CCSI² Carbon Capture Simulation for Industry Impact

Development of Process Model of CESAR1 Solvent System and Validation with Large Pilot Data

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Presentation Outline

- Overview of CCSI² Program
- CESAR1 Solvent Model
  - Background
  - Model Development
  - Model Validation with TCM Pilot Data
- Summary and Future Work

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CCSI² – Carbon Capture Simulation for Industry Impact

- **CCSI² Mission: Accelerate CO_2 Capture Research and Development**
  - Collaboration among national laboratories, academia, and industry
    - Identify novel CCS technologies
    - Reduce scale-up risk through advanced modeling capabilities
  - Development of CCS models, including solvents, sorbents, and membrane technologies
  - Further development of CCSI Computational Toolset
  - FOQUS enables advanced modeling capabilities for process analysis

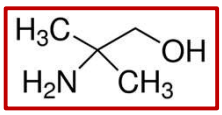
https://github.com/CCSI-Toolset/foqus

https://github.com/CCSI-Toolset/

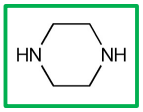
CESAR1 Solvent System

CESAR program funded by EU (2008-2011) tested two novel CCS solvents

- CESAR1: Aqueous blend of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ):



27 wt% AMP



13 wt% PZ

  - Blended system combines advantages of PZ (high reactivity) and AMP (low heat requirement for solvent regeneration)
  - Promising alternative to aqueous MEA as baseline for CO_2 capture applications
- CESAR2: aqueous ethylenediamine (EDA)

Model Development Overview

- Combined PZ-H_2O-CO_2 and AMP-H_2O-CO_2 thermodynamic models developed by Aspen Tech
- Regressed parameters for PZ-AMP interaction to fit thermodynamic data for PZ-AMP-H_2O-CO_2 system
- Adjusted activity-based kinetics expressions for consistency with thermodynamic model
- Correlations used to characterize packing (FLEXIPAC 2X)
  - Mass Transfer and Interfacial Area (BRF-85)
  - Liquid Holdup (BRF-92)
- **Model validated with seven steady-state data cases from Technology Centre Mongstad for natural gas-based flue gas conditions:**
  - **CO_2 capture percentage predicted with average error of 2.4%**
  - **Specific reboiler duty predicted with average error of 4.9%**

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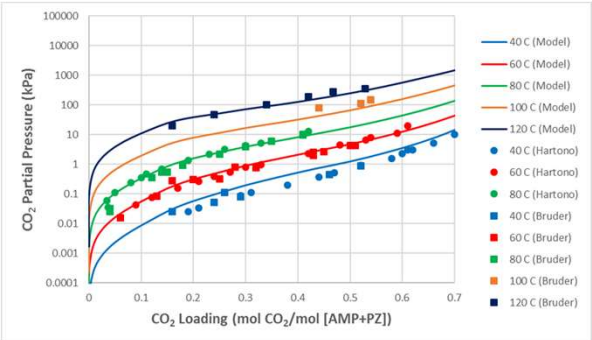
Thermodynamic Model

- CO_2 Partial Pressure (AMP-PZ-H_2O-CO_2 System)



Parameters Regressed:

NRTL/1 (AMP/PZ)	-24.383
NRTL/2 (AMP/PZ)	10000

$A_{ij} = A_{ji}$ and $B_{ij} = B_{ji}$ assumed for AMP/PZ pair

Data Sources:

Hartono et al. (2021). New solubility and heat of absorption data for CO_2 in blends of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) and a new eNRTL model representation, *Fluid Phase Equilibria* 550: 113235. https://doi.org/10.1016/j.fluid.2021.113235

Brúder et al. (2011). CO_2 capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol, *Chem Eng Sci* 66: 6193-6198. https://doi.org/10.1016/j.ces.2011.08.051

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Reaction Kinetics and Equilibrium Chemistry

No	Description	Formula
1	Water Dissociation	$2\ H_2O \leftrightarrow H_3O^+ + OH^-$
2	Bicarbonate Formation	$CO_2 + OH^- \leftrightarrow HCO_3^-$
3	Carbonate Formation	$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$
4	AMP Protonation	$AMP + H_3O^+ \leftrightarrow AMPH^+ + H_2O$
5	AMP Carbamate Formation	$AMP + CO_2 + H_2O \leftrightarrow AMPCOO^- + H_3O^+$
6	PZ Protonation	$PZ + H_3O^+ \leftrightarrow PZH^+ + H_2O$
7	PZ Carbamate Formation	$PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+$
8	PZ Carbamate Protonation	$PZCOO^- + H_3O^+ \leftrightarrow PZH^+COO^- + H_2O$
9	PZ Bi-Carbamate Formation	$PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+$

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7	**PZ Carbamate Formation**	$\boldsymbol{PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+}$
8	PZ Carbamate Protonation	$PZCOO^- + H_3O^+ \leftrightarrow PZH^+COO^- + H_2O$
9	**PZ Bi-Carbamate Formation**	$\boldsymbol{PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+}$

Denotes kinetic reaction

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Kinetic Model Refinement

	$k_{0f,j}$ / $k_{0r,j}$ (kmol/s/m^3)	$E_{f,j}$ / $E_{r,j}$ (cal/mol)	Source
Bicarbonate Formation			
Forward	1.33e17	13249	[1]
Reverse	6.63e16	25656	[1]
AMP Carbamate Formation			
Forward	1e9	8202	[2]
Reverse	1.52e20	12693	[2]
PZ Carbamate Formation			
Forward	1.7e10	319	[1]
Reverse	2.08e22	10610	This work
PZ Bi-Carbamate Formation			
Forward	1.04e14	8038	[1]
Reverse	1.73e24	14092	This work

$$K_j = \exp\left(\frac{-\Delta G_{rxn,j}}{RT}\right) = \prod a_i{}^{\nu_{ij}}$$

$$k_{f,j} = k_{0f,j} \exp\left(\frac{-E_{f,j}}{RT}\right)$$

$$k_{\mathrm{r},j} = k_{0\mathrm{r},j} \exp\left(\frac{-E_{\mathrm{r},j}}{RT}\right)$$

Parameters calibrated to ensure:

$$K_j = \frac{k_{f,j}}{k_{r,j}}$$

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CESAR1 System Data Collected at TCM

Photograph from www.tcmda.com

- Seven data sets collected in 2019 during the ALIGN-CCUS campaign at Technology Centre Mongstad, the world's largest facility for testing CCS systems
- Flue gas composition: ~3.5 % CO_2 by volume (natural gas combined cycle turbine flue gas)
- Includes variation in:
  - Absorber packing height: 12/18/24 meter
  - CO_2 capture percentage: 90-98.5%
  - L:G ratio (mass): 0.57 – 1.09

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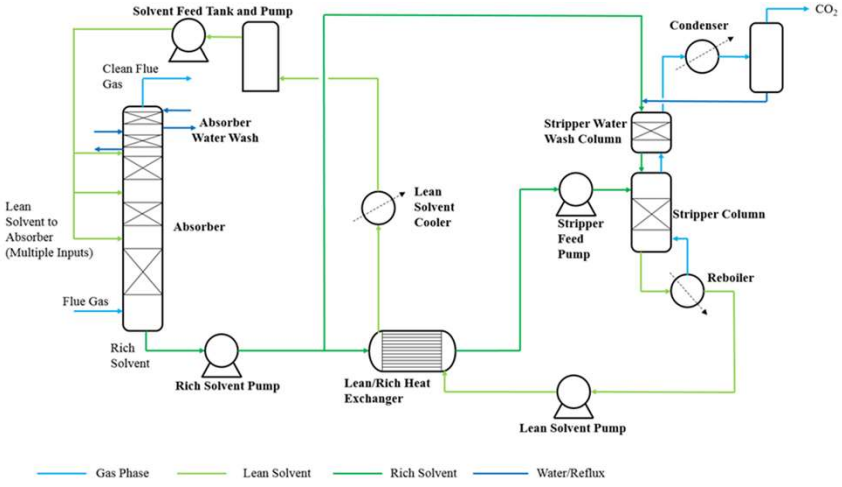
Schematic of TCM Pilot Plant



- Multiple solvent inlets for absorber column enable testing with variable packing height (12, 18, or 24 meter)
- Portion of rich solvent (~20%) bypassed from lean/rich heat exchanger and heated in stripper water wash column

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Process Data

Case Name	C5	D5	E1	F4	AA2	BB3	A5
Absorber Packing Height (m)	18	18	12	18	24	24	24
Flue Gas Flowrate (kg/hr)	59853	59803	59821	70675	60101	60086	60451
Absorber Liquid: Gas Mass Ratio	0.66	0.92	1.09	0.57	0.74	0.58	0.66
Lean CO_2 Loading (mol CO_2/mol alkalinity)	0.135	0.109	0.147	0.087	0.135	0.049	0.176
Rich CO_2 Loading (mol CO_2/mol alkalinity)	0.404	0.314	0.312	0.402	N/A	0.415	0.454
Lean Solvent Molality (AMP/PZ)	5.206/ 2.616	5.077/ 2.669	4.907/ 2.574	5.022/ 2.470	5.460/ 2.482	5.541/ 2.492	4.490/ 2.314
Flue Gas Temperature (°C)	40.00	40.12	40.15	40.20	40.13	40.17	30.43
Stripper Pressure (kPa)	191.9	191.9	191.8	221.4	192.0	192.1	191.4
CO_2 Capture Percent	90.37	97.73	90.69	90.16	92.31	98.44	90.37
Specific Reboiler Duty (MJ/kg CO_2)	3.450	4.531	4.482	3.423	3.514	3.926	3.198

Data set includes:

- Variation in absorber height
  - 3 Beds (24 m): AA2,BB3, A5
  - 2 Beds (18 m): C5, D5, F4
  - 1 Bed (12 m): E1
- Testing with lower flue gas temperature: A5
- Testing with higher stripping pressure: F4
- CO_2 capture levels above 95%: D5, BB3

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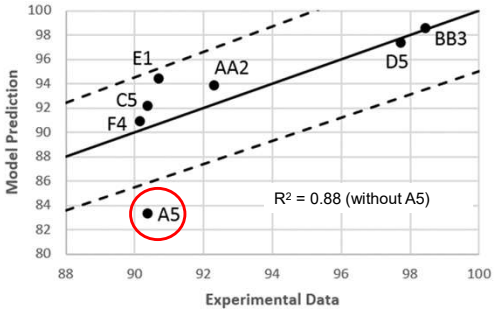
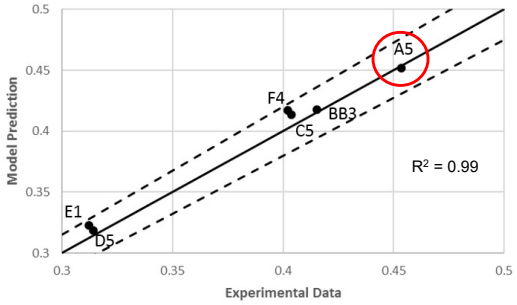
Model Validation - Absorber

CO_2 Capture Percentage



Rich Solvent CO_2 Loading



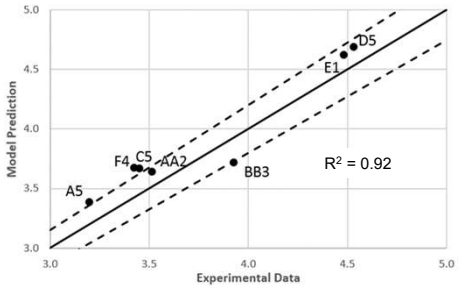
Suspected data uncertainty with Case A5 due to good fit for rich loading vs. relatively poor fit for CO_2 capture

Dashed lines represent ±5% error

- CO_2 capture percentage predicted with average error of 2.4% (maximum of 7.7% for Case A5)
  - Average error is 1.5% if Case A5 is omitted
- Rich solvent CO_2 loading predicted with average error of 2.0% (maximum of 3.8% for Case F4)

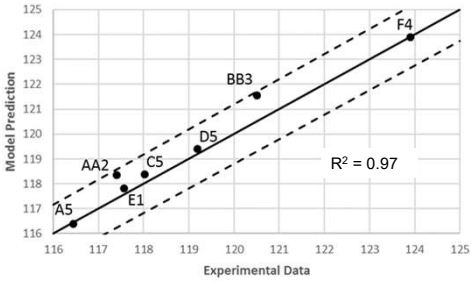
Model Validation - Stripper

Specific Reboiler Duty (MJ/kg CO_2)



Dashed lines represent ±5% error

Lean Solvent Temperature (°C)



Dashed lines represent ±1% error

- Specific reboiler duty predicted with average error of 4.9% (maximum of 7.2% for Case F4)
- Lean solvent temperature predicted with average error of 0.3% (maximum of 0.9% for Case BB3)

Summary and Conclusions

- Model of CESAR1 system developed and validated TCM process data
  - Absorber: CO_2 capture predicted with average percent error of 2.4% and rich loading with average error of 2.0%
  - Stripper: SRD predicted with average percent error of 4.9% and lean solvent outlet temperature predicted with <1% error for all cases
- Future Work
  - Public, open-source release steady-state model to CCSI Toolset
  - Parametric uncertainty quantification in property and process sub-models
  - Application in Sustainable OPEration of post-combustion Capture plants (SCOPE) program: Modeling of water wash section for quantifying solvent emissions

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Carbon Capture Simulation for Industry Impact

For more information
https://www.acceleratecarboncapture.org/

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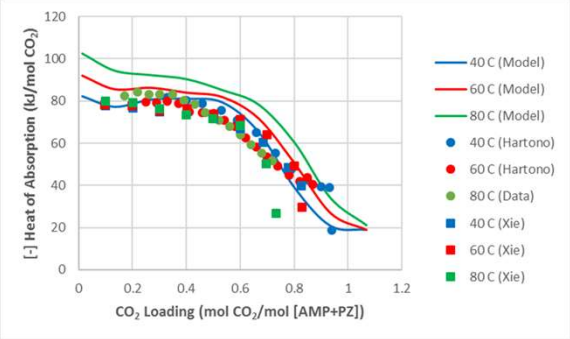
Backup Slides

Thermodynamic Model

- Heat of Absorption(AMP-PZ-H_2O-CO_2 System)



Heat of absorption calculated from energy balance on mixing a differential amount of CO_2 with loaded solvent

Data Sources:

Hartono et al. (2021). New solubility and heat of absorption data for CO_2 in blends of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) and a new eNRTL model representation, *Fluid Phase Equilibria* 550: 113235. https://doi.org/10.1016/j.fluid.2021.113235

Xie et al. (2013). Measurement of heat of CO_2 absorption into 2-amino-2-methyl-1-propanol (AMP)/piperazine (PZ) blends using differential reaction calorimeter, *Energy Procedia* 37: 826-833. https://doi.org/10.1016/j.egypro.2013.05.175

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