Development needs and knowledge gaps of CESAR1 solvent

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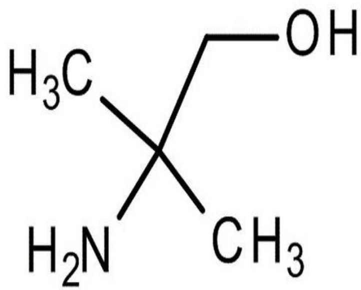
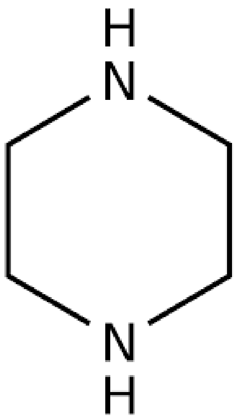
Solvent Chemistry

CESAR1 is an aqueous amine-based solvent for CO_2 capture.



2-amino-2-methyl-1-propanol
(AMP)



Piperazine
(PZ)

Solvent Chemistry

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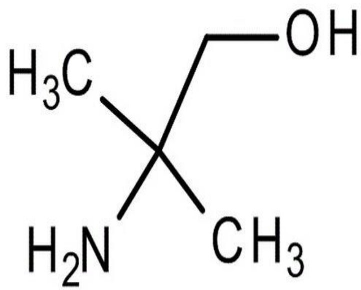

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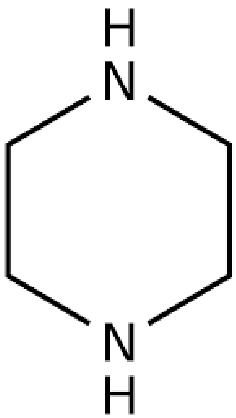


Piperazine
(PZ)

AMP = sterically hindered amine

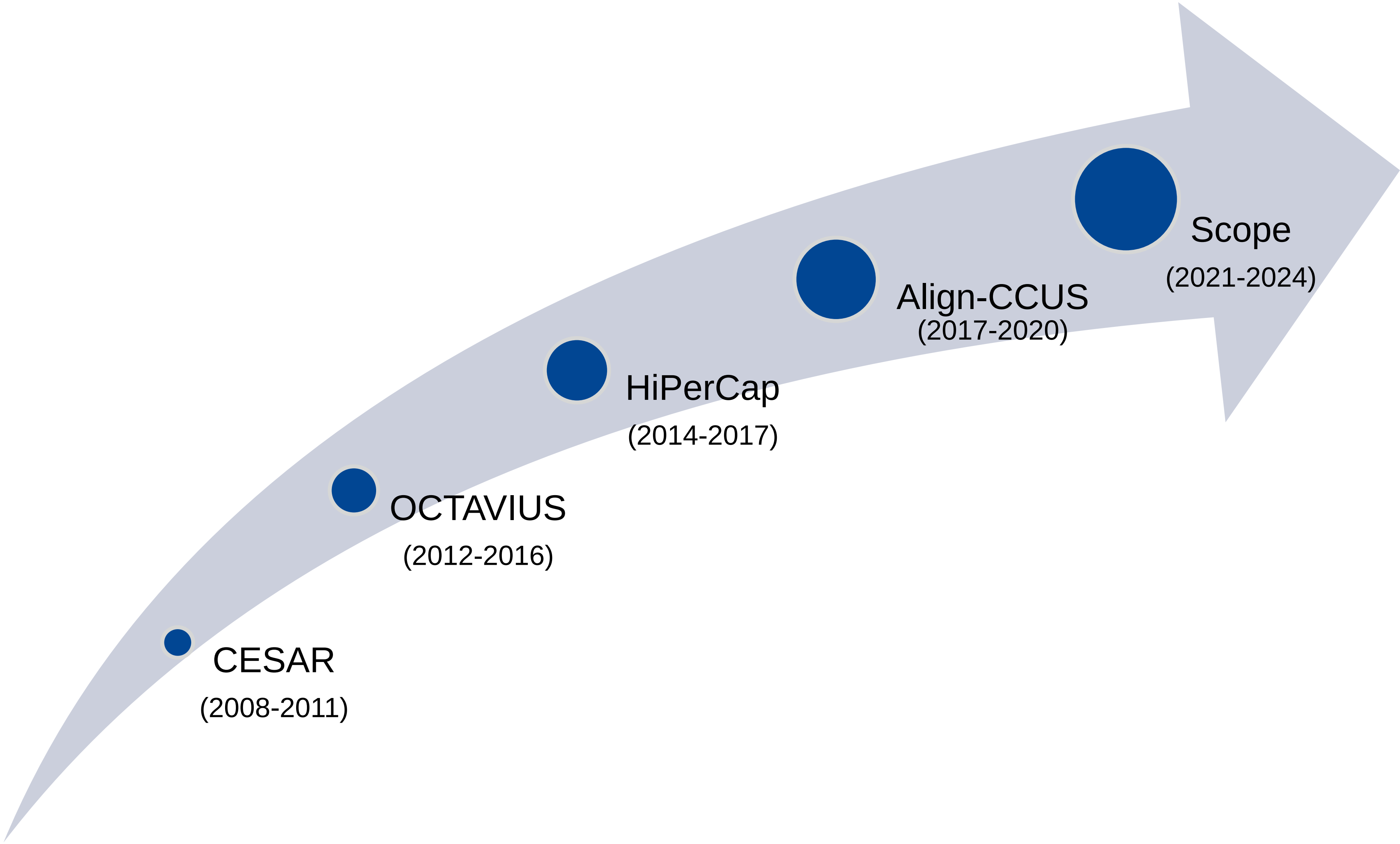
PZ = cyclic bifunctional amine.

CESAR1 is a blend of 3 M AMP and 1.5 M PZ

Why?

MEA vs CESAR1					
Energy Performance	Solvent Stability	Performance at high capture rate	Flexibility	Emission Control	Precipitation
					

History:

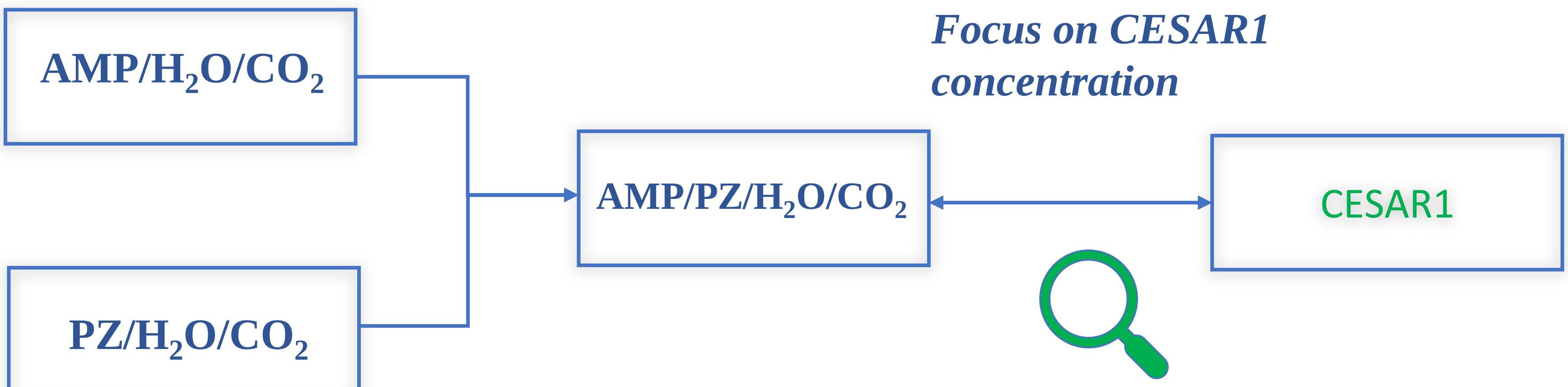

CESAR
(2008-2011)
OCTAVIUS
(2012-2016)
HiPerCap
(2014-2017)
Align-CCUS
(2017-2020)
Scope
(2021-2024)

Nowadays and Scope of the work

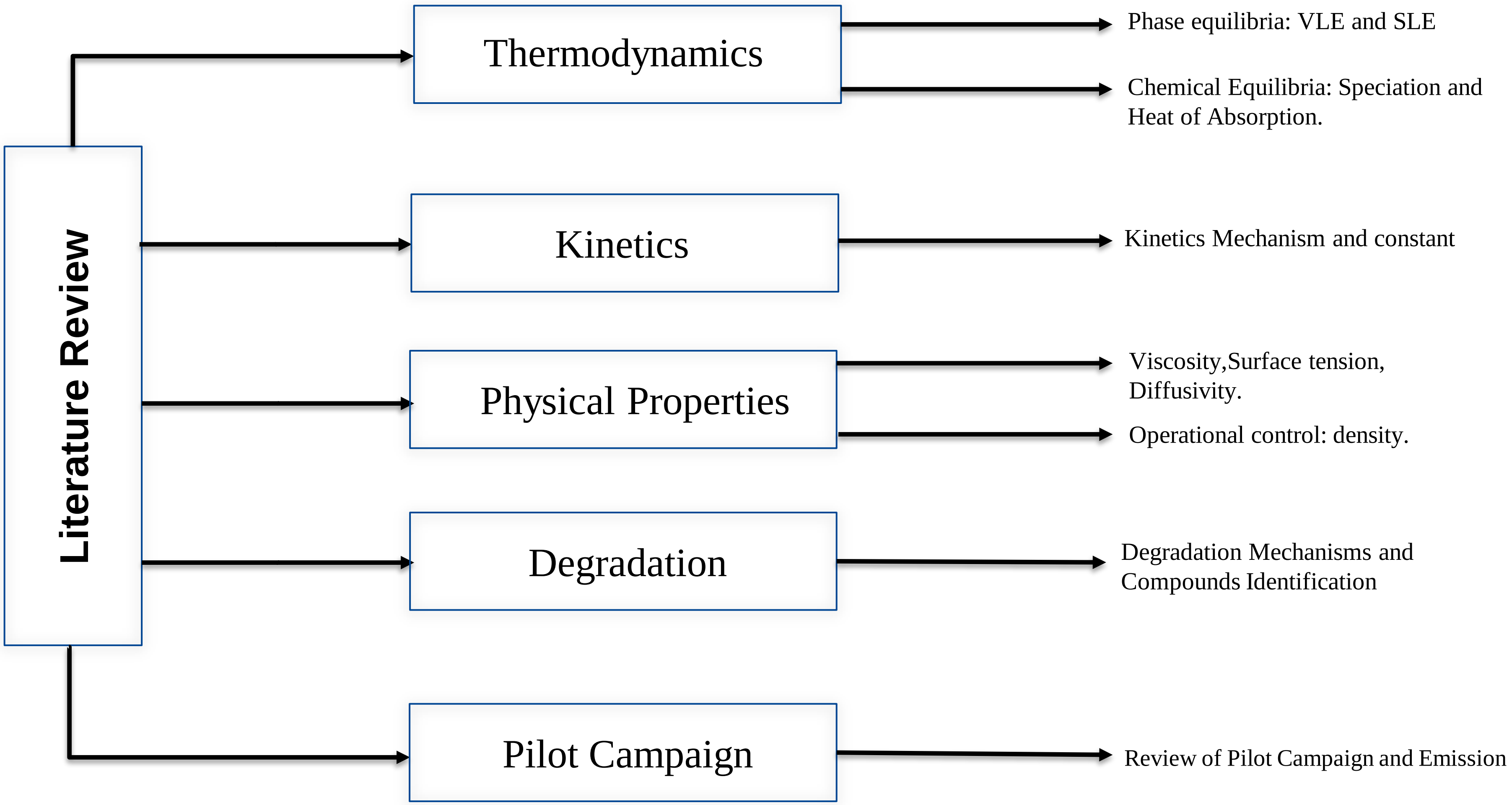
Mission: Development and qualification of CESAR1 solvent

One of the milestones: *Filling the experimental gaps*

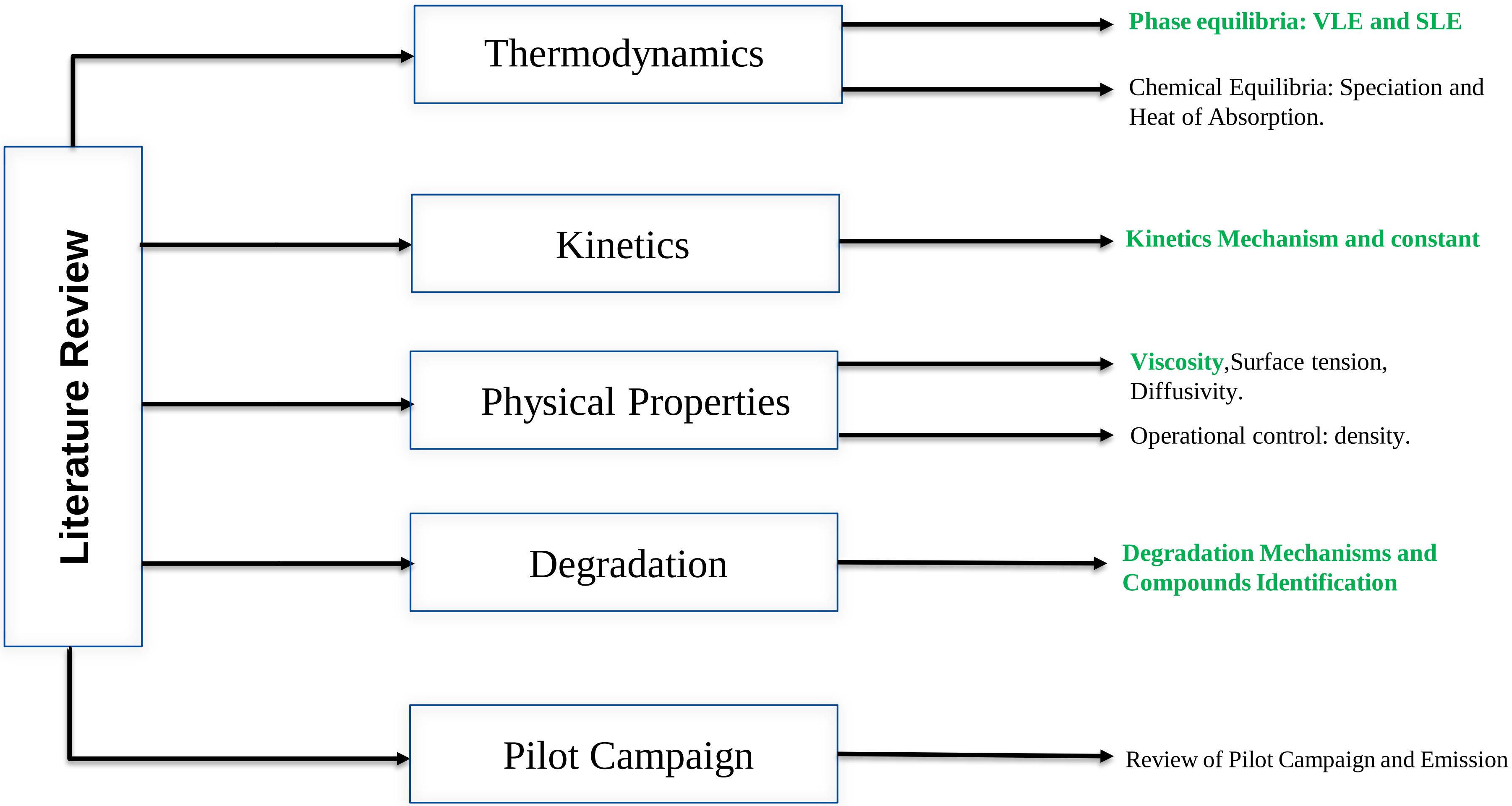
Methodology



Methodology



Outline



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Thermodynamics: VLE for subsystems

AMP

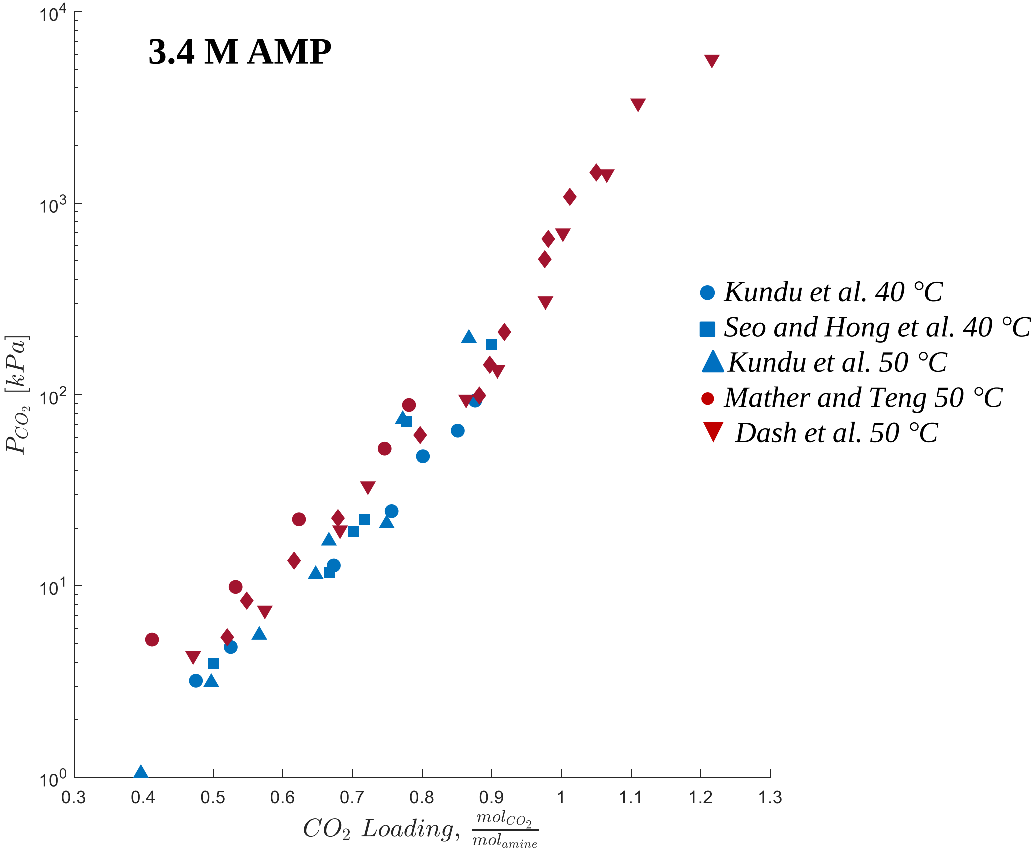
Concentration: from 0.1 M to 5.4 M AMP

Temperature: 20 up to 120 °C

PZ

Concentration: from 0.2 M to 4.9 M

Temperature: 20 up to 190 °C

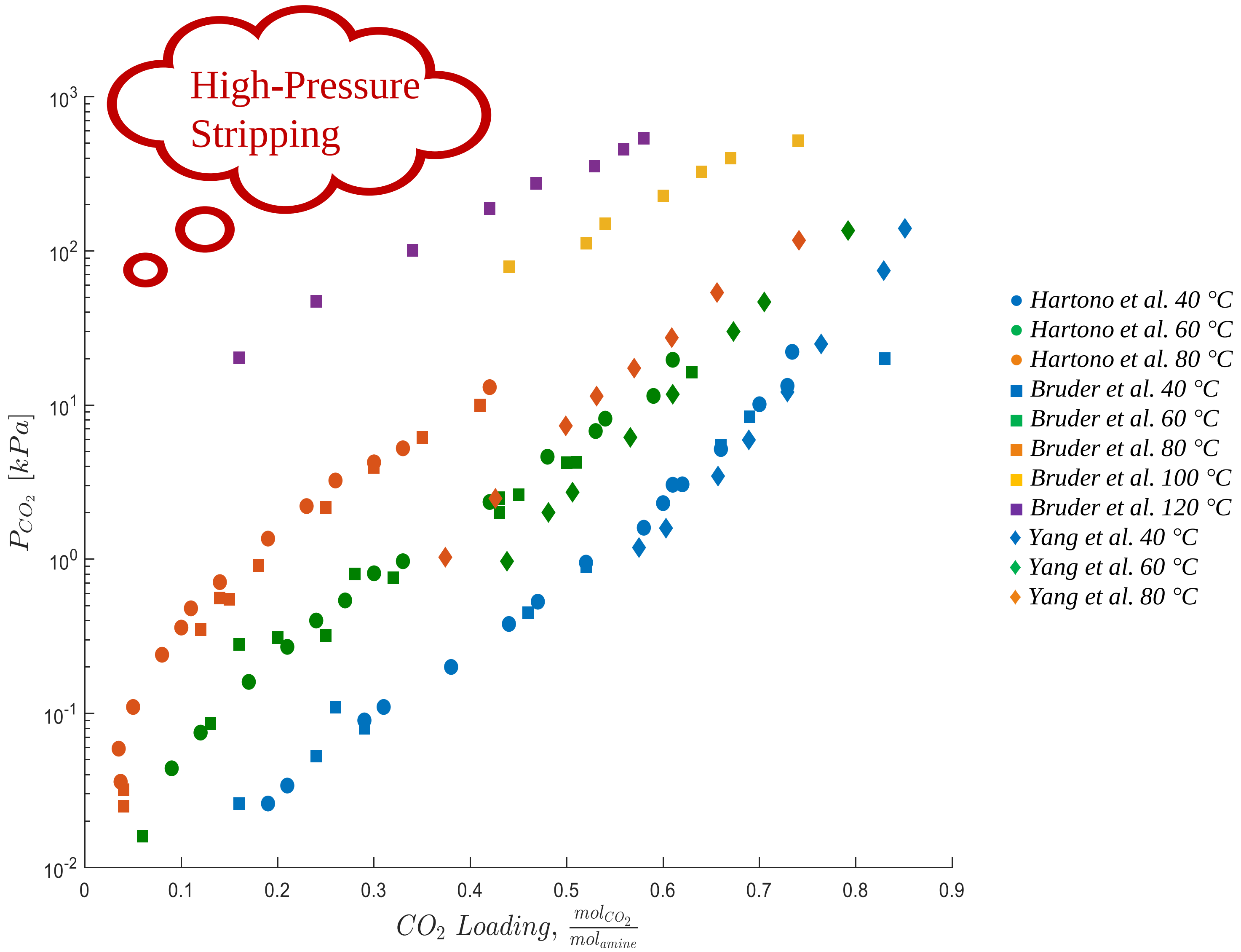


Some inconsistencies regarding AMP VLE data at CESAR1 concentration have been found.

Thermodynamics: VLE for AMP/PZ

System	Experimental Range	Data Type	Instrument	Reference
$AMP/PZ/H_2O/CO_2$	[AMP/PZ] = 3.0/1.5, 4.0/0.5,0.5/4.0,1.5/3.0,2.25/2.25 T = 40÷120 °C α_{CO_2} = 0.035÷1.05	P_{TOT} for T ≥ 100°C P_{CO_2}	Reaction Calorimetry and Vapor recirculation technique	Hartono, Ahmad, et al. (2021)
$AMP/PZ/H_2O/CO_2$	[wf_{AMP}/wf_{PZ}] = 25/5,20/10 % T = 40÷120 °C α_{CO_2} = 0÷0.95	P_{TOT}	Static Analytical Apparatus	Tong et al. (2013)
$AMP/PZ/H_2O/CO_2$	[m_{AMP}/m_{PZ}] = 2.3/5, 4/2 m T = 20÷160 °C α_{CO_2} = 0.268÷0.65	P_{CO_2}	Wetted Wall Column	Li et al. (2013)
$AMP/PZ/H_2O/CO_2$	[wf_{AMP}/wf_{PZ}] = 38/2,35/5,32/8,45/5,42/8 % T = 30÷55 °C α_{CO_2} = 0.22÷1.03	P_{CO_2}	Equilibrium Cell	Dash et al. (2012)
$AMP/PZ/H_2O/CO_2$	[AMP/PZ] = 3.0/1.5 T = 40÷120 °C α_{CO_2} = 0.04÷0.83	P_{CO_2}	Vapor Recirculation Technique	Brúder et al. (2011)
$AMP/PZ/H_2O/CO_2$	[AMP/PZ] = 3.0/1.5 T = 40÷120 °C α_{CO_2} = 0.04÷0.83	P_{CO_2}	Vapor Recirculation Technique	Yang et al. (2010)

Thermodynamics: VLE for CESAR1



Thermodynamics: VLE Detected Gaps

1. Inconsistency for CO_2-solubility data for aqueous AMP solutions at CESAR1 concentration.

2. CO_2 Solubility data at temperature higher than 120 °C.

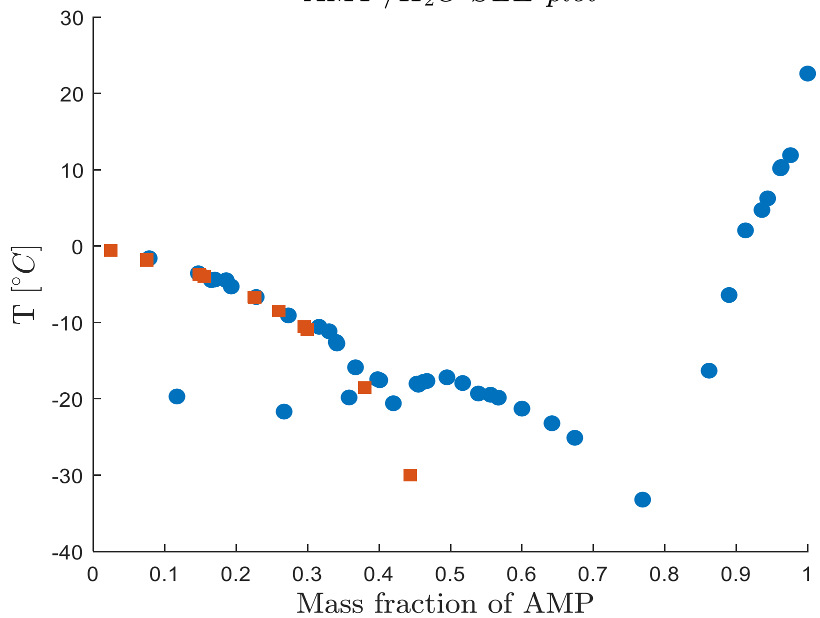
3. Vapor Liquid equilibrium data for diluted CESAR1 solvent.

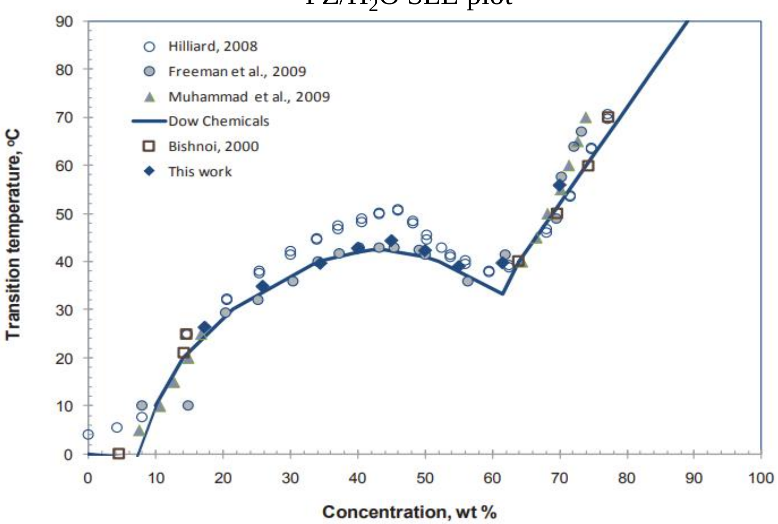
Thermodynamics: SLE Detected Gaps

Formation of slurries and solids downstream may create unforeseen process conditions:

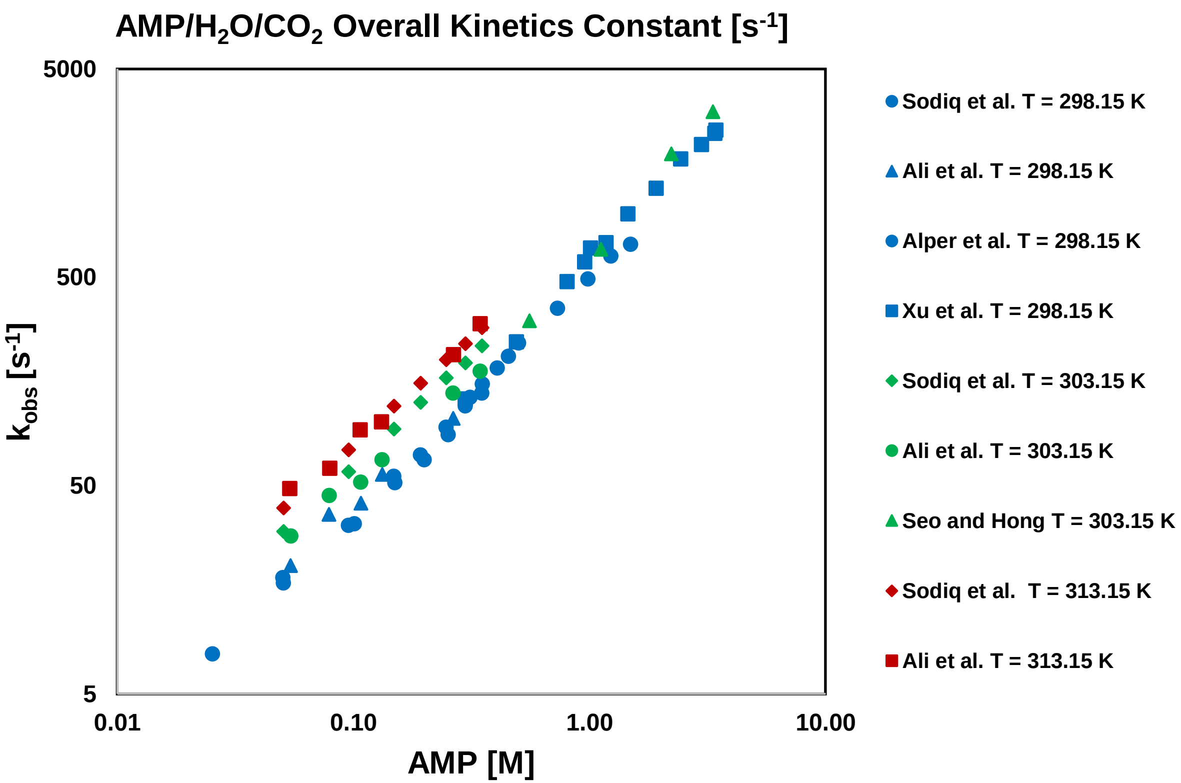
- Decrease equipment Efficiency
- Clogging
- Higher level of risk

- AMP Solid-Liquid Solubility Data ?
- PZ Solid-Liquid Solubility Data ✓
- AMP/PZ Solid-Liquid Solubility Data ?





Kinetics: AMP subsystem



First Order kinetics constant

$$r_{CO_2} = r_{CO_2-AMP} + r_{CO_2-OH^-}$$

$$r_{CO_2} = k_{2,AMP}[AMP][CO_2] + k_{OH^-}[OH^-][CO_2]$$

$$r_{CO_2} = \left(k_{2,AMP}[AMP] + k_{OH^-}[OH^-]\right)[CO_2]$$

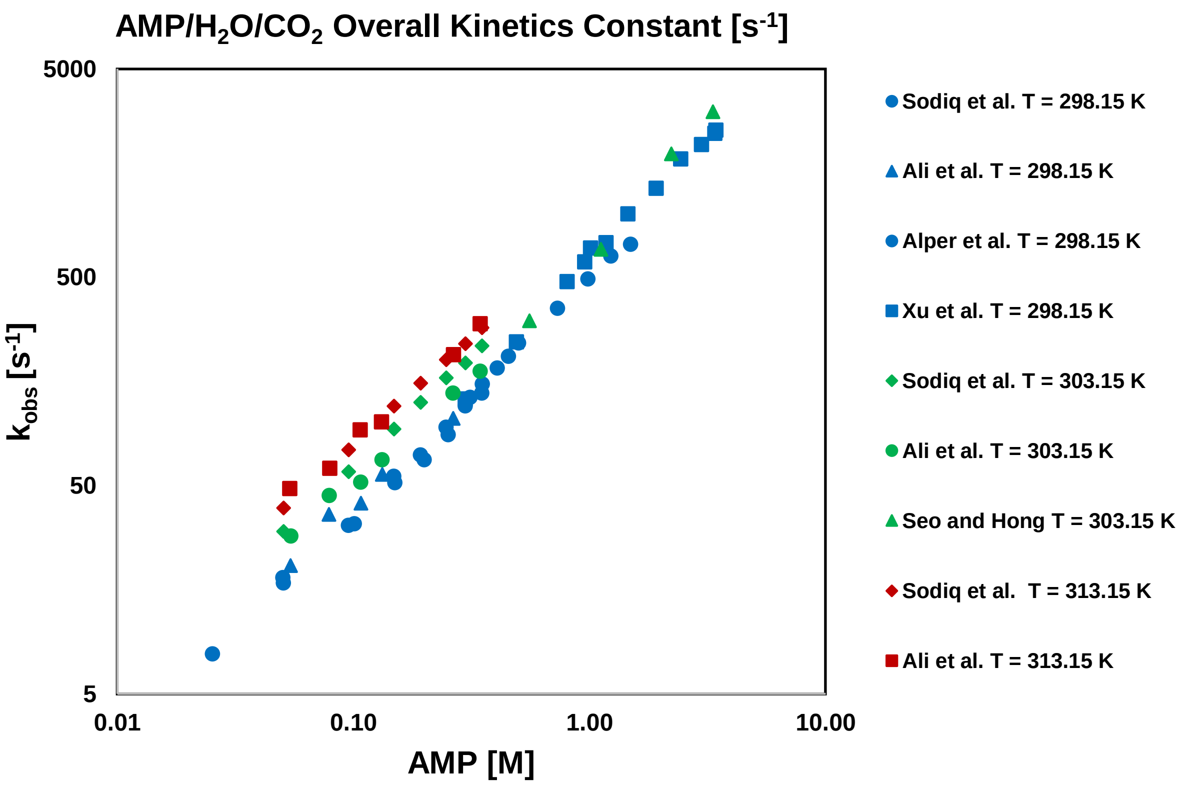
$$k_{obs} = k_{2,AMP}[AMP] + k_{OH^-}[OH^-]$$

Steric hindrance

Kinetics Mechanism

Less basic due to α-Methyl substitutions

Kinetics: AMP subsystem



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$$k_{obs} = k_{2,AMP}[AMP] + k_{OH^-}[OH^-]$$

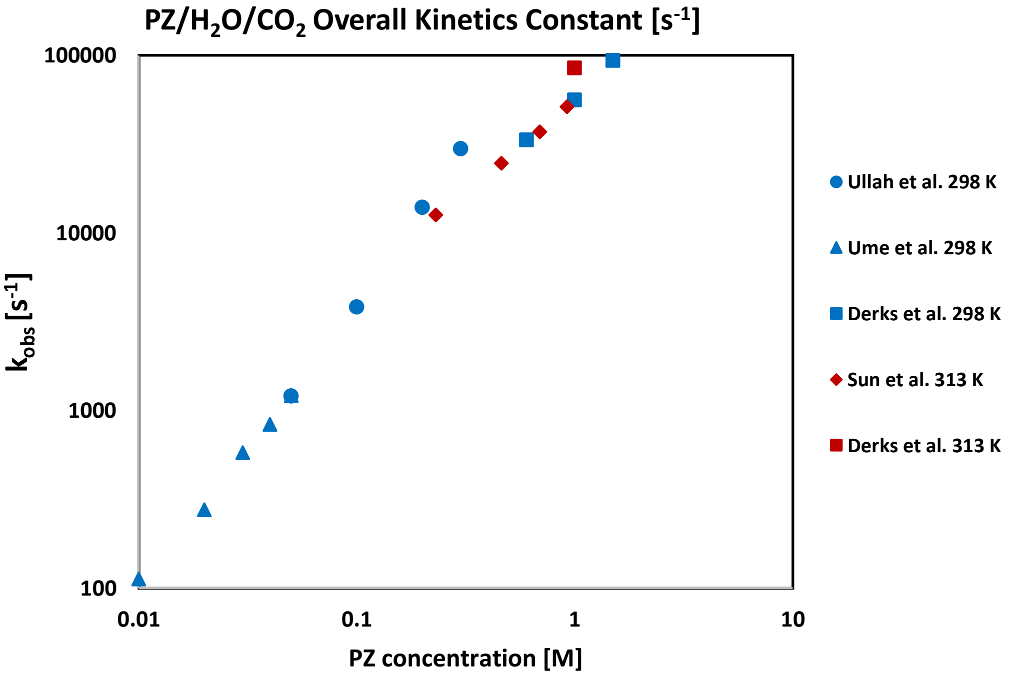
CO_2 unloaded measurements!

$$R_1)\ \boldsymbol{AMP + H_2O + CO_2 \rightleftarrows AMPCOO^- + H_3O^+}$$

$$R_2)\ \boldsymbol{AMP + H_2O + CO_2 \rightleftarrows HCO_3^- + AMPH^+}$$

Higher Loading ↓

Kinetics: PZ subsystem



First Order kinetics constant

$$r_{CO_2} = r_{CO_2-PZ} + r_{CO_2-OH^-}$$

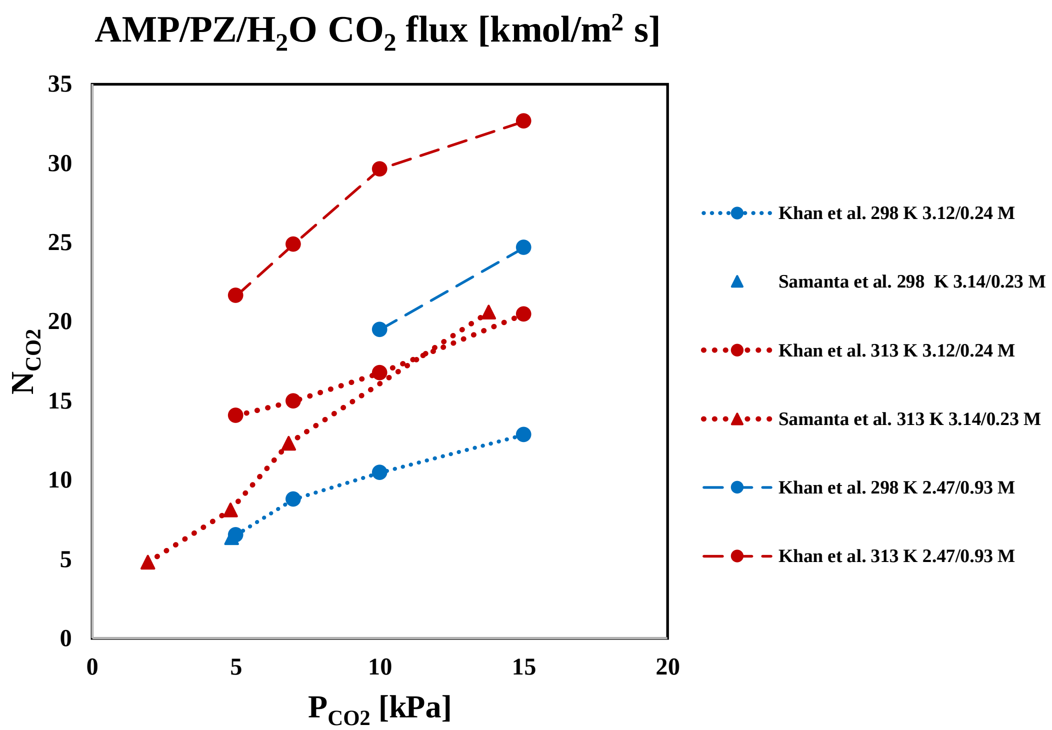
$$r_{CO_2} = k_{2,PZ}[PZ][CO_2] + k_{OH^-}\,[OH^-][CO_2]$$

$$r_{CO_2} = \left(k_{2,PZ}[PZ] + k_{OH^-}[OH^-]\right)[CO_2]$$

$$k_{obs} = k_{2,PZ}[PZ] + k_{OH^-}[OH^-]$$

Many data are available for CO_2-absorption kinetics in aqueous PZ solutions starting from CO_2-unloaded and CO_2-loaded solutions

Kinetics: AMP/PZ subsystem



First Order kinetics constant

$$r_{CO_2} = r_{CO_2-PZ} + r_{CO_2-OH^-} + r_{CO_2-AMP}$$

$$r_{CO_2} = k_{2,PZ}[PZ][CO_2] + k_{OH^-}[OH^-][CO_2] + \mathrm{k}_{2,\mathrm{AMP}}[\mathrm{AMP}][\mathrm{CO}_2]$$

$$r_{CO_2} = \left(k_{2,PZ}[PZ] + k_{OH^-}[OH^-] + k_{2,AMP}[AMP]\right)[CO_2]$$

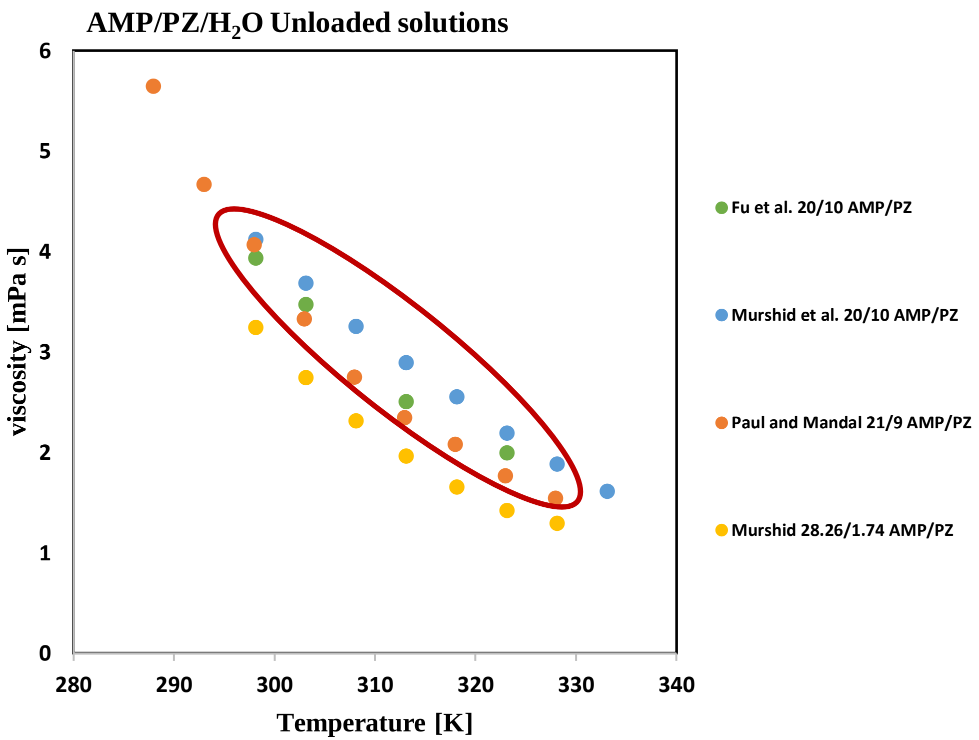
$$k_{ov} = k_{2,PZ}[PZ] + k_{OH^-}[OH^-] + k_{2,AMP}[AMP]$$

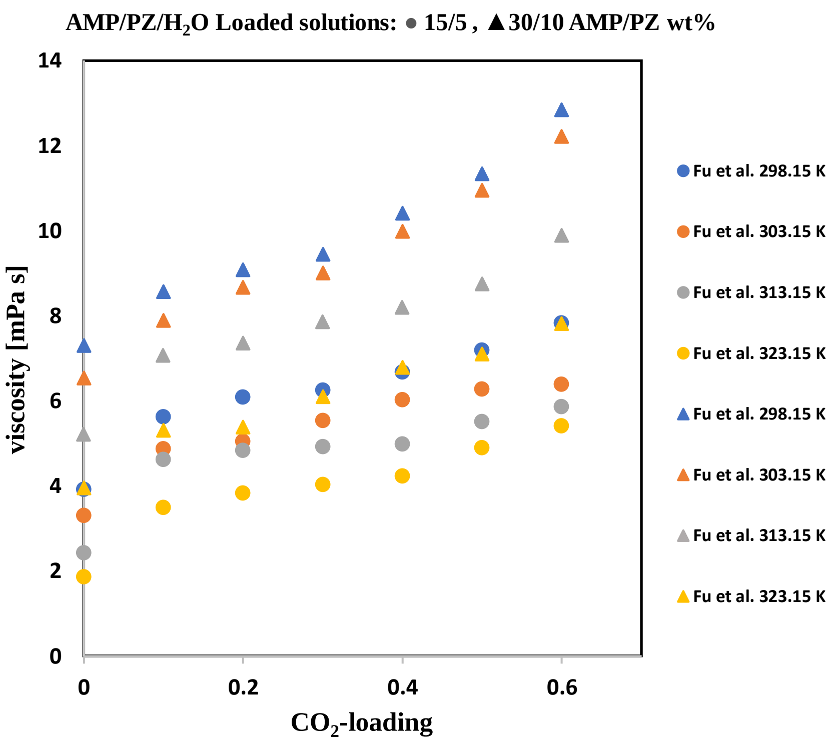
1. Data for blends available up to 1 M concentration of PZ.
2. Data available up to 40 °C.
3. Data available for CO_2-unloaded system.

Kinetics: Detected Gaps

1. Measurements for CO_2-Loaded aqueous AMP solutions.
2. Measurements for CO_2-Loaded and CO_2-unloaded CESAR1 solutions are required
3. Extend temperature framework for blend kinetics measurements.

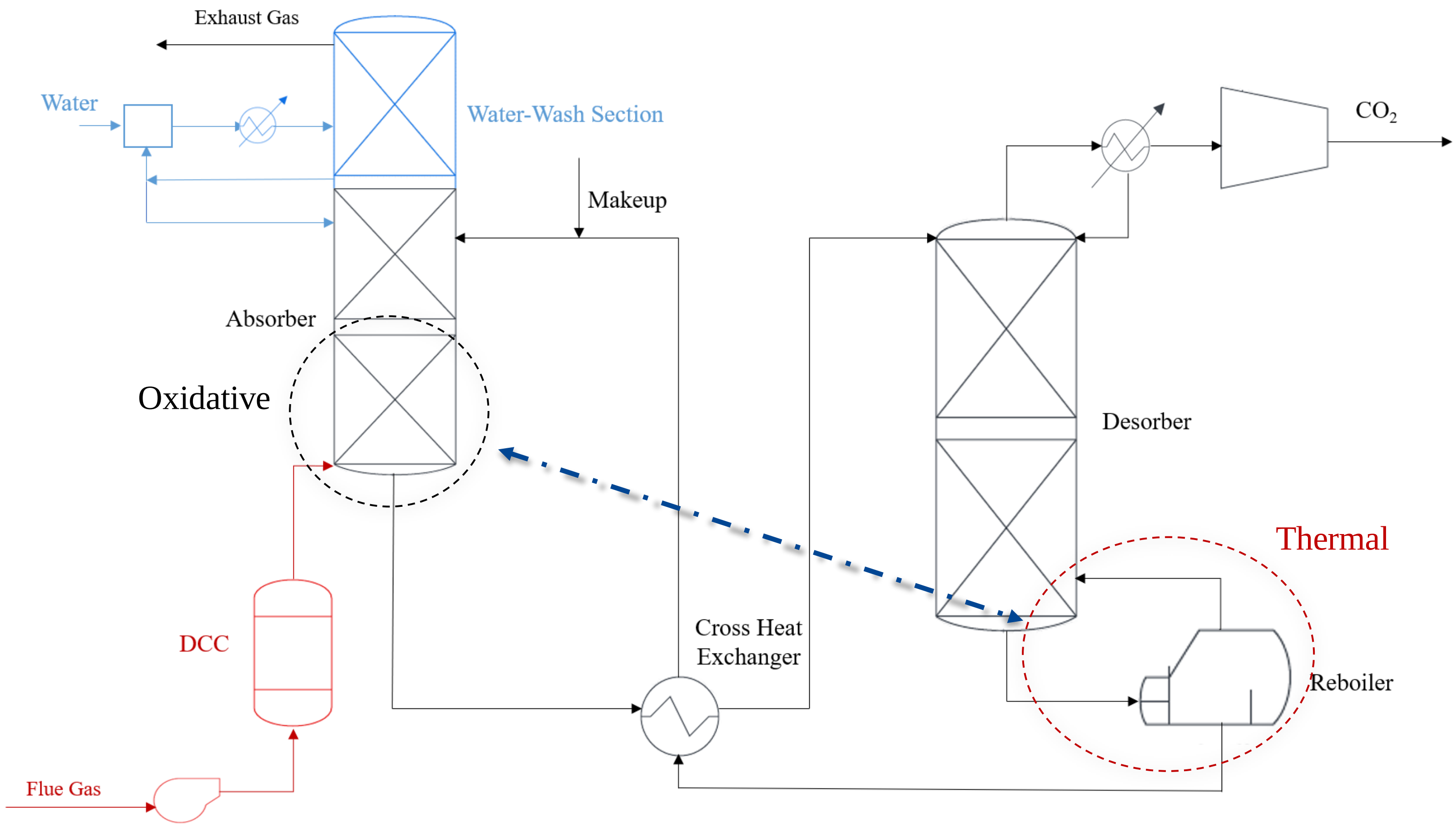
Viscosity: Detected Gaps



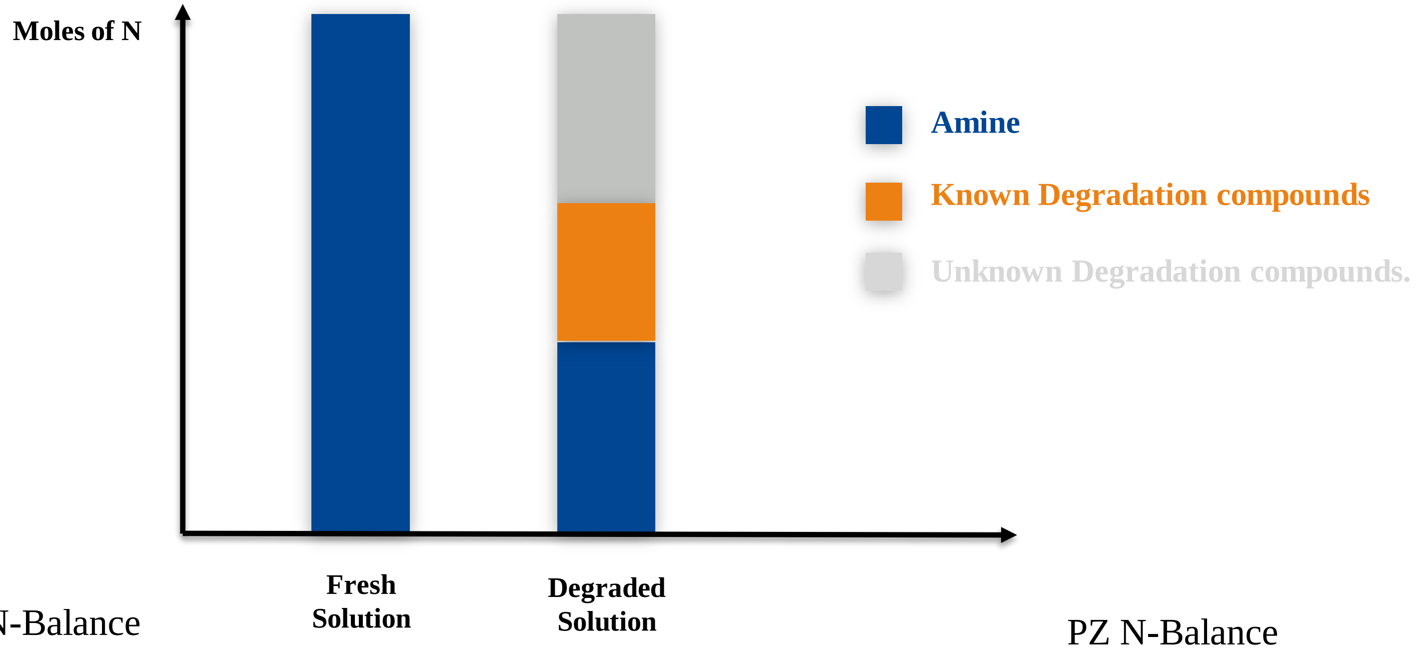


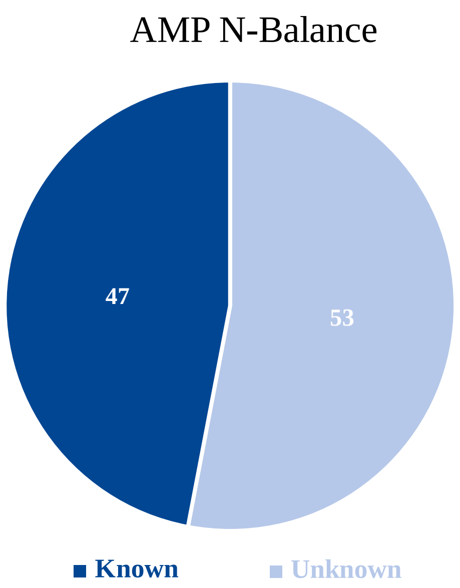
Data at CESAR1 concentration at CO_2-Loaded and CO_2-unloaded conditions are necessary

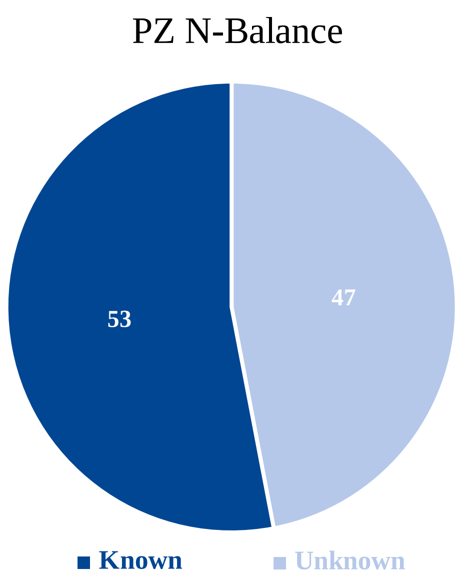
Amine Degradation



Degradation of AMP and PZ







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Main Gaps Qualitative Review

Legend

Available | Gaps detected | Not available

Property	AMP/H_2O	PZ/H_2O	$AMP/PZ/H_2O$	$AMP/H_2O/CO_2$	$PZ/H_2O/CO_2$	$AMP/PZ/H_2O/CO_2$
Density	Available	Available	Available	Gaps detected	Available	Gaps detected
Viscosity	Available	Available	Gaps detected	Not available	Available	Gaps detected
Diffusivity	Available	Gaps detected	Gaps detected	Not available	Not available	Not available
Kinetics	Available	Available	Gaps detected	Not available	Gaps detected	Not available
VLE	Available	Available	Available	Available	Available	Gaps detected
Speciation				Available	Available	Gaps detected
ΔH_{abs}				Available	Available	Available
$\mathcal{H}$	Available	Available	Gaps detected	Available	Not available	Not available
Degradation	Gaps detected	Gaps detected	Gaps detected	Gaps detected	Gaps detected	Gaps detected

QUESTIONS?
Thank you!

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