DEVELOPMENT OF NEW SOLVENTS FOR CO_2 CAPTURE USING MOLECULAR SIMULATIONS

C&EN WEBINAR

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MARCH 23, 2021

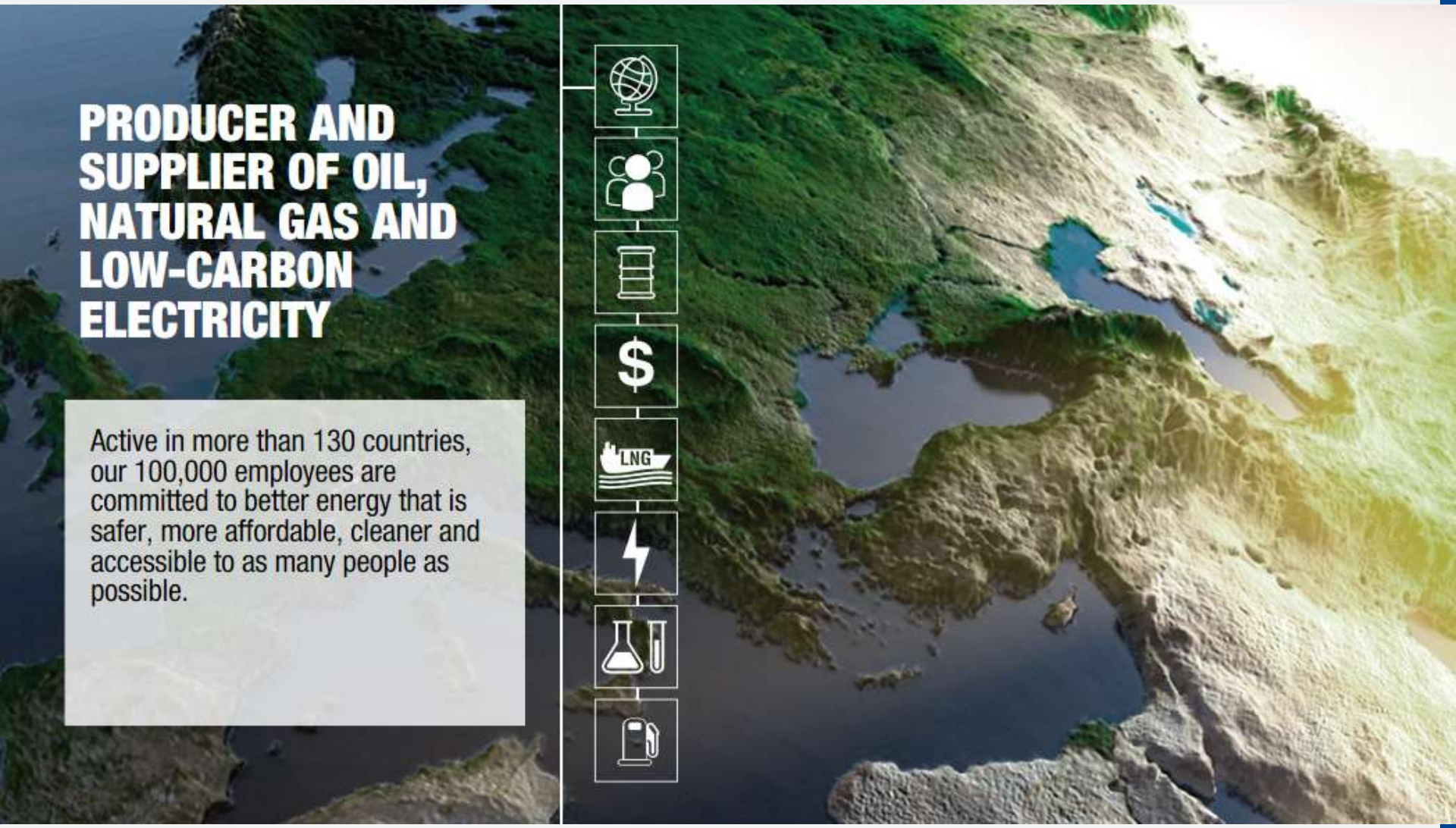
OUTLINE

TOTAL AND CCUS

MOLECULAR SIMULATIONS IN SOLVENT DEVELOPMENT

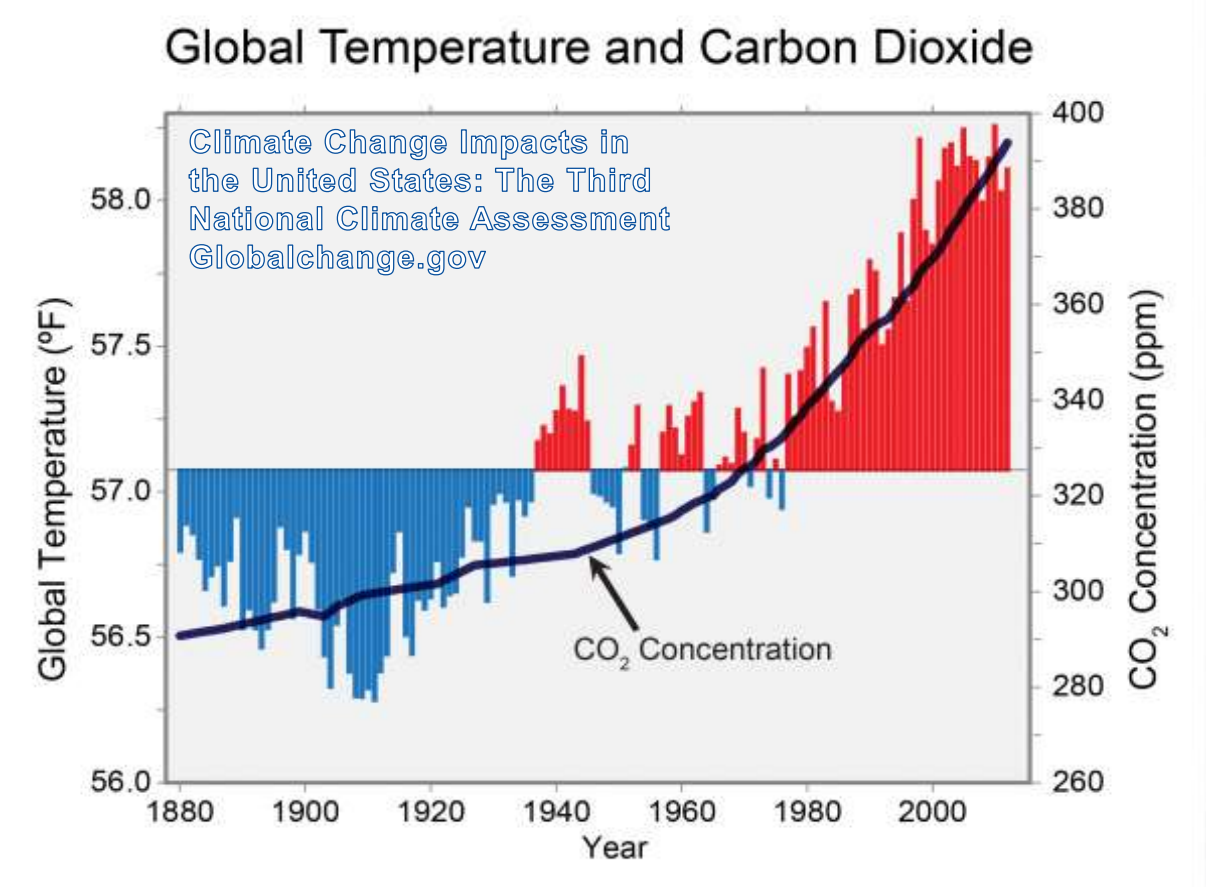
WAY FORWARD & CONCLUSIONS


TOTAL,
A MAJOR
ENERGY
PLAYER


PRODUCER AND SUPPLIER OF OIL, NATURAL GAS AND LOW-CARBON ELECTRICITY
Active in more than 130 countries, our 100,000 employees are committed to better energy that is safer, more affordable, cleaner and accessible to as many people as possible.
$
LNG


OUR
AMBITION?
TO BECOME
THE RESPONSIBLE
ENERGY MAJOR

FAST CHANGING ENVIRONMENT CLIMATE CHALLENGE



FAST CHANGING ENVIRONMENT ACCEPTABILITY CHALLENGE

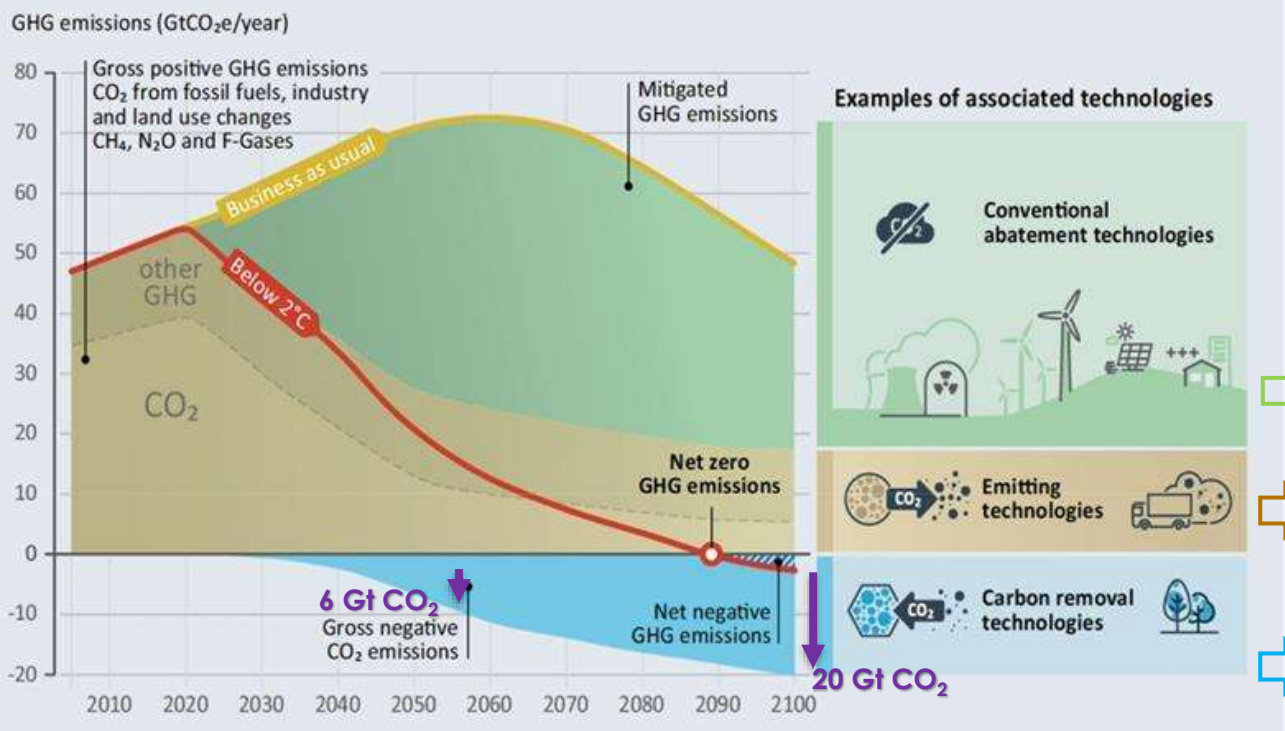
GETTING TO NET ZERO

Total shares the ambition to get to Net Zero by 2050 together with society for its global business

3 major steps to get Total to Net Zero

1	Net Zero on Operations by 2050 or sooner
2	**Net Zero in Europe by 2050 or sooner** (operations and products)
3	**60% or more Net Carbon Intensity reduction by 2050** (operations and products): **less than 27.5 gCO2e/MJ**

THE ROLE OF CO_2 REMOVAL IN CLIMATE CHANGE MITIGATION

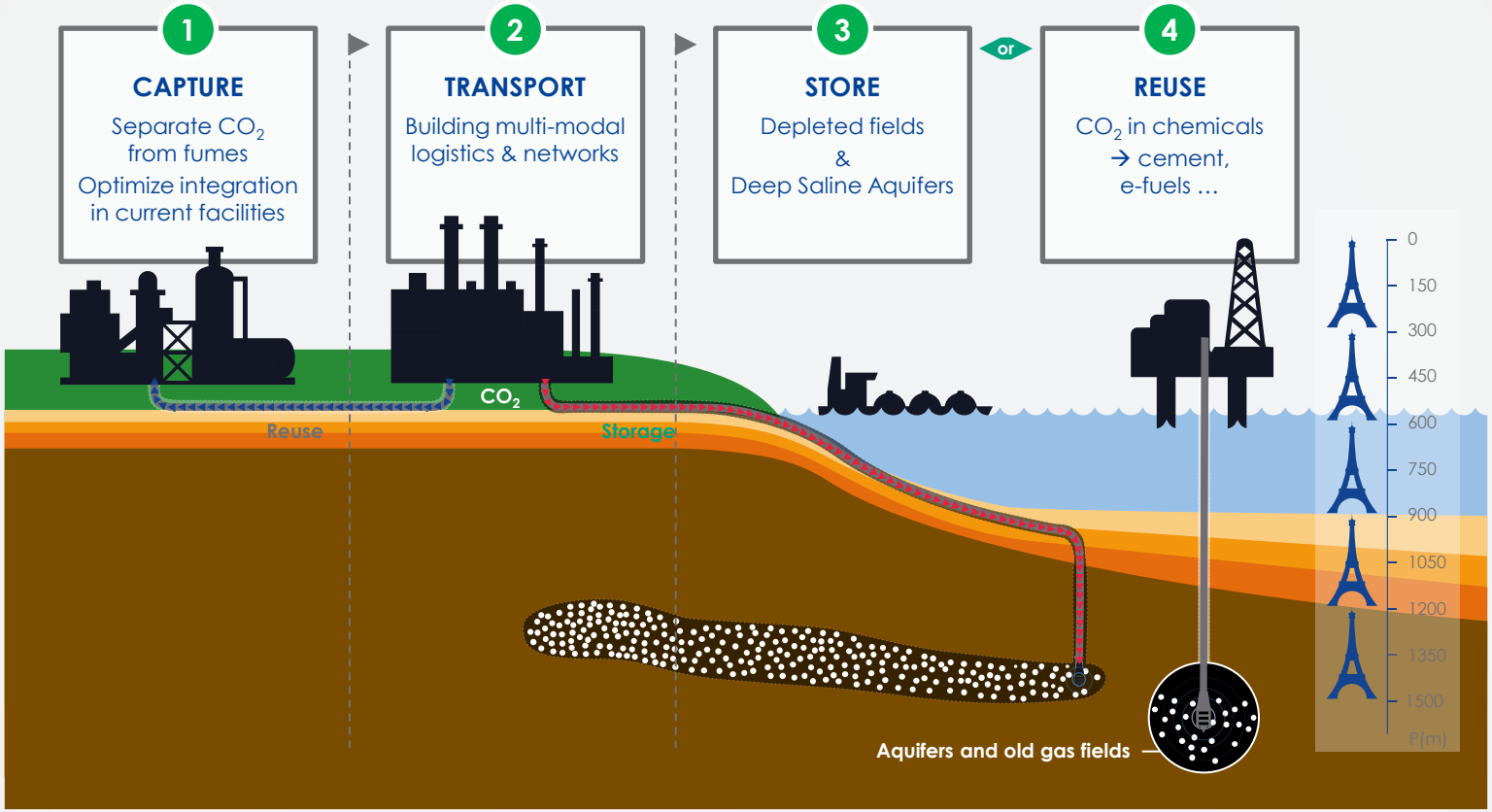


- Mitigated emissions **Including CCUS**
- Residual emissions difficult or too expensive to avoid
- To achieve Net Zero ➔ need Negative Emissions Technologies (NETs)

Carbon Dioxide Removal is required to reach Net Zero Emissions

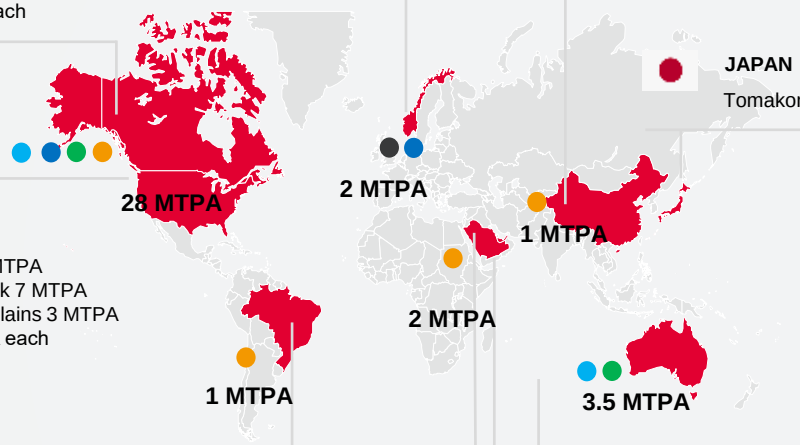
Source: The Emissions Gap Report 2017. United Nations Environment Program (UNEP 2017)

CCUS: MANAGING CARBON VIA A COMPLEX CHAIN



25 CCUS PROJECTS IN OPERATION WORLDWIDE

SOURCE: GLOBAL CCS INSTITUTE (NOVEMBER 2019) + TOTAL R&D



NORWAY 1.7 MTPA
2 projects ≤ 1MTPA each

CANADA 2.8 MTPA
6 projects ≤ 1MTPA each

USA 23 MTPA
Oxy - Century Plant 8.4 MTPA
ExxonMobil – Shute Creek 7 MTPA
Dakota Gas Cy – Great Plains 3 MTPA
6 other projects ≤ 1MTPA each

BRAZIL 1 MTPA
Lula oil field

SAUDI ARABIA 0.8 MTPA
Ghawar field

CHINA 0.8 MTPA
2 projects ≤ 1MTPA each

JAPAN 0.1 MTPA
Tomakomai project

AUSTRALIA 3.5 MTPA
Chevron - Gorgon 3.5 MTPA

UAE 0.8 MTPA
Al Reyadah

35 MTPA @ present

operated by

24% Oxy
19% Exxon
10% Chevron
5% Equinor
3% Petrobras
3% Shell

Only 4 projects ≥ 1.5 MTPA each

79% USA + Canada

79% EOR (Enhanced Oil Recovery)

2030: x3 in volume

+60 MTPA in studies
>30 projects avge size 1.5 MTPA

At various stages of development

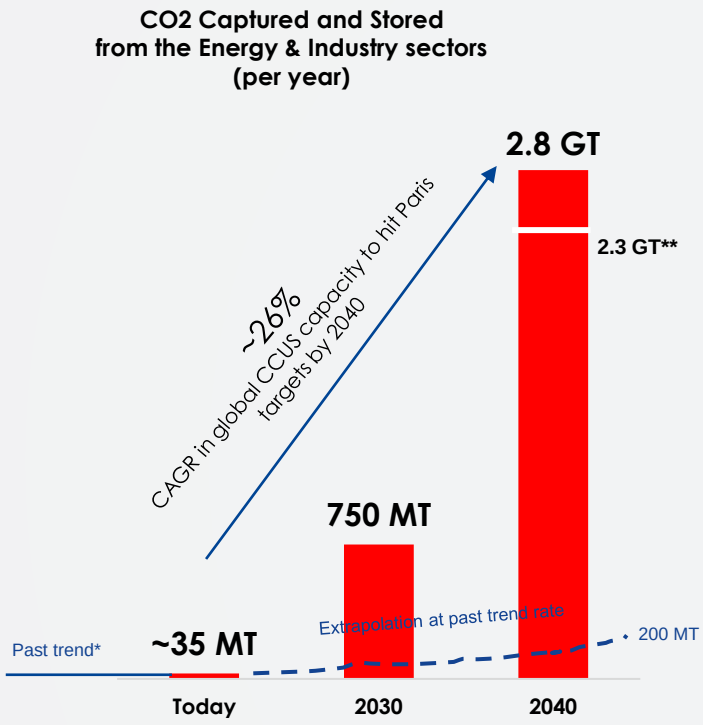
(inventory from Global CCS Institute)

EOR	19
Subsidies	9
Tax or emissions credit	9
Regulatory requirement	4
Carbon tax	2

2030: ~100 MTPA expected capacity (vs. 750 MTPA IEA SDS <2°C)

* Reported design CO_2 capacity

SCALING-UP CCUS



*Past trend including EOR

**CO2 captured and stored from fossil energies

IEA SDS scenario requires CCUS to grow

× 20 by 2030 (vs. × 25 solar PV in 2008/17)

× 80 by 2040 (vs. × 5 oil production in 1950/72)

Source: DG / STI / R&D / IST

1 Worldwide 750 MTPA in 2030 requires

1500 capture projects (0.5 MTPA each)

+ 150 storage projects (≥ 5 MTPA each)

Meaning a capital intensity of:

- 1 MTPA project ≈ 1 G€ investment (1000 €/ton)
- 750 MTPA projects over 10y → **75 G€/year investment**

2 EU vision 300 MTPA in 2050 requires

600 capture projects (0.5 MTPA each)

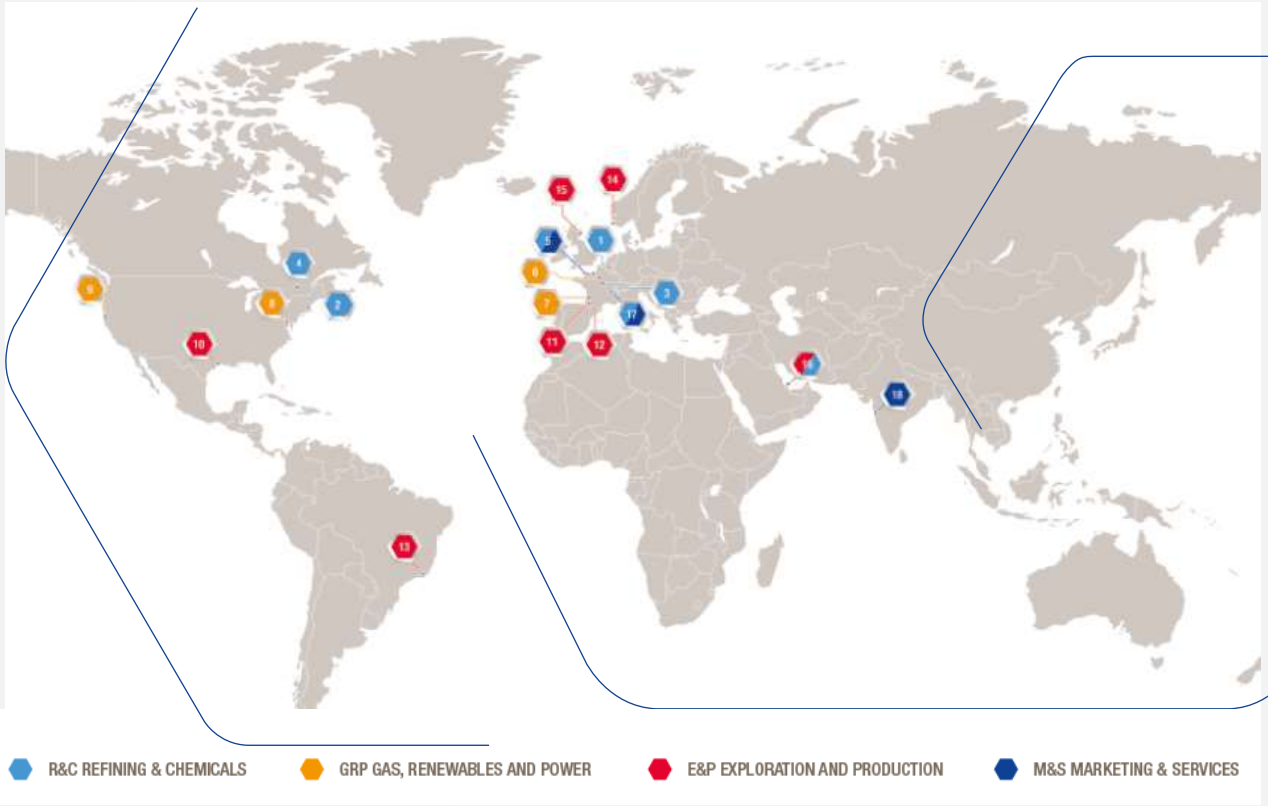
+ 60 storage projects (≥ 5 MTPA each)

Meaning a capital intensity of:

- 300 MTPA projects over 20y → **15 G€/year investment**

IEA SDS requires CCS growth @ solar rate and massive investment

TOTAL R&D WORLDWIDE AT A GLANCE



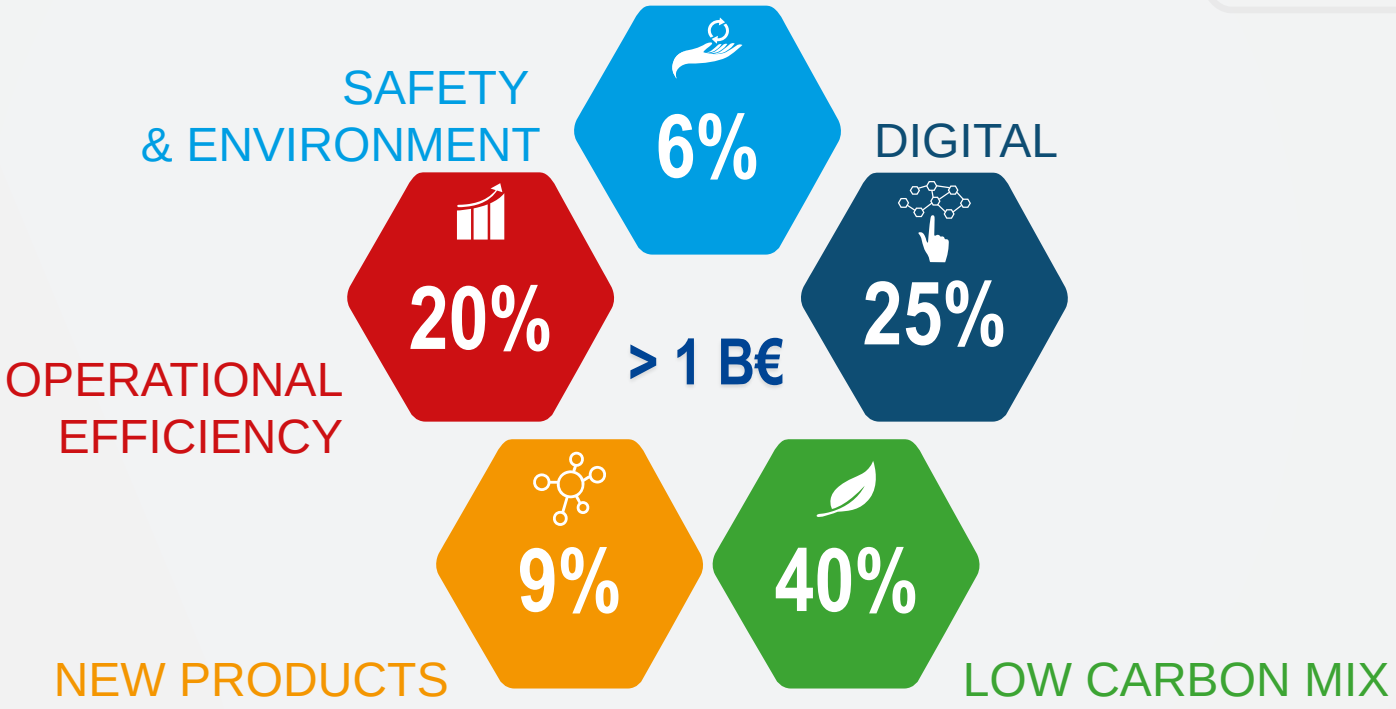
18
R&D centers, &Technological development centers

4300
researchers

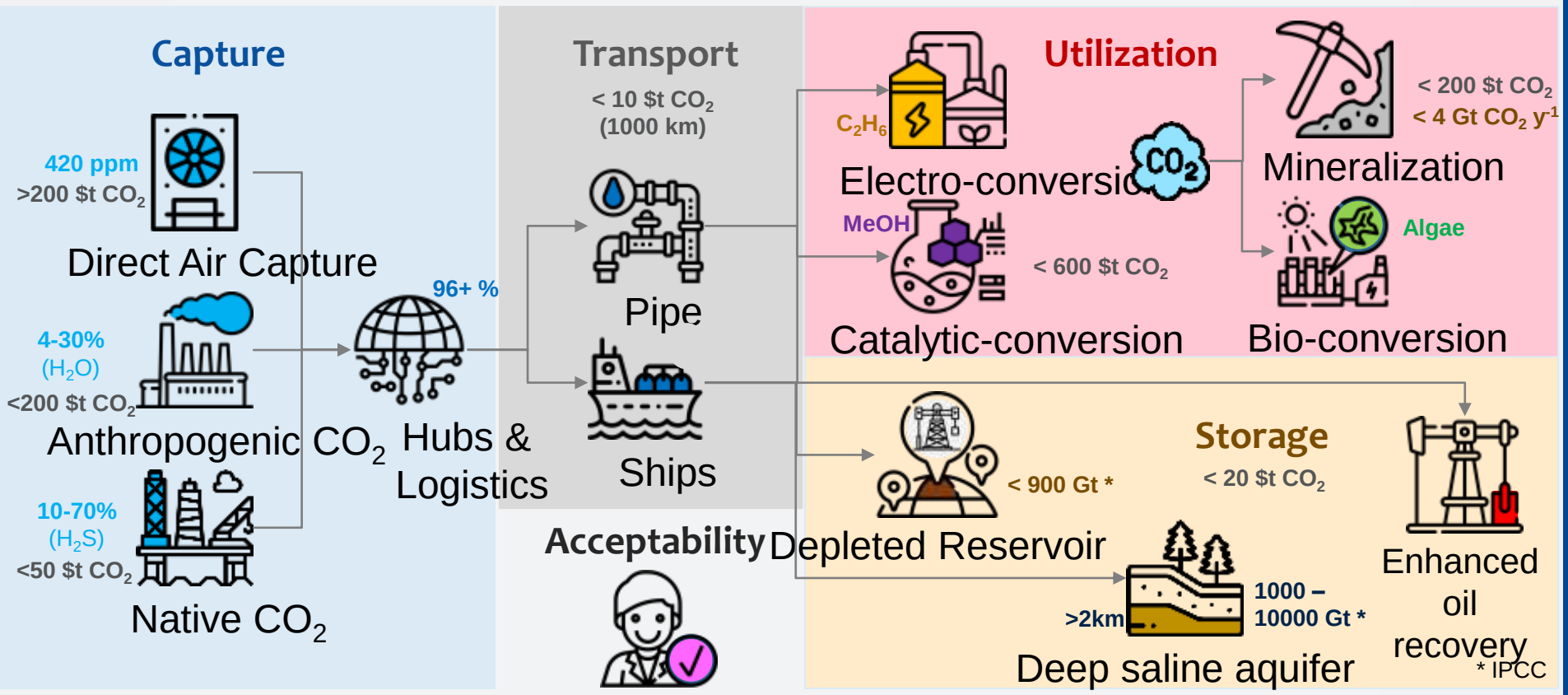
> 200
patents / year

300
PhDs & post doctorates

2020 INVESTMENTS FOR THE FUTURE BY FOCUS AREA



CCUS R&D @ TOTAL: A MULTIDISCIPLINARY APPROACH TO ASSESS THE COMPLEX CARBON MANAGEMENT CHAIN



INVESTING IN R&D TO LOWER COSTS OF CCUS

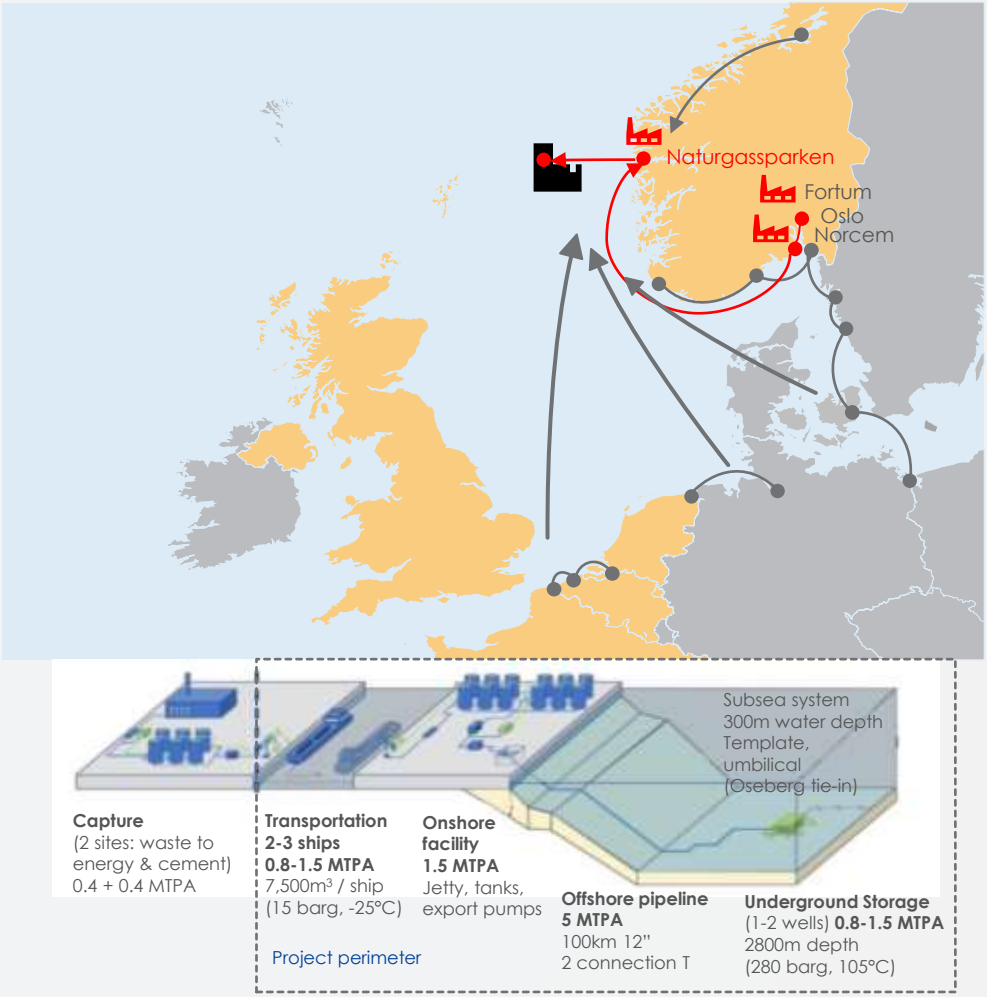
- **New materials for better energy efficiency on CCUS value chain**

- **Speed up research results from lab to industrial projects:**
  - **Research partnerships**
  - **Development projects with start ups**
  - Member of **CO_2 capture technology demonstration facilities:** National Carbon Capture Center (NCCC) in Alabama-US and Technology Center Mongstad (TCM) in Norway

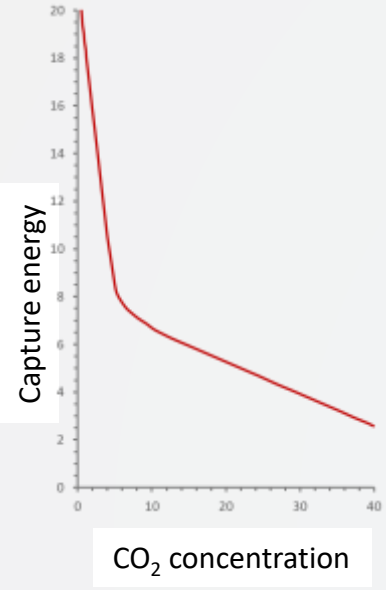
NORTHERN LIGHTS A FIRST OF A KIND.

- Norway & Total historic CCS partners since 1996

- **Northern Lights**
  - A country's ambition supported by the industry
  - Partners FID (0.8 G$) taken on 15 May 2020
  - Parliament/EU approval processes underway
  - A commercial ambition serving European Net Zero objectives
    - Industrial decarbonation
    - Creating negative emissions
    - Phase 1: ~0.7 $MtCO_2$/y capacity available for European emitters

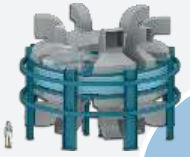


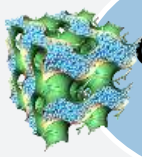
CARBON CAPTURE



% CO_2	Source
0.04	Air / DAC
4	**NGCC**
8-10	**FCC**, Waste to Energy
15-20	**SMR**, Steel, Cement, Coal
35	Biogas
1-70 at high pressure	**Native CO_2**

Cost, Footprint





Toolbox of solutions

- Amine scrubbing
- Other solvents : demixing green
- Adsorption : PSA, TSA
- Calcium looping
- Membranes
- MCFC
- Chemical looping (Cheers)
- Oxycombustion

Key hurdles to deployment

- Cost
- Energy
- Environmental impact / Emissions
- Source vs Solution
- Intensification
- Architecture / Integration

Scientific Challenges

- Solvent → *e.g.* green
- Sorbent → e.g. H_2O stable
- Contactor design → Flow, 3D printing
- Process vs Source
- Energy Integration
- Intensification
- RPB, rapid TSA

TOTAL AND CCUS

MOLECULAR SIMULATIONS IN SOLVENT DEVELOPMENT

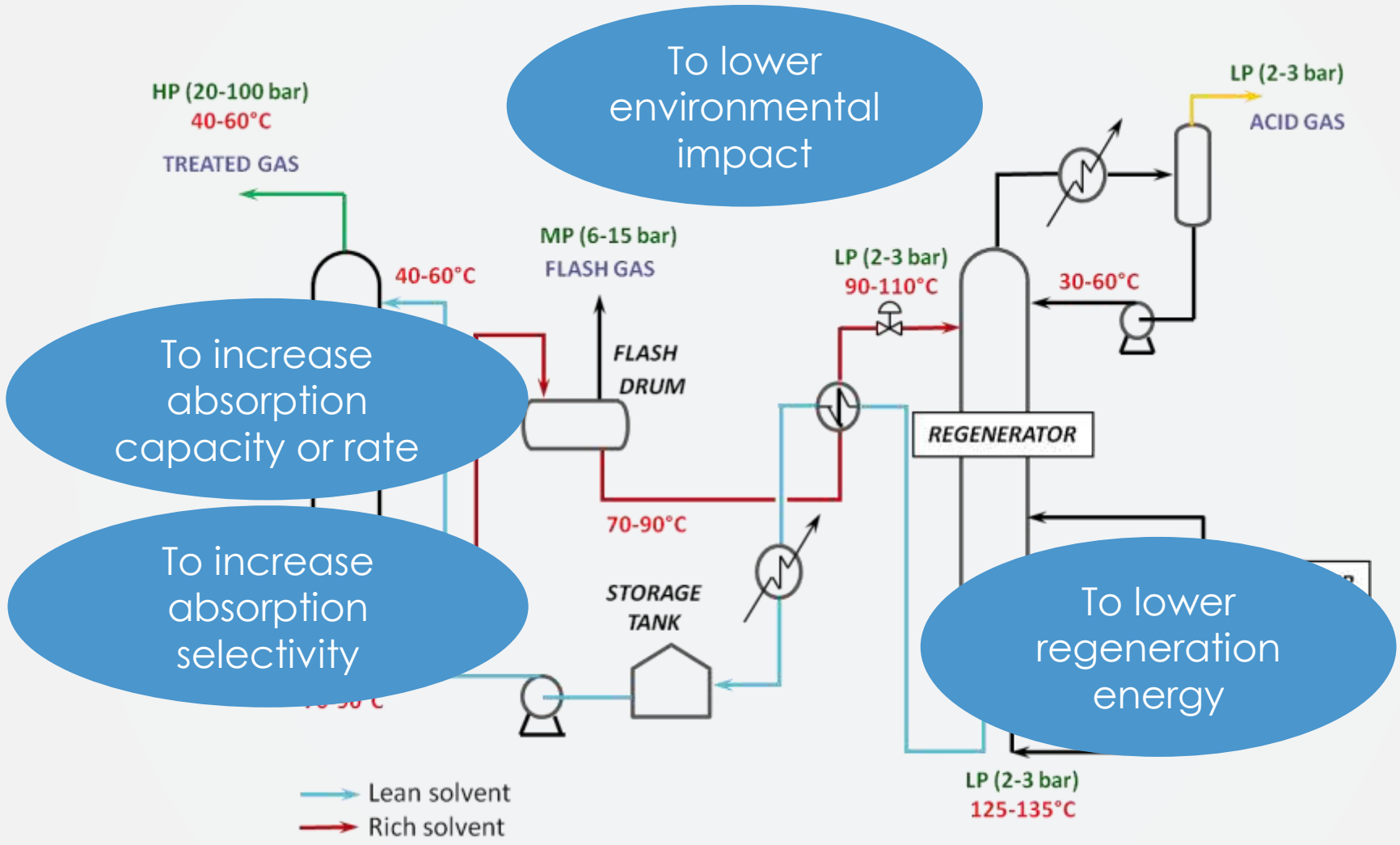
WAY FORWARD AND CONCLUSIONS

EXAMPLE OF ACID GAS REMOVAL UNIT (AGRU) - OPERATING CONDITIONS

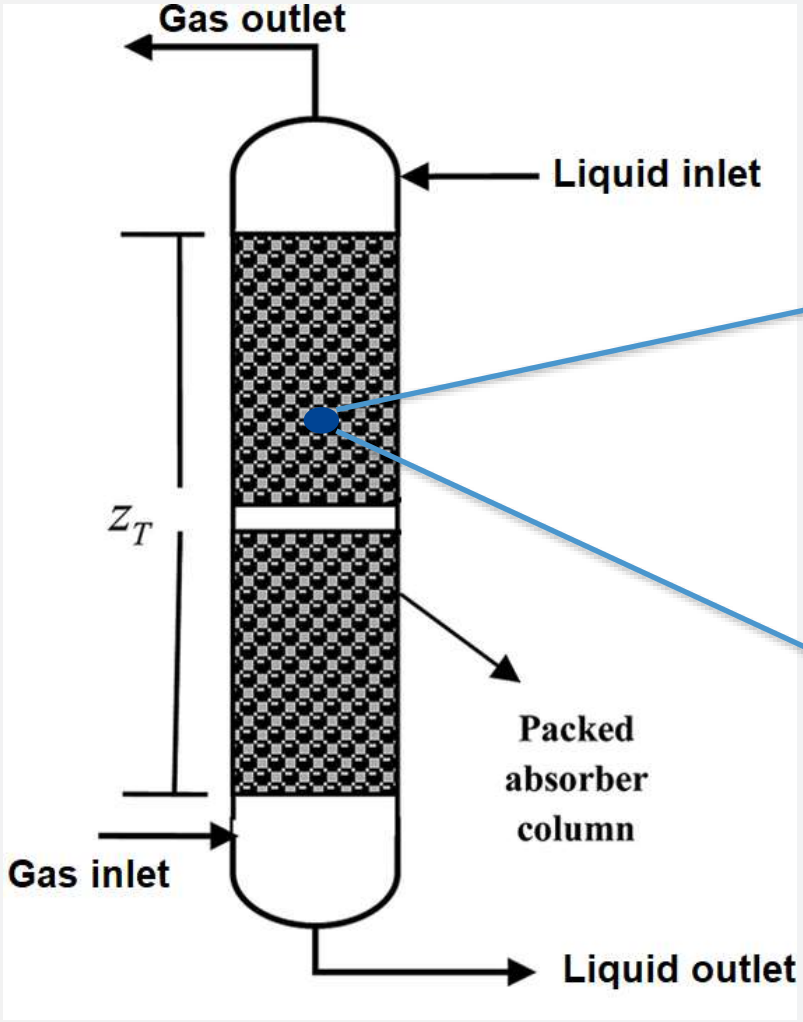
Absorption/regeneration with aqueous amine is most mature technology in industry

HP operating conditions for natural gas, same scheme for flue gas, but at LP.

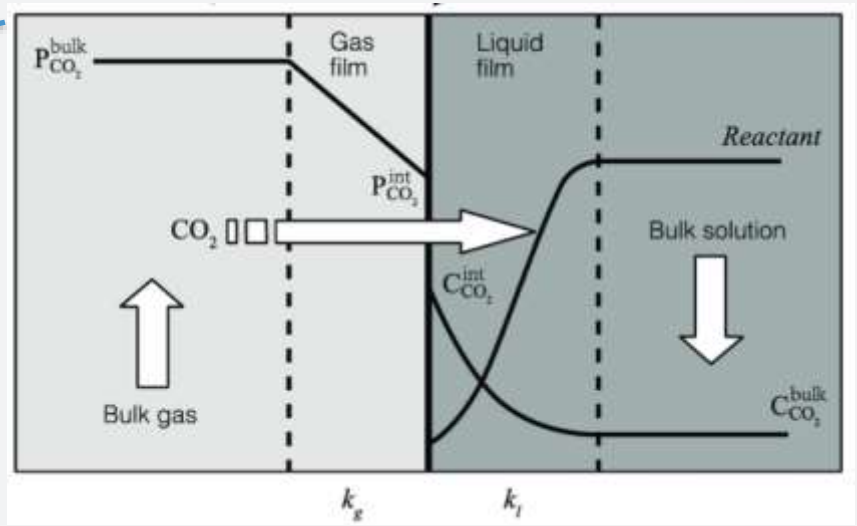
THE SEARCH FOR NEW SOLVENTS



MASS TRANSFER



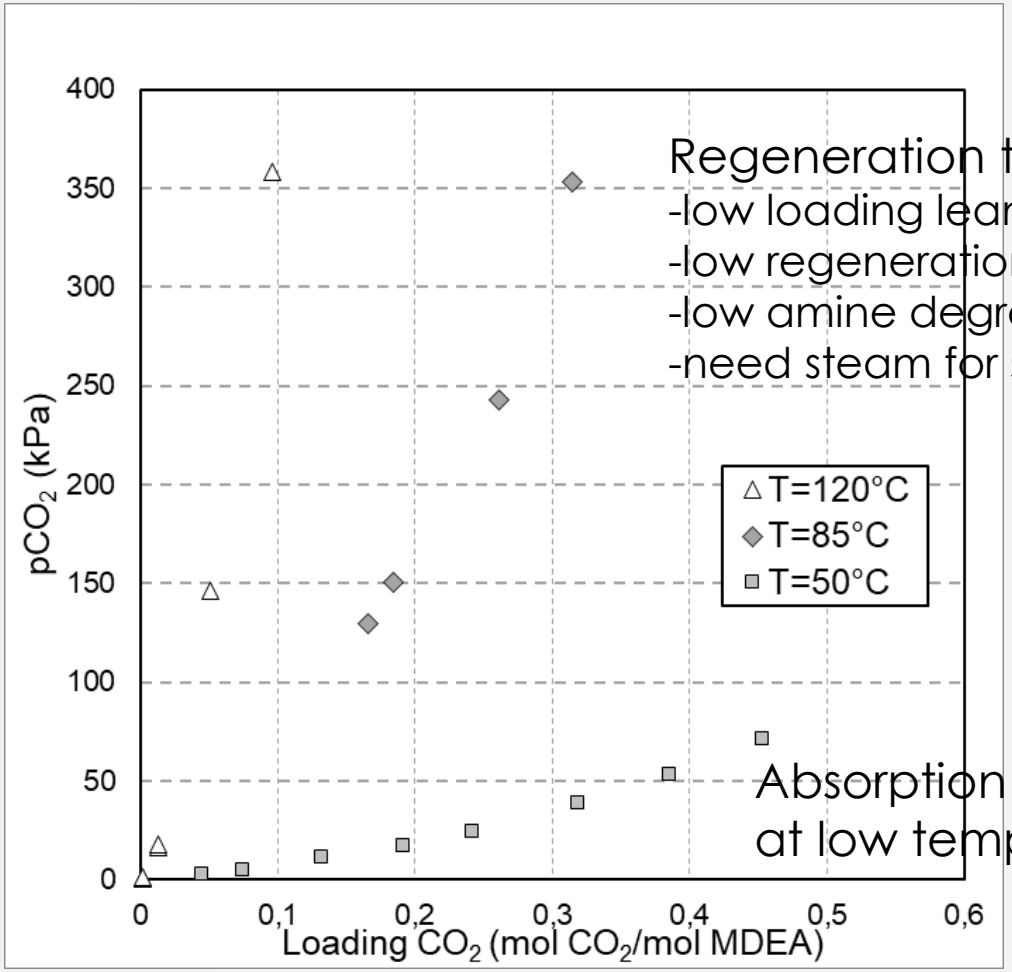
CO_2 absorption is typically limited by liquid-phase mass transfer



From: Review on the mass transfer performance of CO2 absorption by amine-based solvents in low- and high-pressure absorption packed columns Morteza Afkhamipour and Masoud Mofarahi RSC Advances, 29, 2017

THERMODYNAMICS

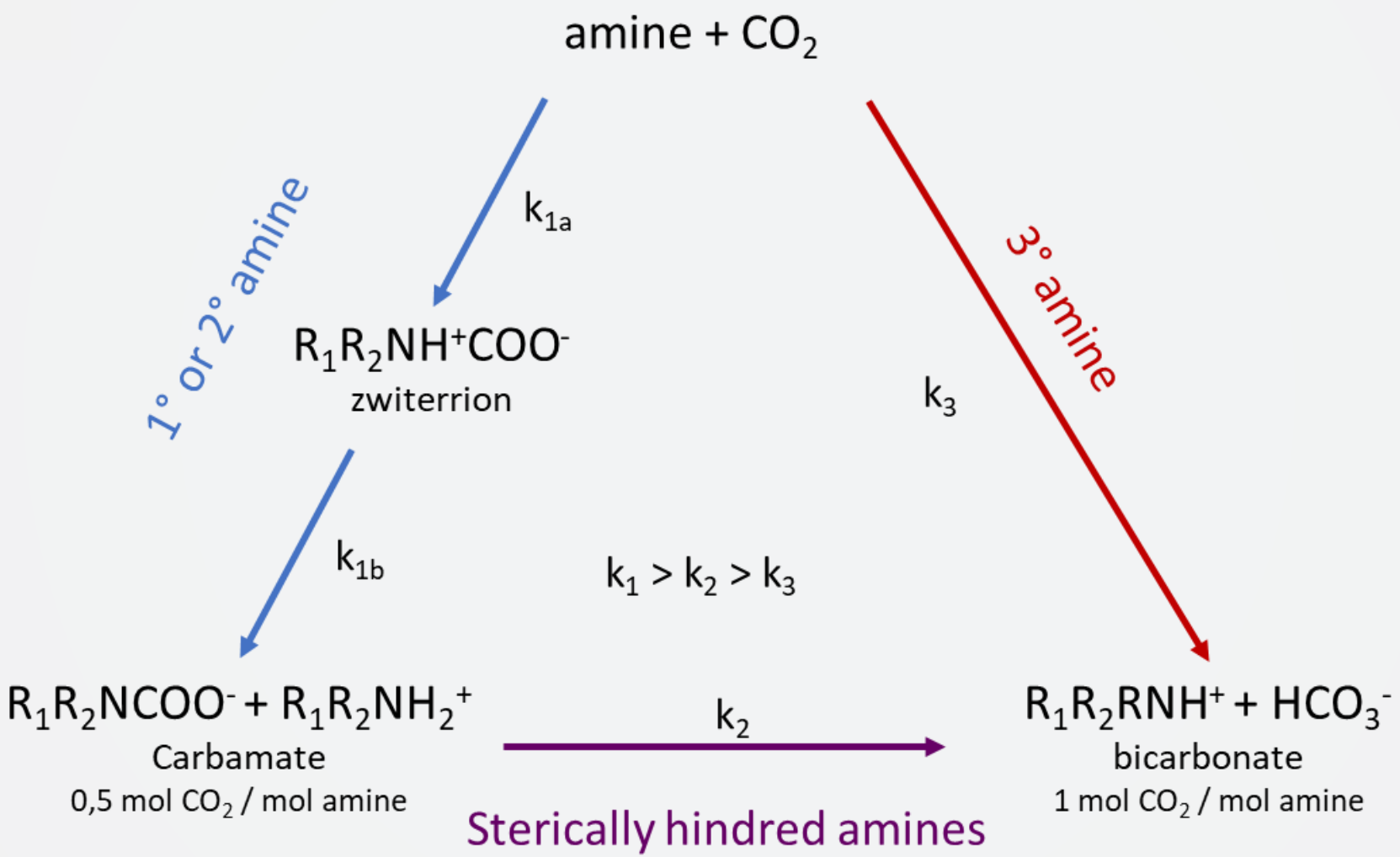
Desorption (endothermic) at high temperature (120°C)



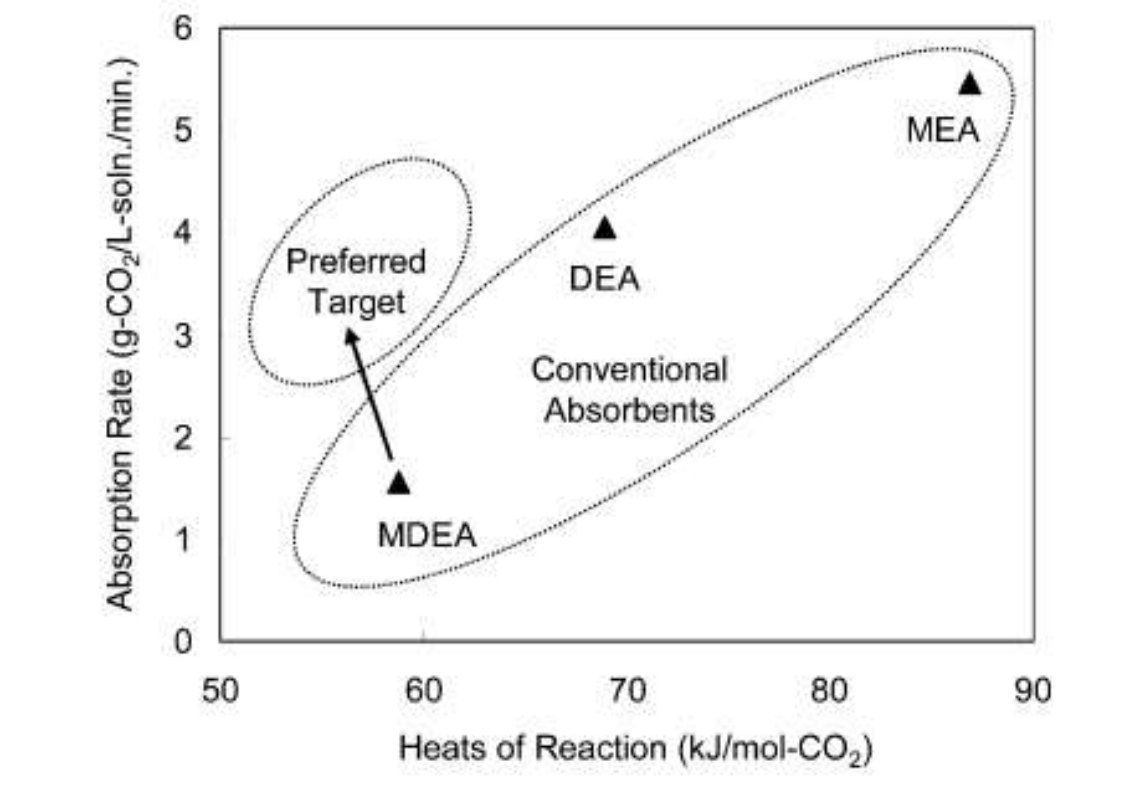
Regeneration temperature is trade-off between:
-low loading lean amine (high temp)
-low regeneration energy (low temp)
-low amine degradation (low temp)
-need steam for stripping (>100°C)

Absorption (exothermic)
at low temperature (50°C)

REACTION MECHANISM



PURPOSE: BETTER KINETICS & LOW REACTION HEATS



Chowdhury *et al. Ind. Eng. Chem. Res.* **2013**, *52*, 8323

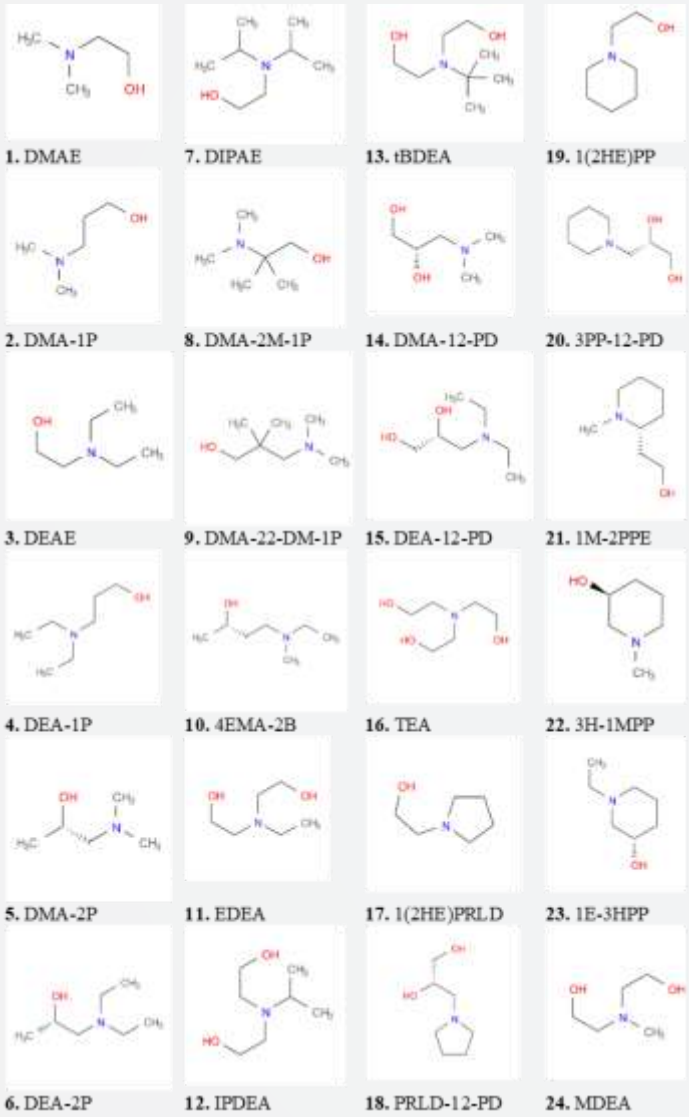
MEA: fast absorption, but high heat of reaction (lean amine loading ~0,2 mol CO_2/molMEA)

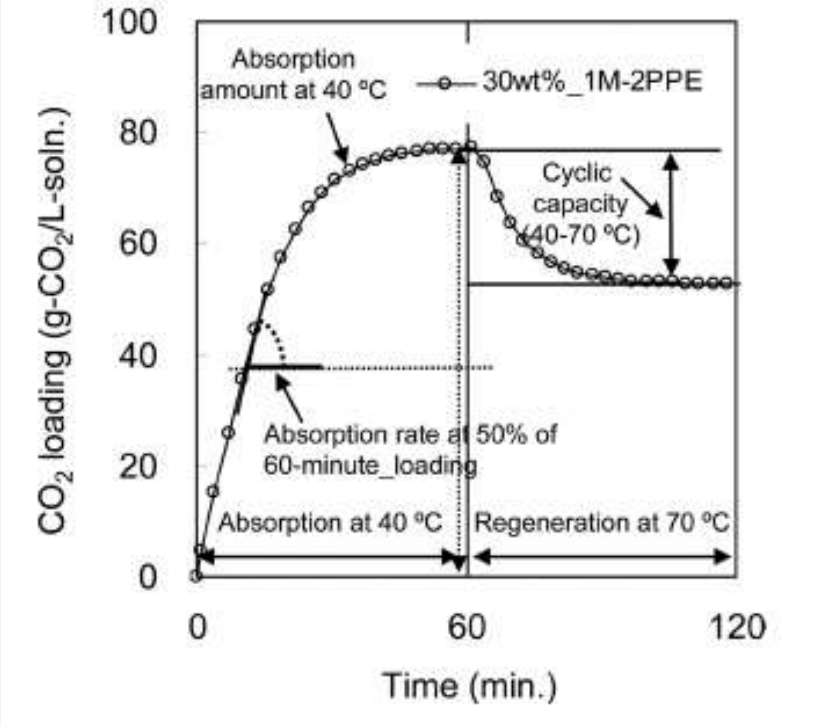
MDEA: slow absorption, but lower reaction heat (lean amine loading <0,01 mol CO_2/molMDEA)

Faster absorption (smaller columns, less solvent (CAPEX))
Low reaction heat (OPEX+CAPEX)

Alternatives : catalysis or addition of activators/promotors like Piperazine

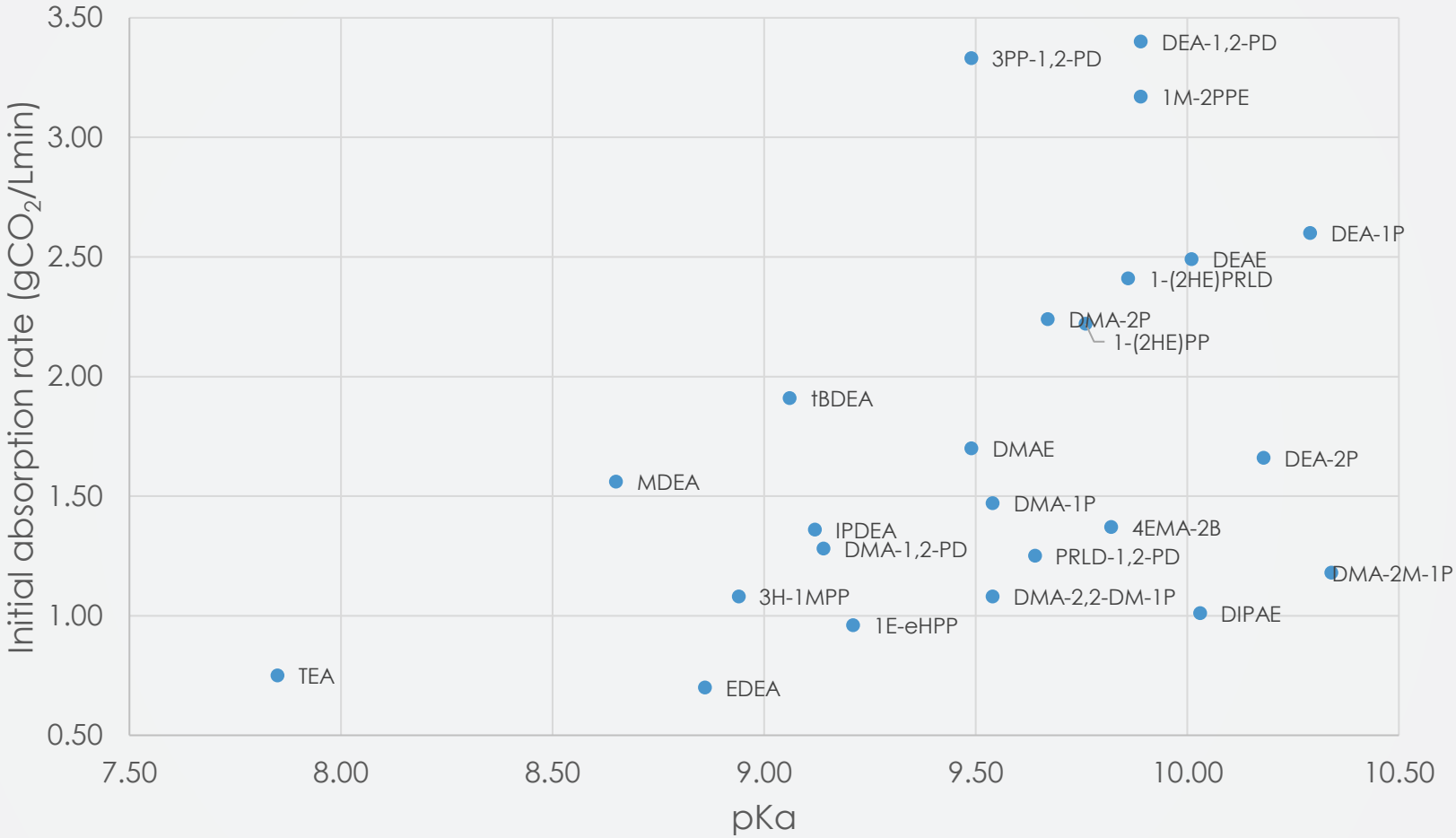
KINETIC EXPERIMENTS OF CHOWDHURY ET AL.





Chowdhury *et al. Ind. Eng. Chem. Res.* **2013**, *52*, 8323

IMPACT OF PK_A (BASICITY OF AMINE)



Experimental data: Chowdhury *et al. Ind. Eng. Chem. Res.* **2013**, *52*, 8323

QSPR MODELING OF ABSORPTION RATE: CHALLENGING

Full Paper www.molinf.com

DOI: 10.1002/minf.201600143

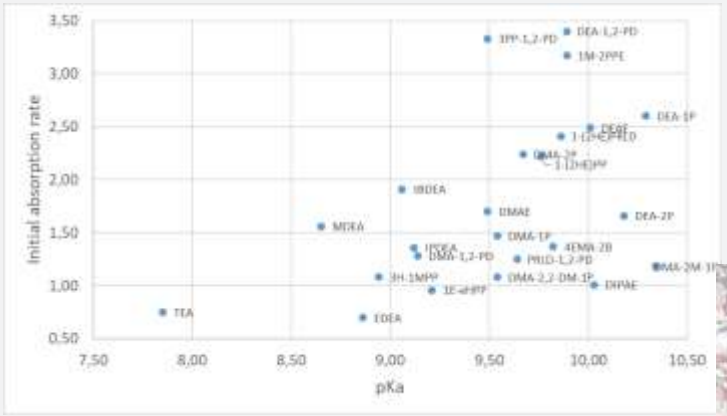
Cheminformatics Modeling of Amine Solutions for Assessing their CO_2 Absorption Properties

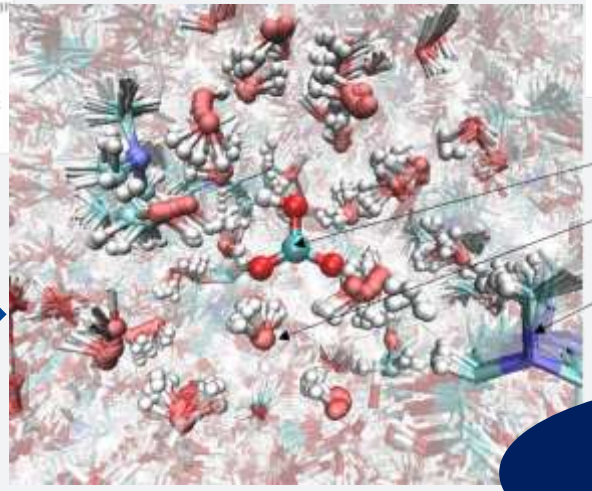
Melaine A. Kuenemann[a] and Denis Fourches*[a]

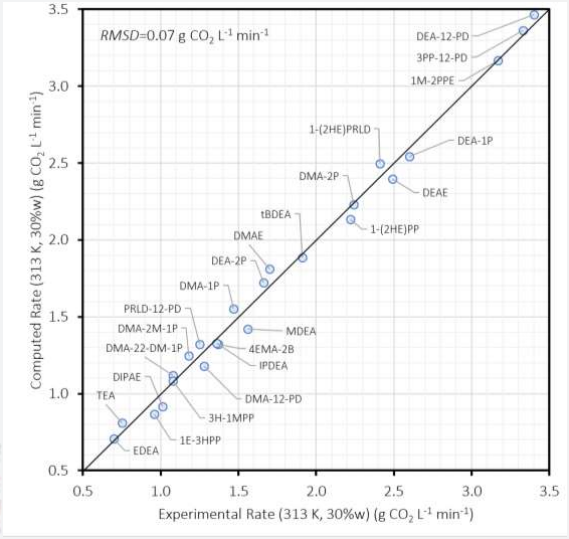
Kuenemann, M. A.; Fourches, D. *Mol. Inform.* **2017**, *36* (7), 1600143. https://doi.org/10.1002/minf.201600143.

Paper	Number of amines	Types of amines	Algorithm	Descriptors	Q^2_{LOO}	$Q^2_{10\text{-}CV}$	RMSE gCO_2/Lmin
Kuenemann et al.	37	tertiary (68%) secondary (27%) primary (5%)	Random Forest	RDKit	0.45	0.4	0.22
			Neural Network	RDKit	0.60	0.52	0.19

APPROACH BASED ON MOLECULAR SIMULATIONS







Develop Molecular Simulation based model to predict CO_2 absorption rates

Validate new model

significant breakthrough!

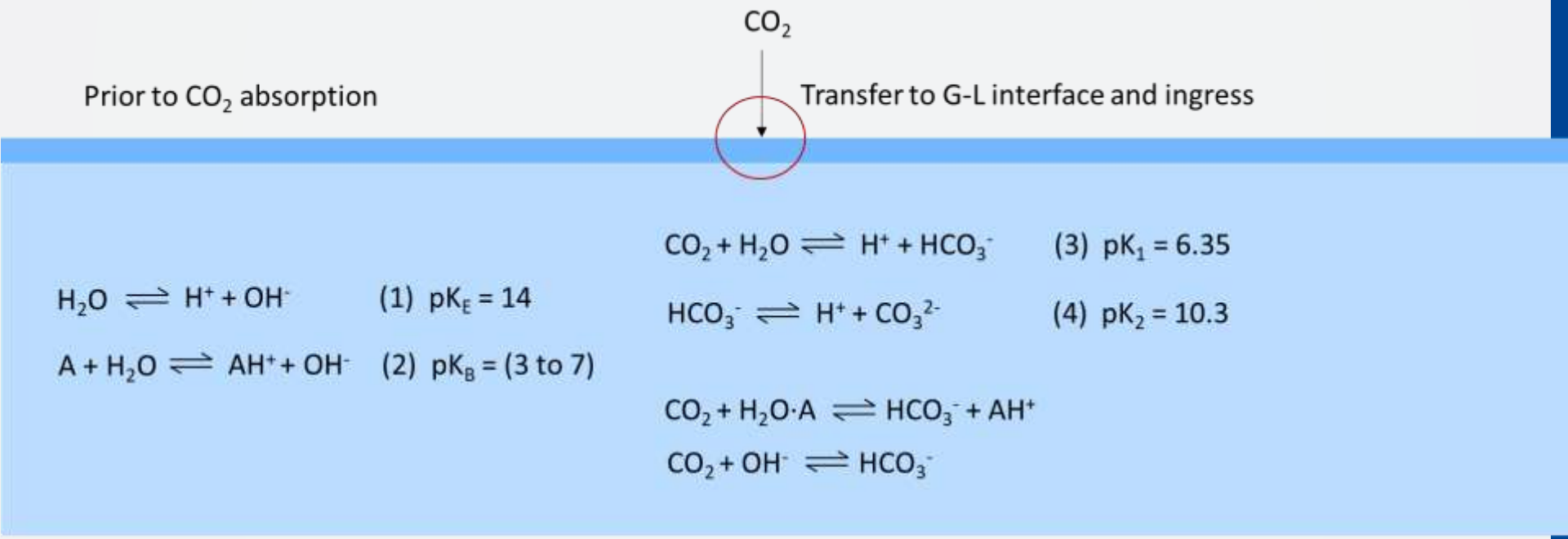
Experimental data: Chowdhury *et al. Ind. Eng. Chem. Res*. **2013**, *52*, 8323

MASS TRANSFER, THERMO AND KINETICS

$$r = A \exp(-\Delta G^{\#}/RT)\ ([OH^-]\ [CO_2]+B)$$

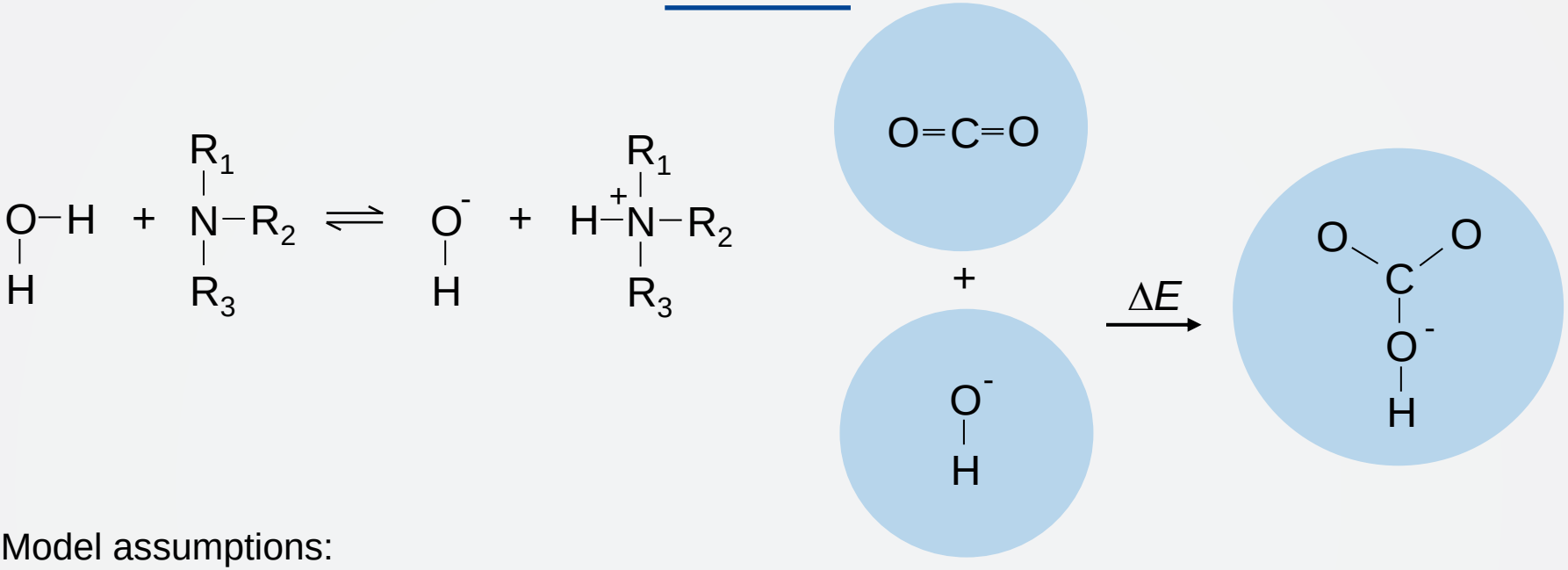
Evans-Polanyi principle and solvation free energies of reactants and products (MolSim)

From a set of equations: pK_a, pK_1, pK_2, pK_E equations, Henry's law, mass balances, neutral solution.



Species: H_2O, H^+, OH^-, CO_2, HCO_3^-, CO_3^{2-}, A, AH^+

CONCEPT CO_2 ABSORPTION MODEL



Model assumptions:

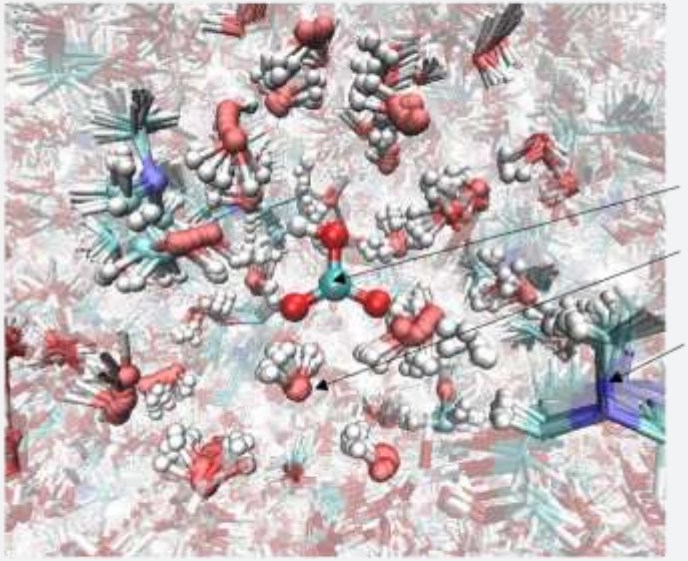
1. The reaction of CO_2 with OH^- to HCO_3^- dominates the absorption.
2. The energy barrier of this reaction hinges on the difference in the energy of solvation of the reactants (CO_2 and OH^-) and the product (HCO_3^-).
3. The absolute value of the barrier is calibrated with the experimental value of CO_2 in pure water.
4. The solvation energies depend on the molecular structure of the amine-water solvent and can be accurately computed using molecular dynamics.
5. The concentration of OH^- is determined by the concentration of the amine and its pK_a (and CO_2 gas pressure).

KINETICS OF CO_2 ABSORPTION

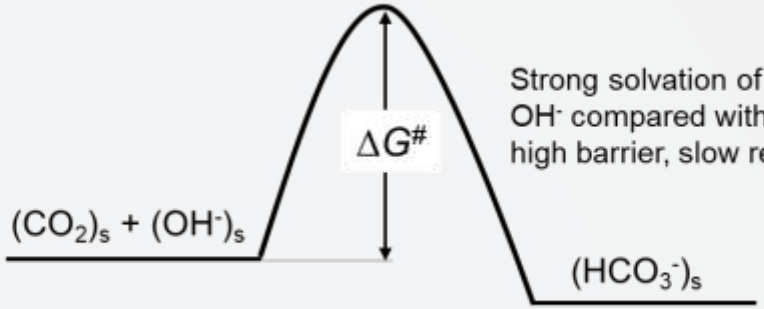
Key reactions:

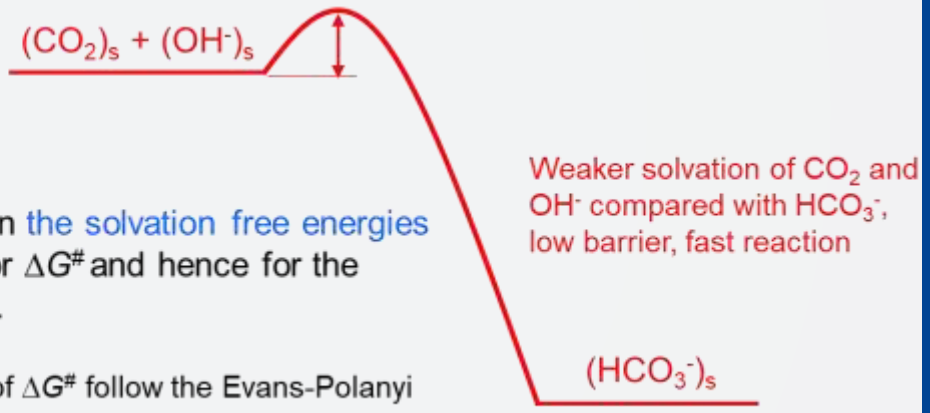
Protonation of Amine: $NR_3 + H_2O \rightleftharpoons HNR_3^+ + OH^-$

Carboxylation of CO_2: $CO_2 + OH^- \rightleftharpoons HCO_3^-$



Superposed snapshots from molecular dynamics simulations of HCO_3^- in a solvent containing MDEA, water, and ethylene glycol. Note the dynamic screening of the anion by water molecules.



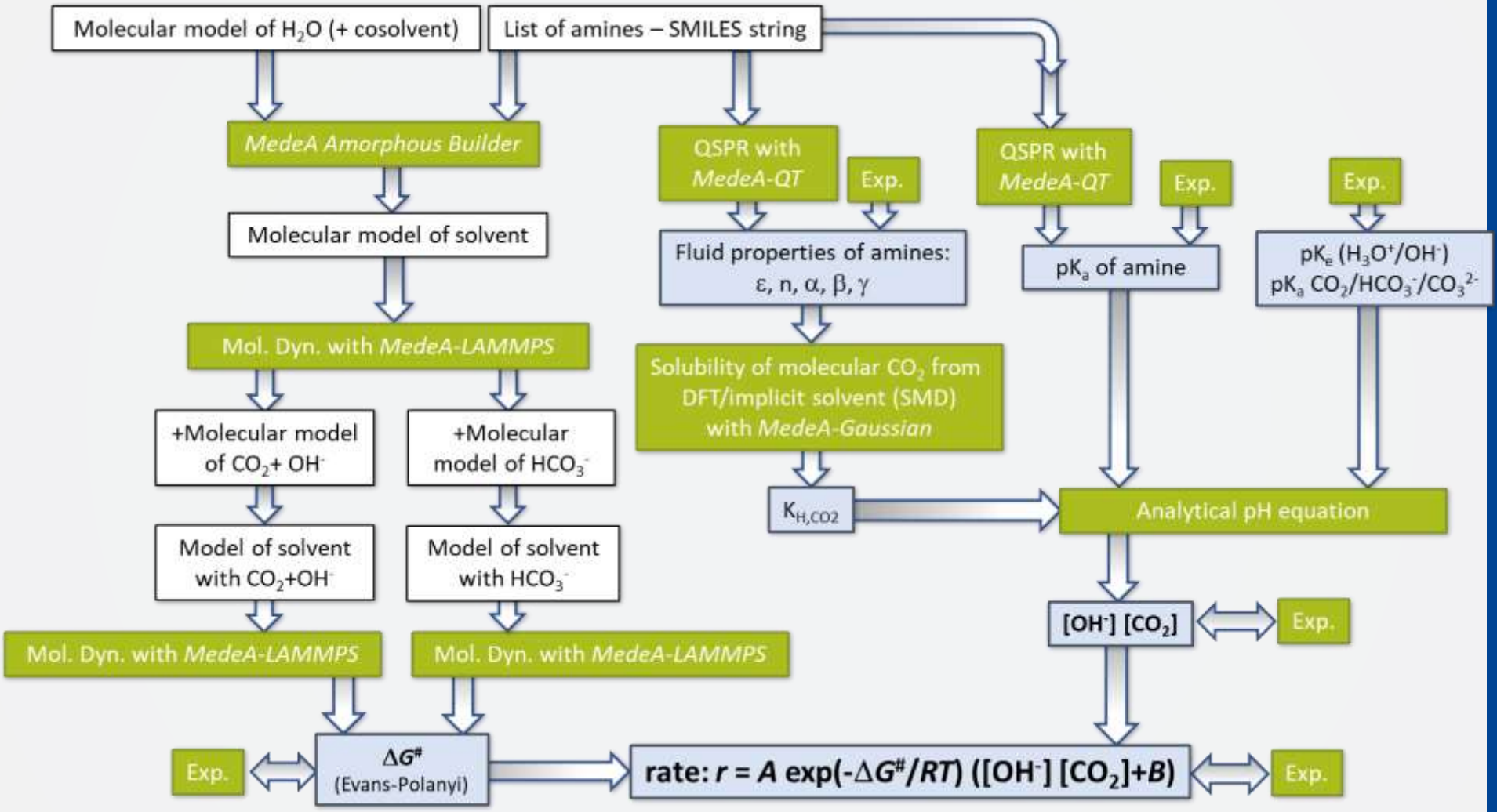


Differences in the solvation free energies are critical for $\Delta G^{\#}$ and hence for the reaction rate.

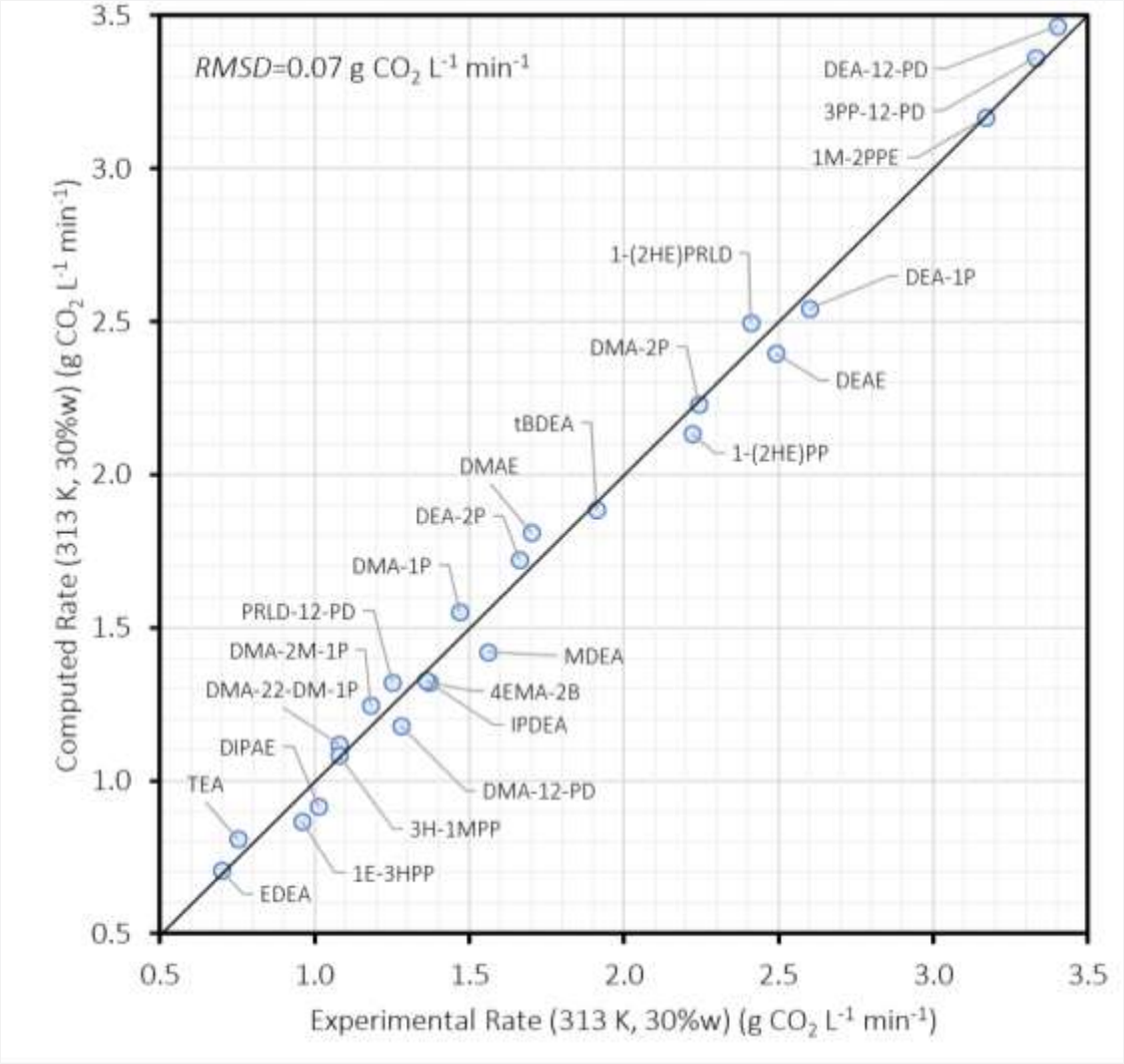
The changes of $\Delta G^{\#}$ follow the Evans-Polanyi principle.

- The energies of solvation of CO_2 + OH^- and of HCO_3^- in an aqueous amine solution (with/without co-solvents) are computed accurately by molecular dynamics. (Accuracy activation energies < 1kJ/mol))
- Using models with several hundred molecules per simulation box and sampling about 40 million configurations, the statistical fluctuations are reduced to about 1 kJ/mol.
- Each simulation can be accomplished in about 40 hours using standard computer clusters.

WORKFLOW


Molecular model of H_2O (+ cosolvent)
List of amines – SMILES string
MedeA Amorphous Builder
QSPR with MedeA-QT
Exp.
QSPR with MedeA-QT
Exp.
Exp.
Molecular model of solvent
Fluid properties of amines: ε, n, α, β, γ
pK_a of amine
pK_e (H_3O^+/OH^-) pK_a $CO_2/HCO_3^-/CO_3^{2-}$
Mol. Dyn. with MedeA-LAMMPS
Solubility of molecular CO_2 from DFT/implicit solvent (SMD) with MedeA-Gaussian
+Molecular model of CO_2+ OH^-
+Molecular model of HCO_3^-
$K_{H,CO2}$
Analytical pH equation
Model of solvent with CO_2+OH^-
Model of solvent with HCO_3^-
$[OH^-]$ $[CO_2]$
Exp.
Mol. Dyn. with MedeA-LAMMPS
Mol. Dyn. with MedeA-LAMMPS
Exp.
$\Delta G^{\#}$ (Evans-Polanyi)
rate: $r = A \exp(-\Delta G^{\#}/RT)$ $([OH^-][CO_2]+B)$
Exp.

EXPERIMENTAL VALIDATION



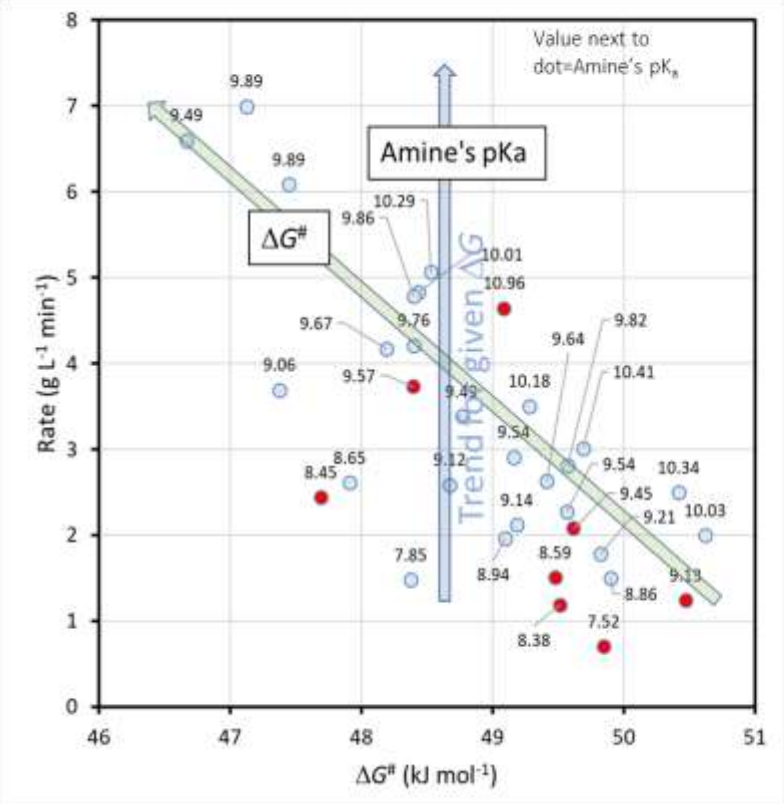
-Training set of 10 amines, validation set of 14 amines

-Different training/validation sets

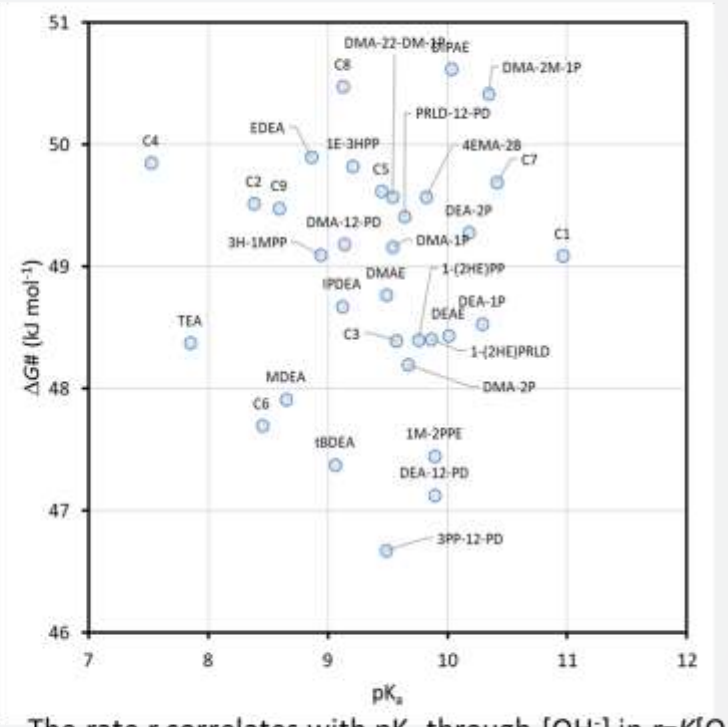
-Accuracy activation energies < 1kJ/mol

ANALYSIS OF RESULTS

$\Delta G^{\#}$ as a function of the CO_2 rate, together with amine's pK_a values

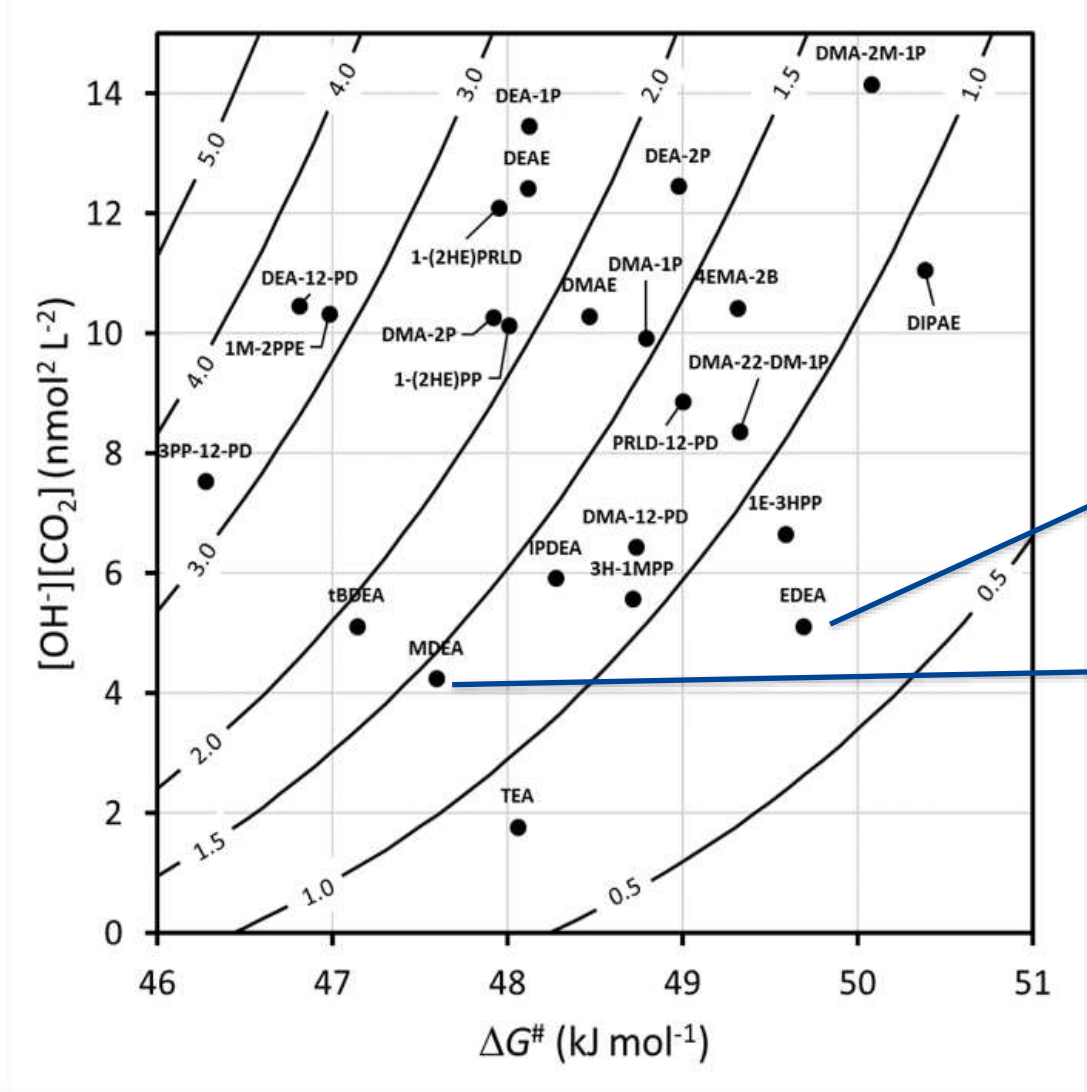


There is no correlation between $\Delta G^{\#}$ and amine's pK_a

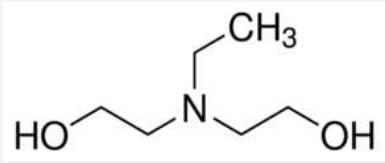


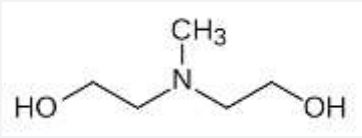
The rate r correlates with pK_a through $[OH^-]$ in $r=K[OH^-][CO_2]$

ANALYSIS OF RESULTS



Example: EDEA and MDEA have similar basicity, but $-CH_2-$ increases activation energy



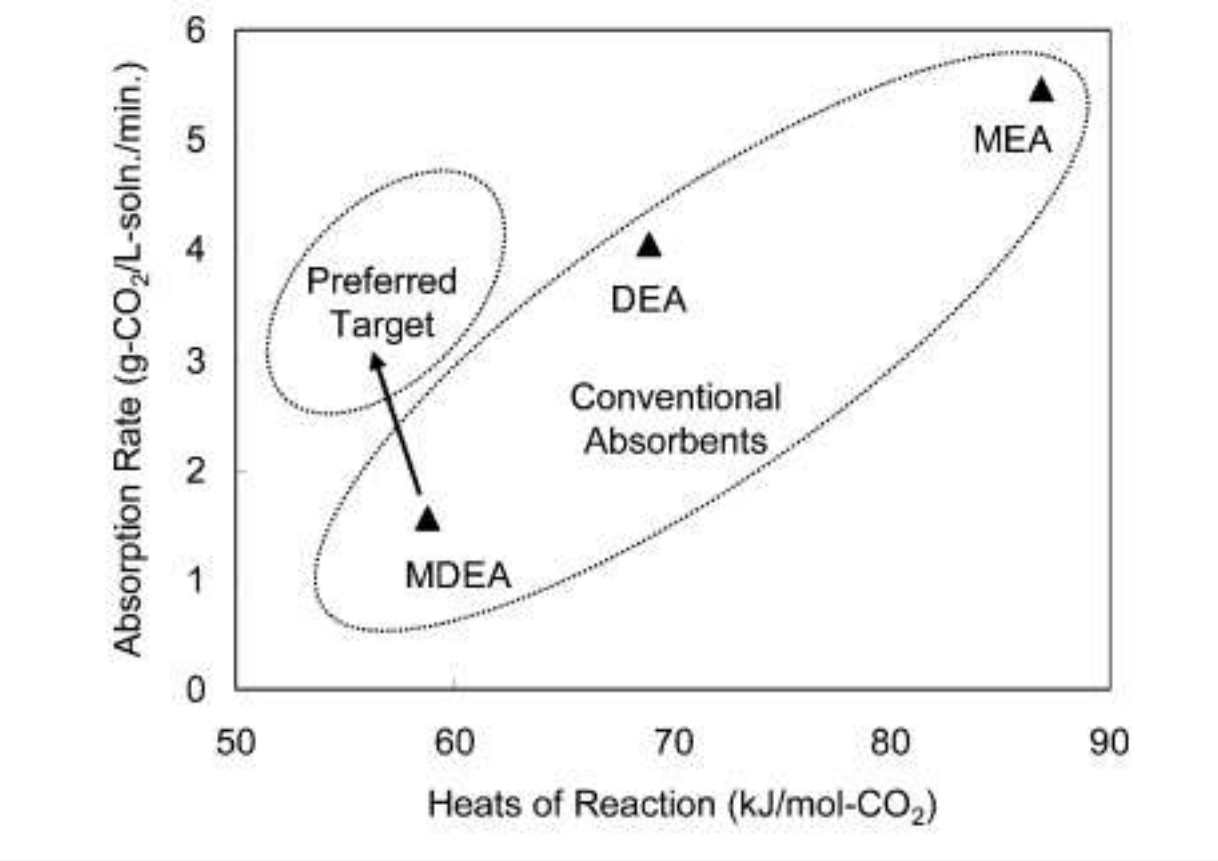


TOTAL AND CCUS

MOLECULAR SIMULATIONS IN SOLVENT DEVELOPMENT

WAY FORWARD & CONCLUSIONS

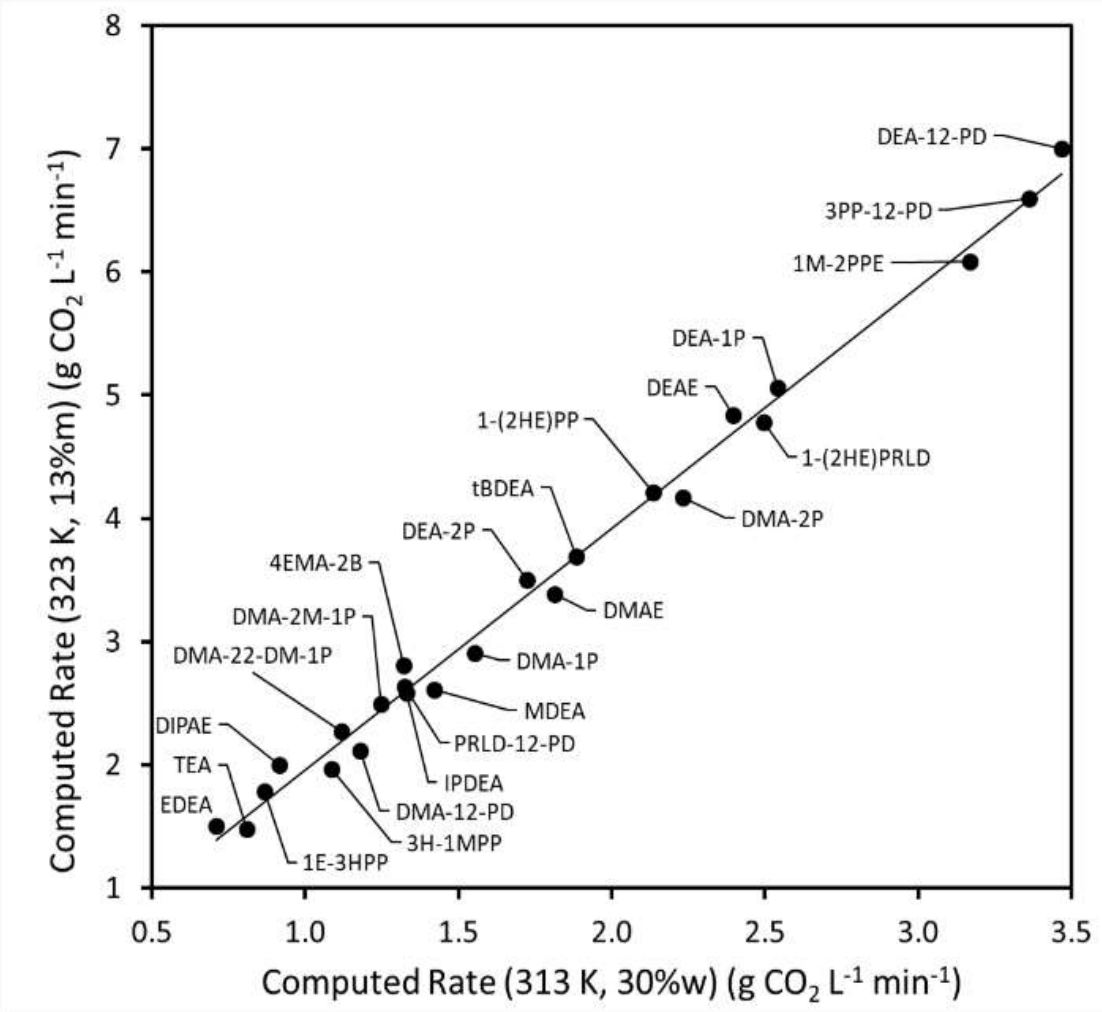
PURPOSE: BETTER KINETICS & LOW REACTION HEATS



Chowdhury *et al. Ind. Eng. Chem. Res*. **2013**, *52*, 8323

SIMULATIONS AT 50°C, 13 MOL% AMINE

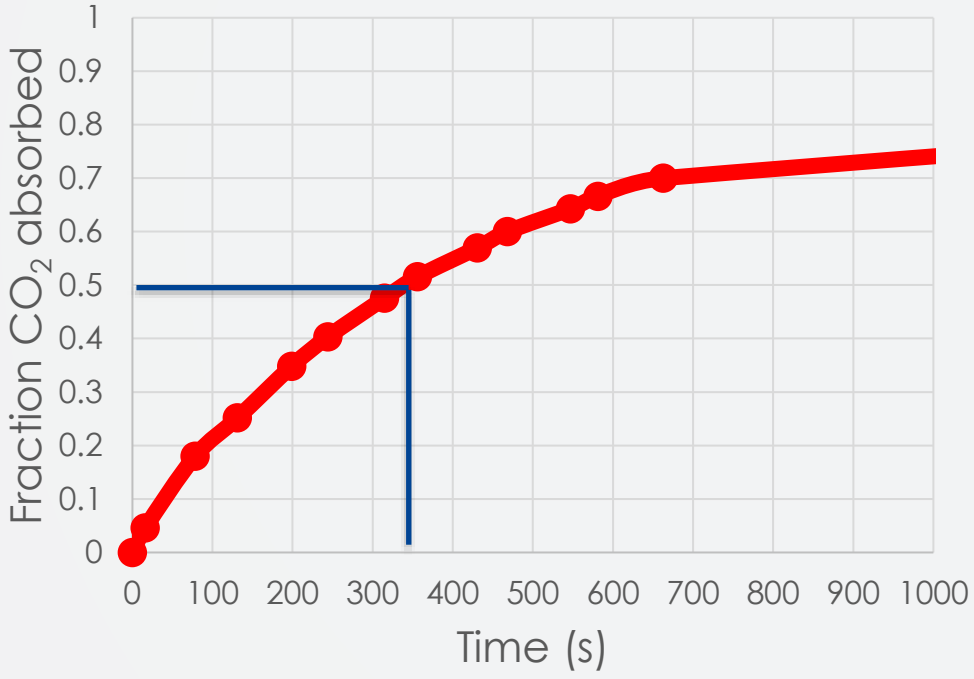
Better to compare kinetics at same amine mol%
50°C is closer to industrial conditions



KINETIC EXPERIMENTS

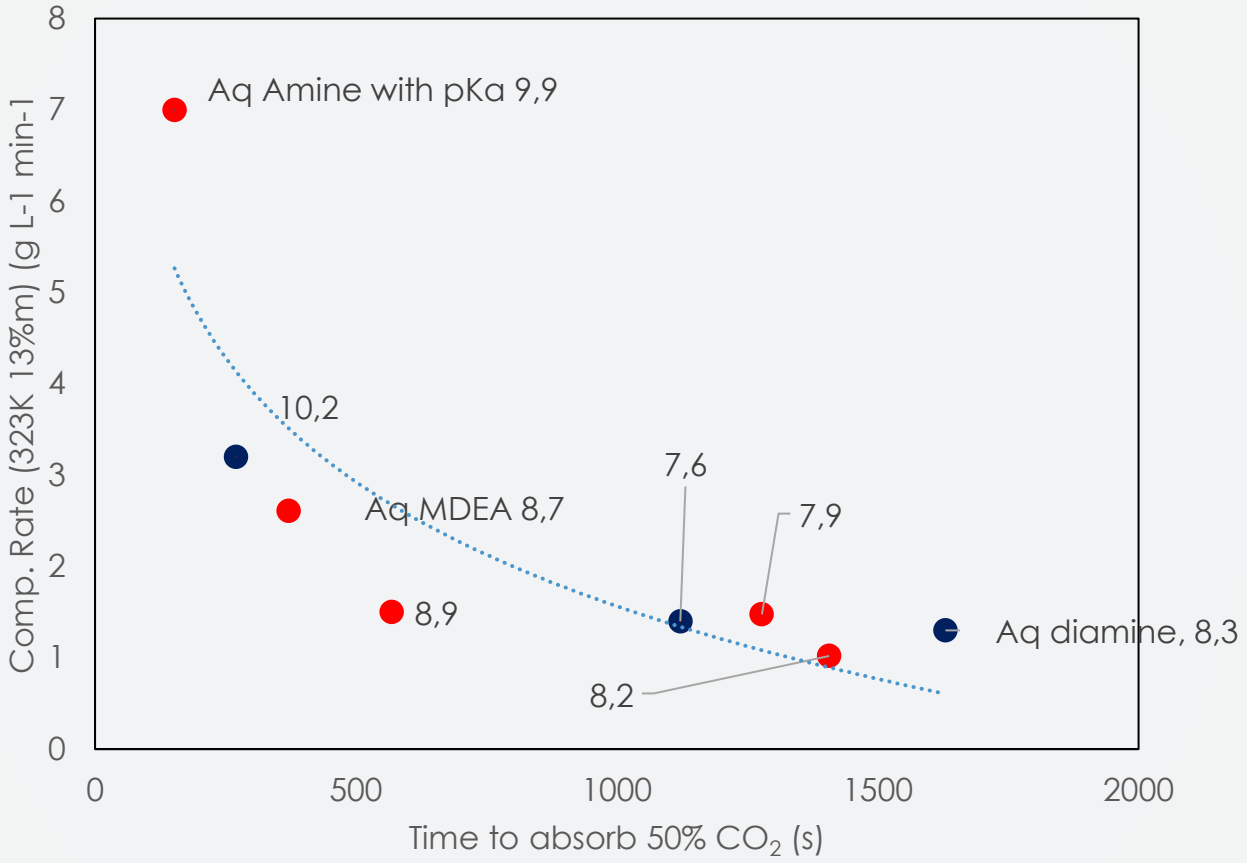
Main aim: have a reliable and quick experimental tool to screen solvents based on kinetic (and thermodynamic) performance.

An experimental set-up has been put in place at Armines (Paris) to monitor CO_2 absorption as function of the time



We look at the time to absorb 50% of CO_2.

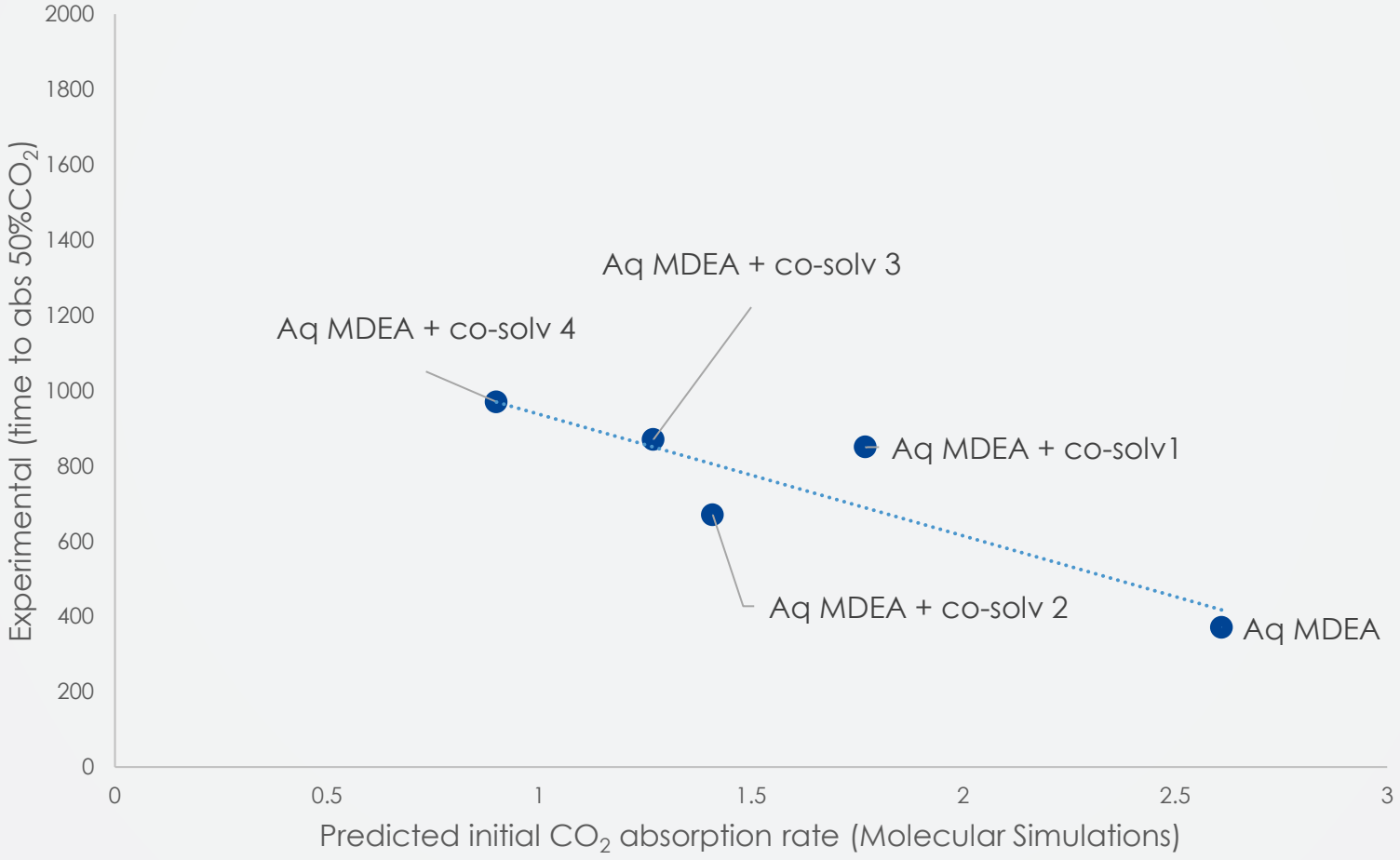
FIRST RESULTS: AQUEOUS 13MOL% AMINES



- Amines from Chowdhury paper
- Other amines

FIRST RESULTS IMPACT OF CO-SOLVENT

-Co-solvents might reduce regeneration energy (lower Cp value)
-Understand/Predict how co-solvents impact the absorption rate of CO_2

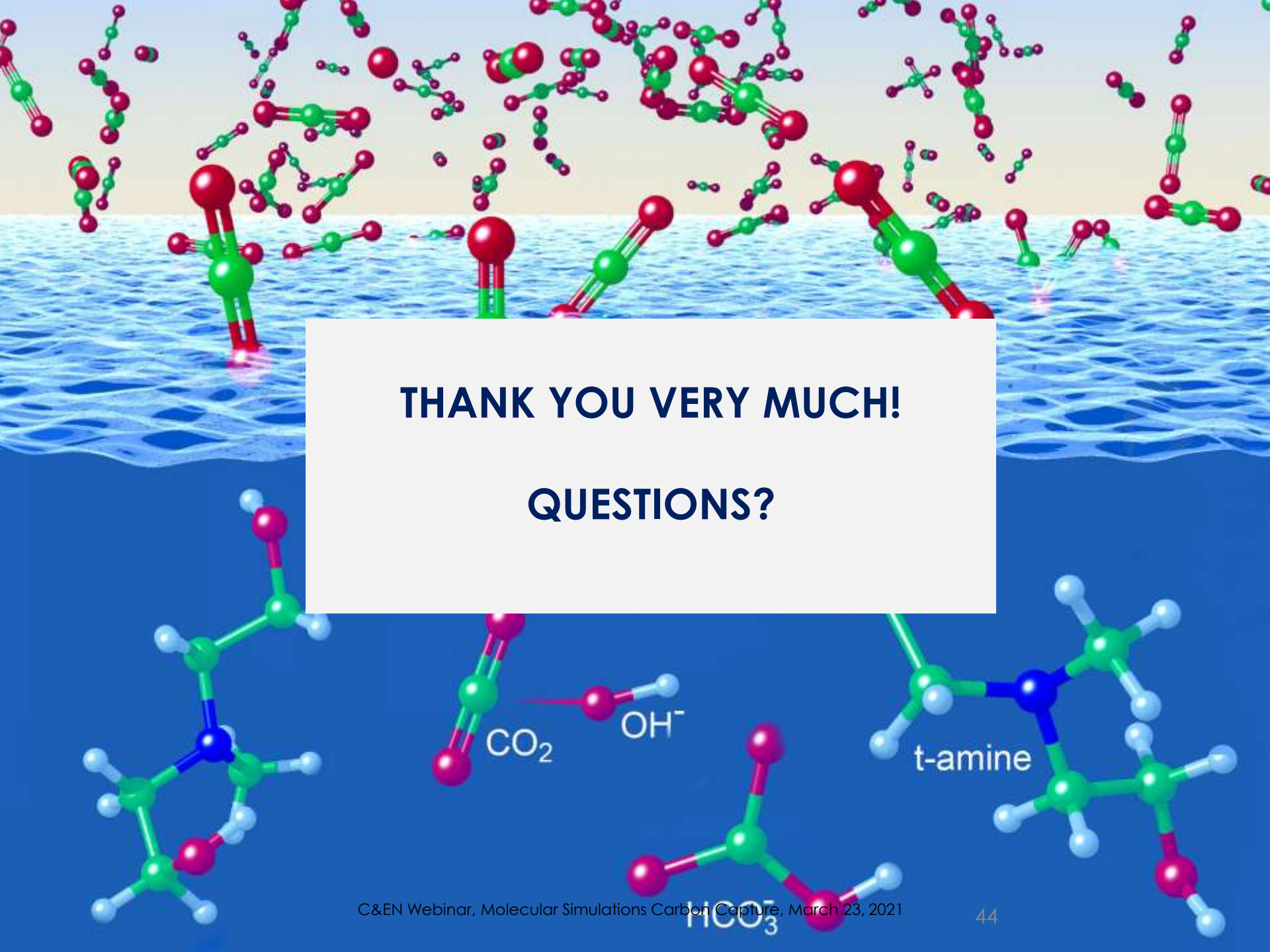


CONCLUSIONS

- A molecular approach allows for a solvent development based on a more thorough understanding of the chemical/physical process.

- Digital tools (molecular simulations, chemoinformatics) might help guiding the experiments (targeted experiments) and might reduce the number of experiments.

- However, developing digital tools is also time consuming and they require significant a priori chemical/physical insight of the systems as well as reliable experimental data as input and for validation.


THANK YOU VERY MUCH!
QUESTIONS?
CO_2
OH^-
t-amine
HCO_3^-