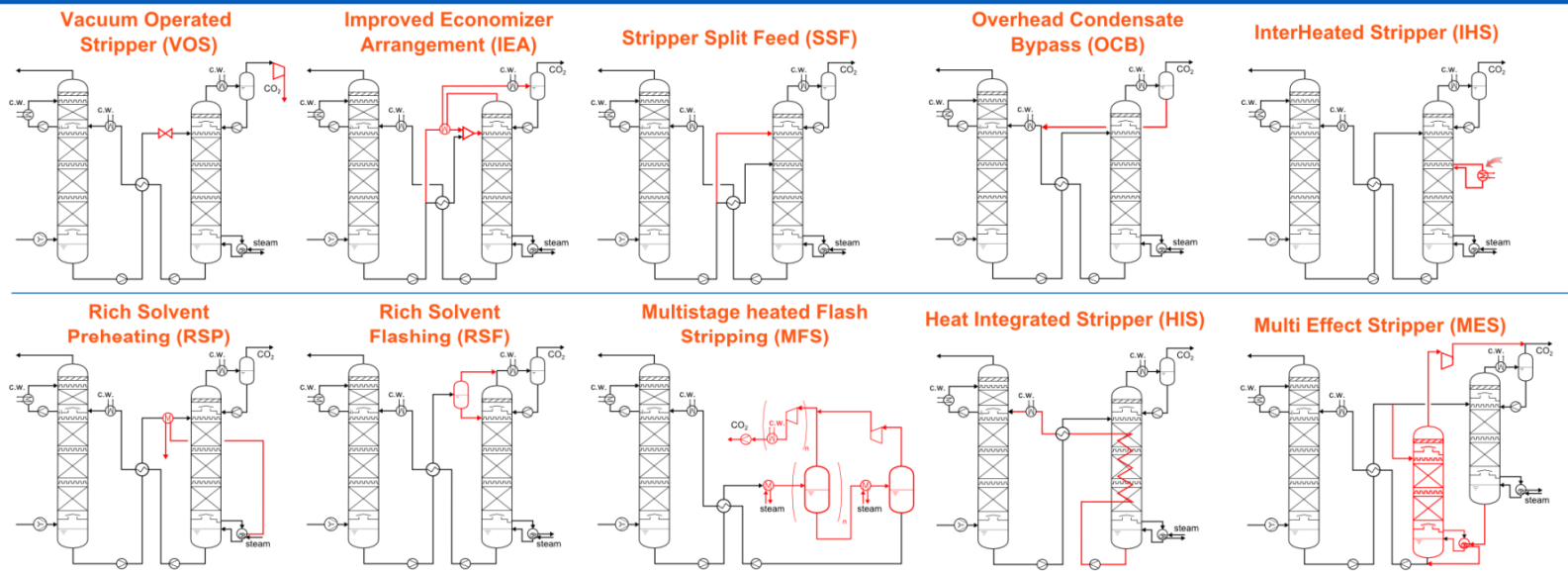
Data from Dubois et Thomas (2012), Lepaumier (2008), Aronu et al. (2011), Chen et al. (2011), Dash et al. (2012)

# OVERVIEW OF SINGLE PROCESS MODIFICATIONS

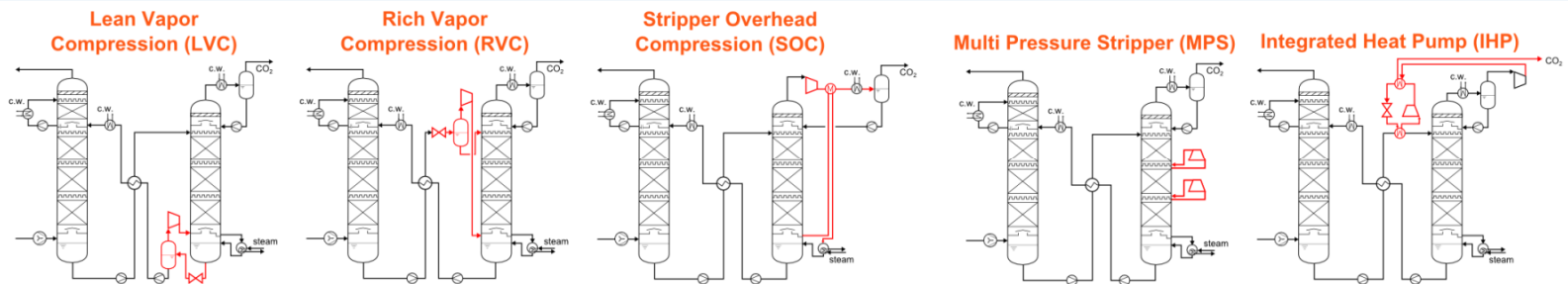
## Absorption enhancement



## Heat integration



## Heat pumps



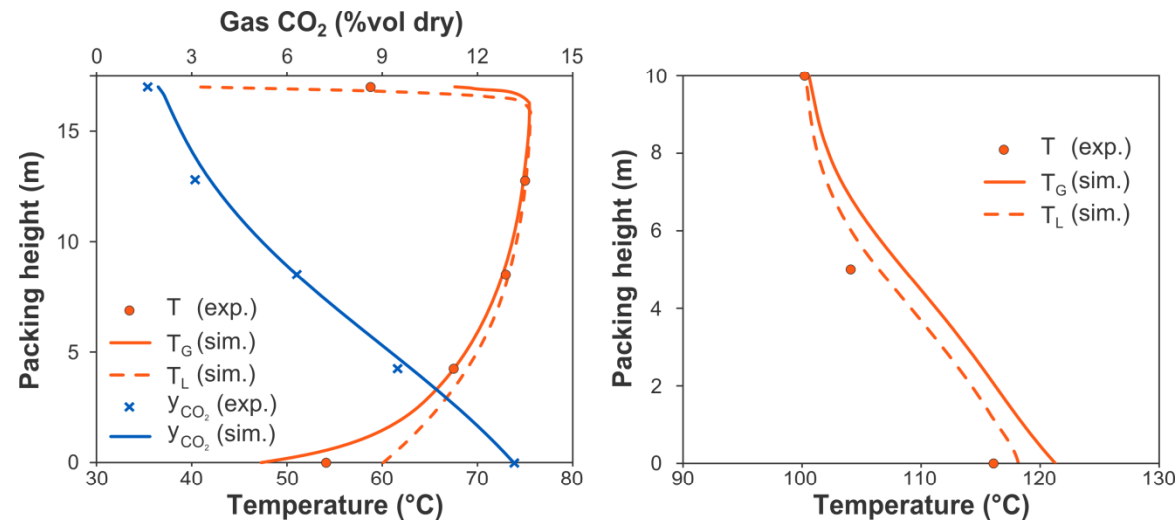
# METHODOLOGY USED FOR PROCESS EVALUATION

## ■ Phenomenological modeling<sup>1</sup>

- In-house simulation and optimization tool (in Fortran)
  - e-UNIQUAC model for electrolyte solutions
  - Rate-based formulation for heat & mass transfer
  - Chemical enhancement in liquid film
- Absorption & stripping models validated against literature data (Esbjerg and NTNU pilot plants)

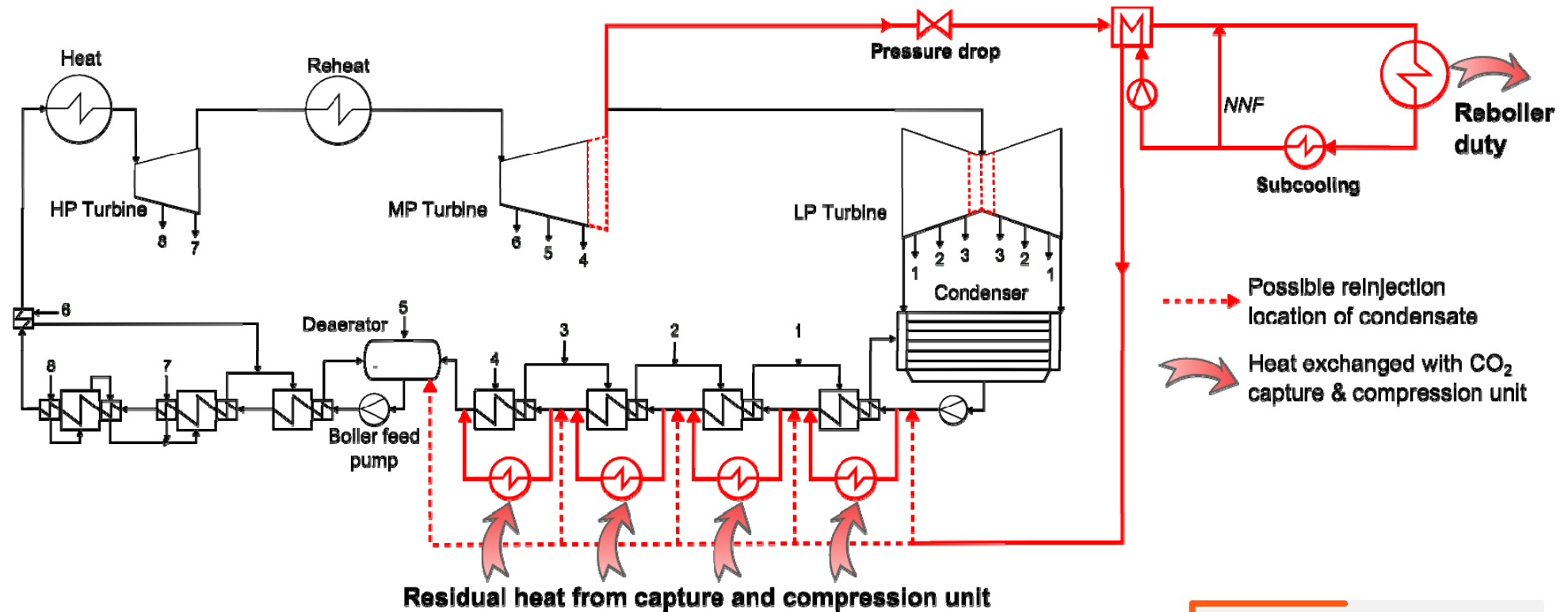
## ■ Evaluation of energy penalty

- Total equivalent work (kWh/t<sub>CO2</sub>), including
  - **Parasitic load** (reboiler duty + vapor quality)
  - **CO<sub>2</sub> compression work** up to 110 bars
  - **Auxiliary work** of capture unit (e.g. pumps, fans, additional compressor)
  - **Heat integration** between power plant and capture unit
- Derivation of new correlations



Validation of absorber (left) and stripper (right) packing model on Esbjerg pilot data

# THERMAL INTEGRATION WITH POWER PLANT



## Integration strategy between capture unit and power plant

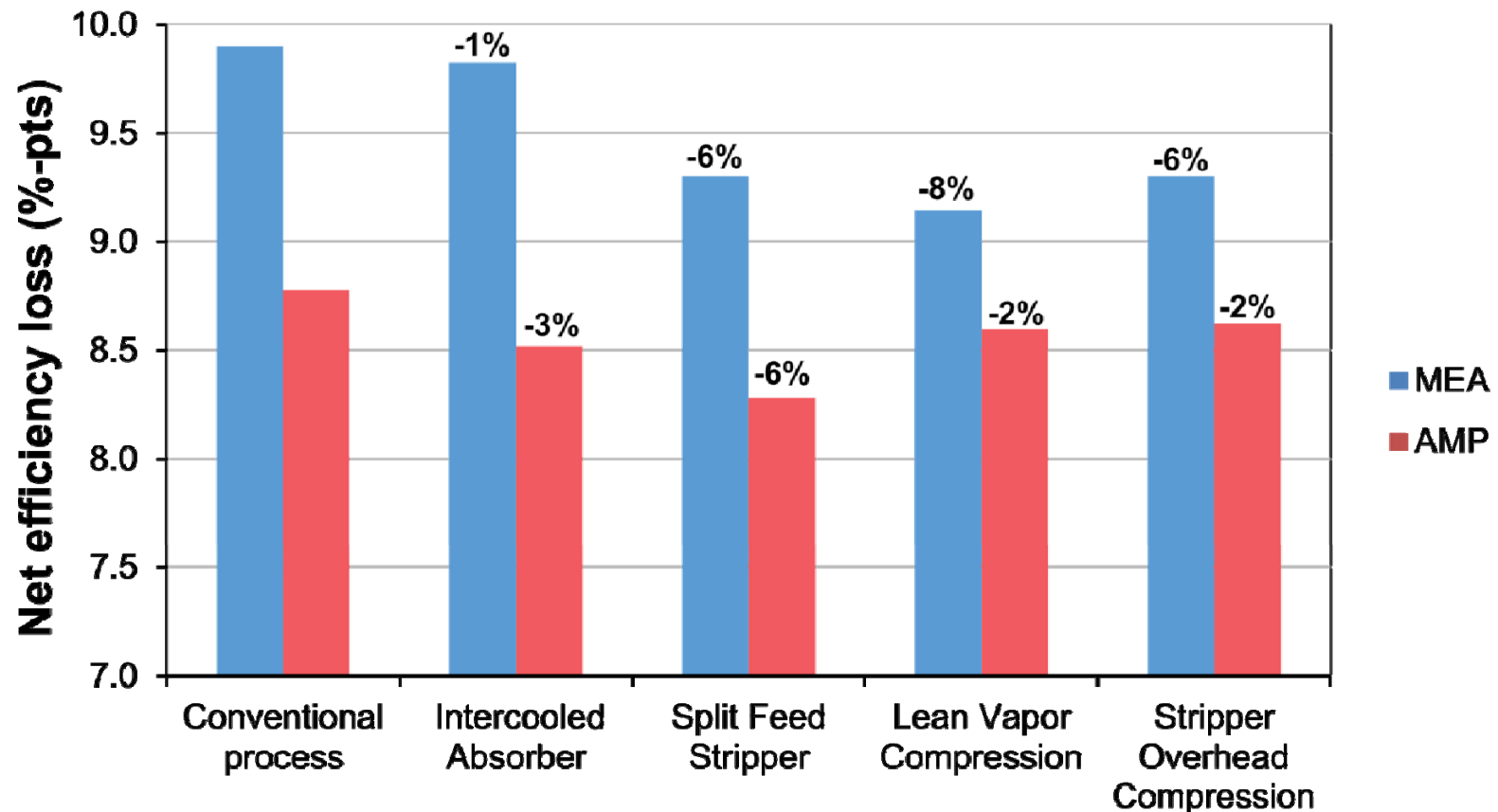
- Steam extraction at the required pressure level
- Steam desuperheating with the reboiler condensate
- Reinjection in the feedwater preheaters at the proper temperature level
- Subcooling of reboiler condensate possible (for some particular capture processes)
- Residual heat of capture and compression unit **integrated into feedwater preheaters**

An **advanced integration strategy** for new-built power plants

# ENERGETIC SIMULATION RESULTS FOR MEA & AMP

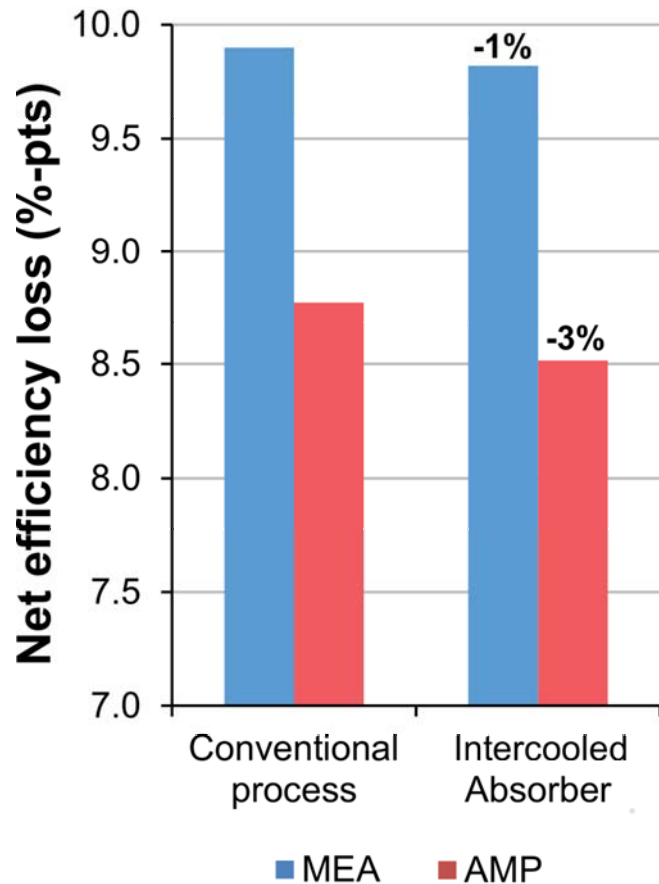
## ■ Conventional process + 4 process modifications evaluated for 30wt% MEA & 40wt% AMP solutions

- Process equipment designed with chemical engineering heuristics
- Operating parameters optimized with respect to energy penalty with a dedicated algorithm (fixed design)



Energetic simulation results of five flow schemes (percentages are reductions with respect to conventional process)

# COMMENTS ON LIMITING PHENOMENA



## ■ MEA to AMP shift

- Lower heat of absorption
- Higher cyclic capacity → sensible heat reduced
- But higher absorber required

## ■ Absorption enhancement

- Absorber intercooler favor driving force
- More efficient for AMP (3% reduction) than for MEA (1%)
- Efficient for thermodynamic-driven mass transfer



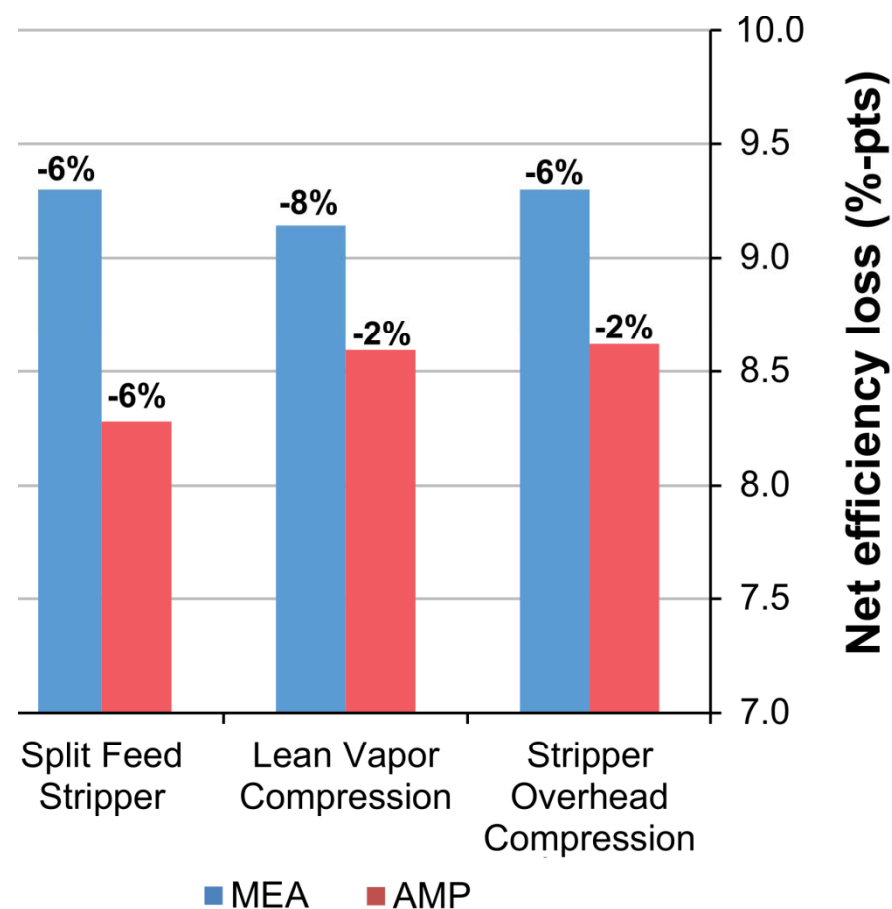
# COMMENTS ON LIMITING PHENOMENA

## ■ Heat integration (Split Feed Stripper)

- Improve heat exchange in economizer
- pre-condensate steam in stripper top
- Generic enhancement, efficient for both amine (6%)

## ■ Heat pump effect (Lean Vapor Compression & Stripper Overhead Compression)

- Rise heat quality through mechanical work
- Generate steam to provide part of reboiler duty
- More efficient for MEA (6-8%) than for AMP (2%)
- Efficient for high heat of absorption solvents



# NEED FOR A SYSTEMATIC OPTIMIZATION

## ■ Limitations of energetic approach

- Only production loss is evaluated
- No consideration of additional CAPEX
- No consideration of other OPEX (e.g. solvent loss)

Need to consider both  
**CAPEX** and **OPEX**

→ **LCOE**

→ **Cost of avoided CO<sub>2</sub>**

## ■ A global technical-economic approach

- Numerous parameters → need for a systematic method
- **Simultaneous optimization of design and operating parameters**
- NLPQLP<sup>1</sup> method used for non-linear optimization

## ■ Technical-economic assumptions for cost estimation<sup>2</sup>

- Supercritical pulverized coal
  - Simulated with recommendations from EBTF
  - Equipped with SCR, ESP and FGD
  - 46.1 %<sub>LHV</sub>, 1082 MW<sub>gross</sub>, 975 MW<sub>net</sub>, 755 t<sub>CO2</sub>/h
- 90% CO<sub>2</sub> capture, amine post-combustion
- LCOE evaluated in constant €<sub>2011</sub>
- Nth-of-a-kind plant, 40 years lifetime
- 7600 operation hours per year
- 8% discount rate, no inflation
- Fuel price = 10 €/MWh<sub>LHV</sub>
- TOC = 1.9 x Installed Cost
- Contingencies = 10% x EPC
- No transport and storage cost considered

<sup>1</sup> Dai et Schittkowski, 2008. *Pacific Journal of Optimization*, 4:335–351,

<sup>2</sup> In compliance with Rubin et al., 2013. *Int. J. Greenh. Gas Con.*, 17:488-503

# OPTIMAL DESIGN OF A CONVENTIONAL PROCESS

## ■ Design parameters

	Original	Optimized	
▪ Absorber height ( $Z_{\text{abs}}$ )	15 m	→ 20.0 m	→ allow to maximize rich loading
▪ Stripper height ( $Z_{\text{strip}}$ )	10 m	→ 16.2 m	→ higher to provide pre-condensate area due to relatively cold rich solvent inlet (cf. economizer)
▪ Economizer pinch ( $\Delta T_{\text{eco}}$ )	10 K	→ 28.1 K	→ reduce eco. CAPEX & provide colder rich solvent
▪ Reboiler pinch ( $\Delta T_{\text{reb}}$ )	10 K	→ 5.7 K	→ trade-off CAPEX/OPEX favorable to OPEX
▪ Condenser pinch ( $\Delta T_{\text{cond}}$ )	10 K	→ 5.0 K	→ trade-off CAPEX/OPEX favorable to OPEX

## ■ Operating parameters

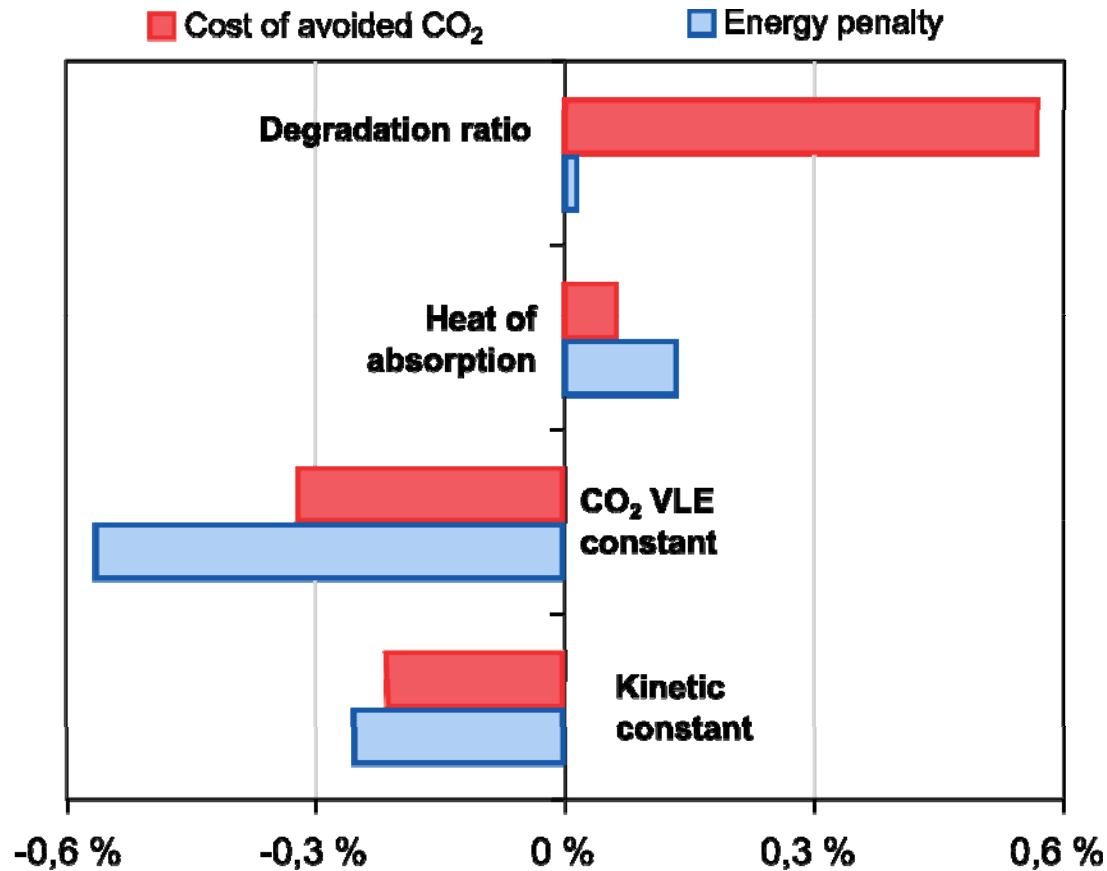
▪ Lean loading ratio ( $\alpha_{\text{lean}}$ )	0.24	→ 0.20	→ lower solvent flow rate, reducing equipment sizes
▪ Reboiler pressure ( $P_{\text{reb}}$ )	2.1 bar	→ 2.1 bar	→ limitation due to solvent degradation

■ Energy penalty	9.9 %-pts	→ 8.5 %-pts
Cost of avoided CO <sub>2</sub>	100 %	→ 91 %

## ■ Optimal design parameters are quite “unusual”

- Mainly due to power plant integration → favor cold rich solvent at stripper top
- Substantial **energy gain 1.4 %-pts** and reduction of cost of avoided CO<sub>2</sub> of **9 %**

# SENSITIVITY TO SOLVENT PROPERTIES



Influence of a 10% change of MEA properties  
on energy penalty and cost of avoided CO<sub>2</sub>

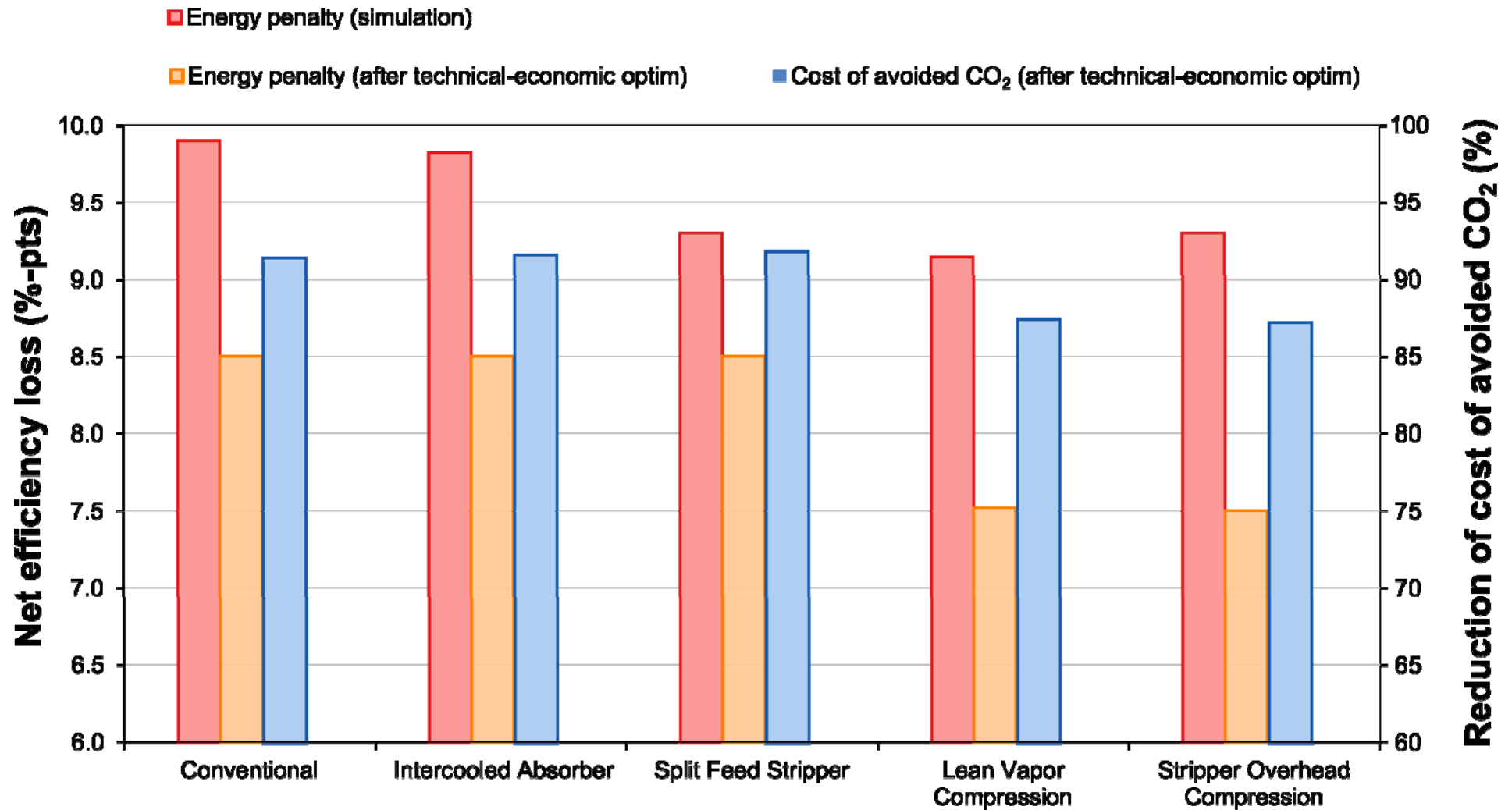
## MOST SENSITIVE PARAMETERS

**Degradation ratio**  
for cost of avoided CO<sub>2</sub>

**CO<sub>2</sub> solubility**  
for energy penalty



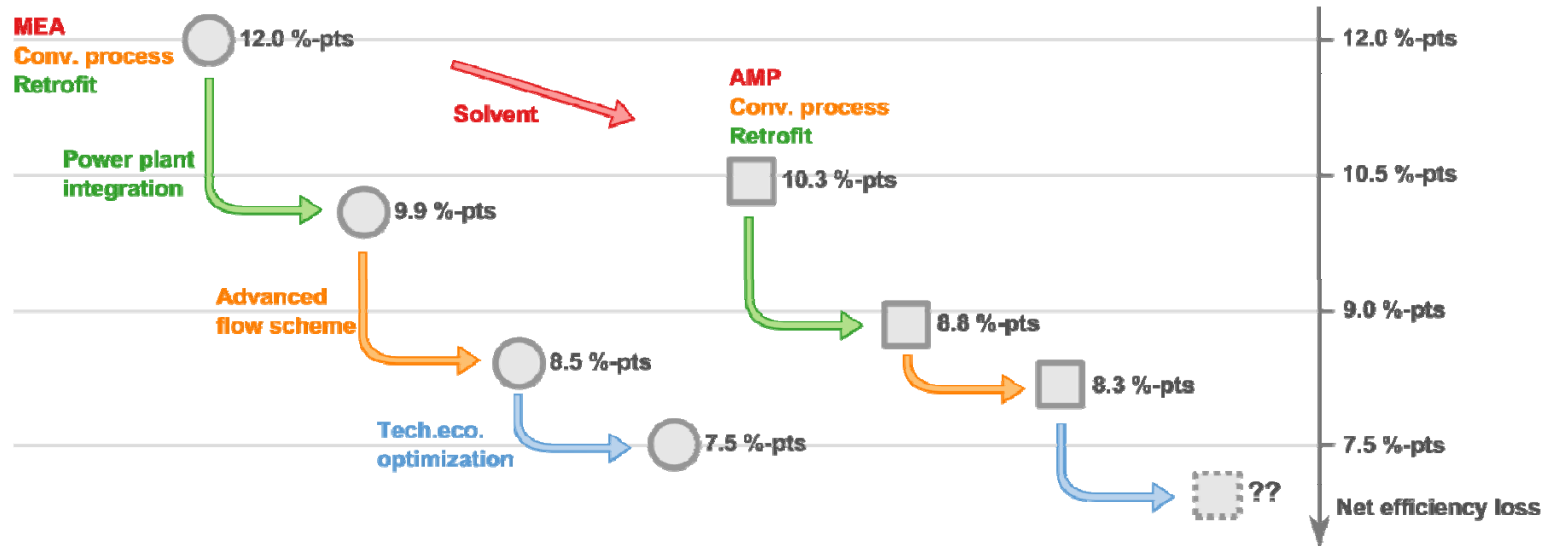
# OPTIMIZATION RESULTS FOR MEA



# SYNTHESIS

## ■ Three ways of performance improvement : Solvent | Power plant integration | Process flow scheme

→ Need to consider all aspects in order to evaluate the potential of a solution



## ■ Perspectives

- Implement other fully characterized solvents
- Evaluate **advanced architecture** by coupling process modifications with **synergetic effects**

## A RELEVANT APPROACH

- **Technical-economic analysis**
  - Coupled with a **systematic optimization** algorithm
  - Simultaneous resolution of **design** and **operating** parameters

# THANK YOU FOR YOUR ATTENTION !

## Any questions?

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