DOCCSS Support for PNNL CO2BOLs Solvents

Zhijie (Jay) Xu, Pacific Northwest National Lab (PNNL)
Sham Bhat, Los Alamos National Lab (LANL)
Gary Rochelle, University of Texas at Austin (UT)

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Introduction

Objective

Understanding transformational solvents → Predicting performance via multiscale modeling → Targeting optimal system design

Computational Tools:

- Uncertainty Quantification (UQ) analysis for full-scale process model
- Computational Fluid Dynamics (CFD) model for device-scale mass transfer
- Lost work analysis of water-lean solvent CO2BOL

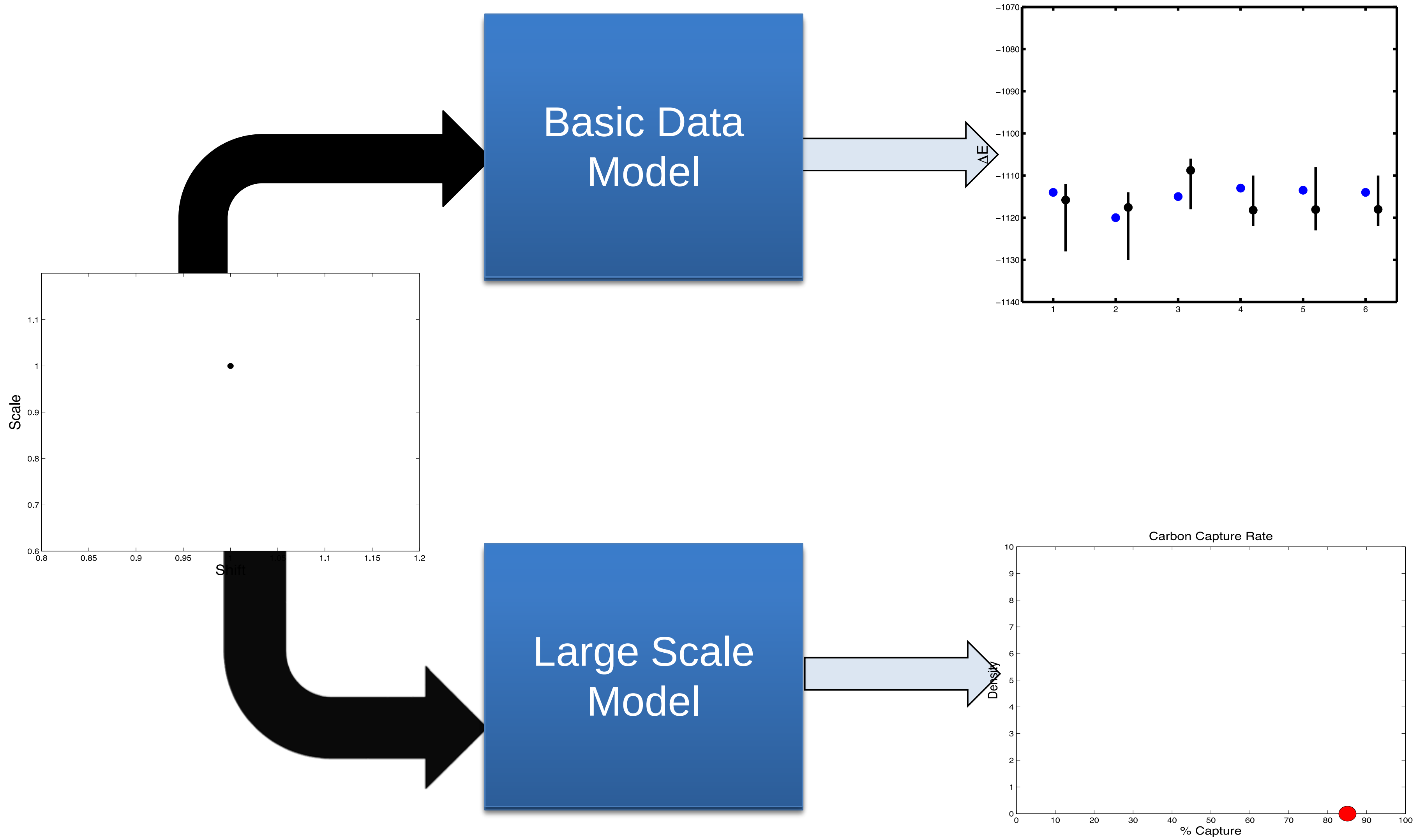
Outline

- **UQ analysis for full scale process model with CO2BOL**

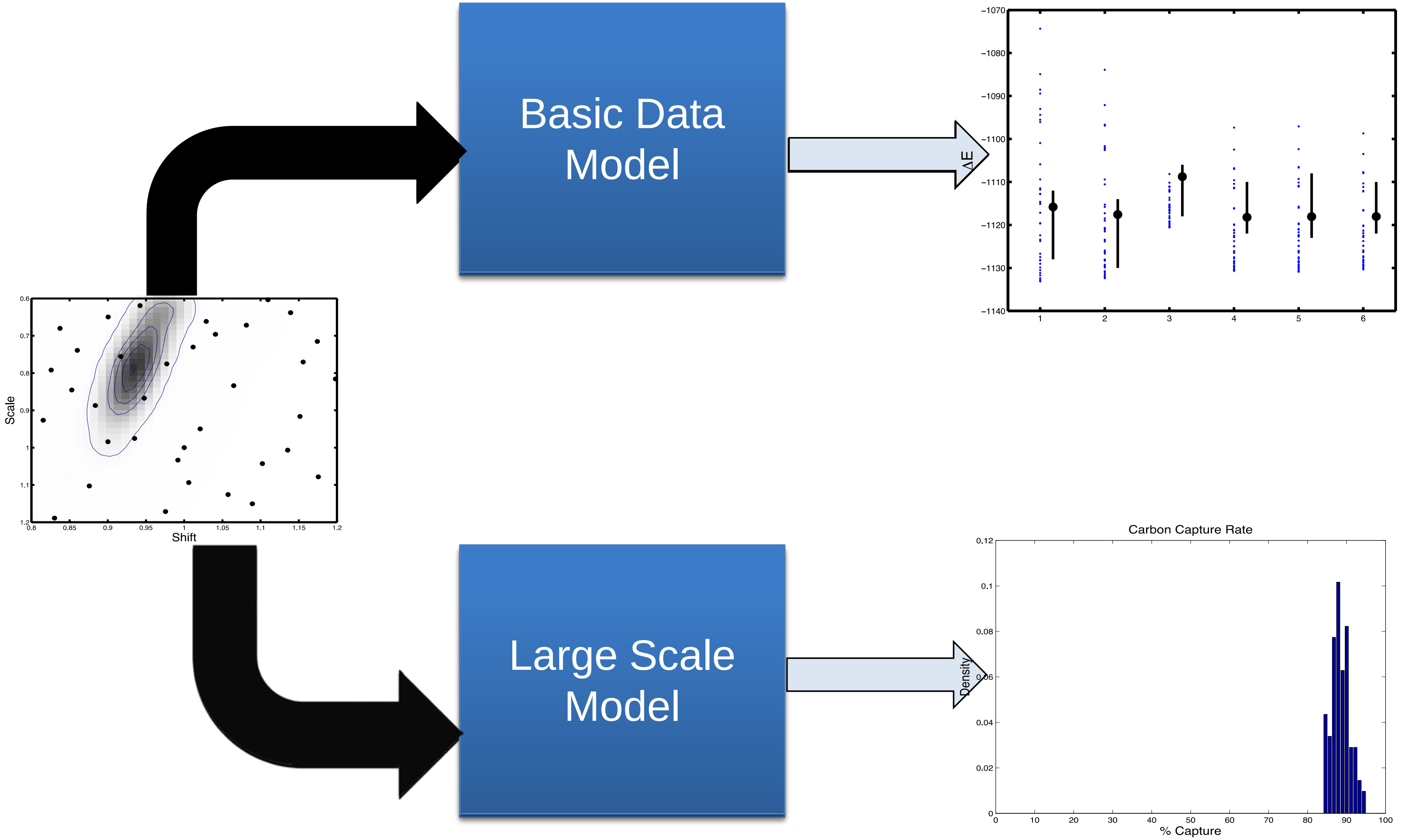
- **CFD models for mass transfer of CO2BOL**
  - Model description
  - Model validation
  - Preliminary results for CO2BOL

- **Lost work analysis of water-lean solvent CO2BOL**

Standard Practice: Least Squares Fit



Uncertainty Quantification



Procedure for using UQ methods

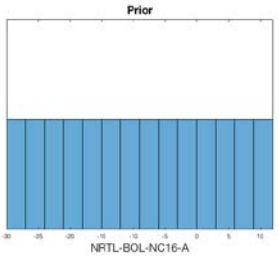
1. At Each Stage, Identify Relevant System Information and Ranges for Parameters/Inputs
2. Identify Prior Distributions for Model Parameters
3. Develop a "Space-Filling" Design to Train Surrogate Model
4. Run Model (Aspen) at Designed Parameter/Input Values Adjusting if Needed
5. UQ Analysis: Calibrate the Model to Data to Compute Parameter Distributions
6. Get Output Predictions with Uncertainty
7. Propagate Results to Full-Scale Model

UQ: Working with Novel Solvent Systems

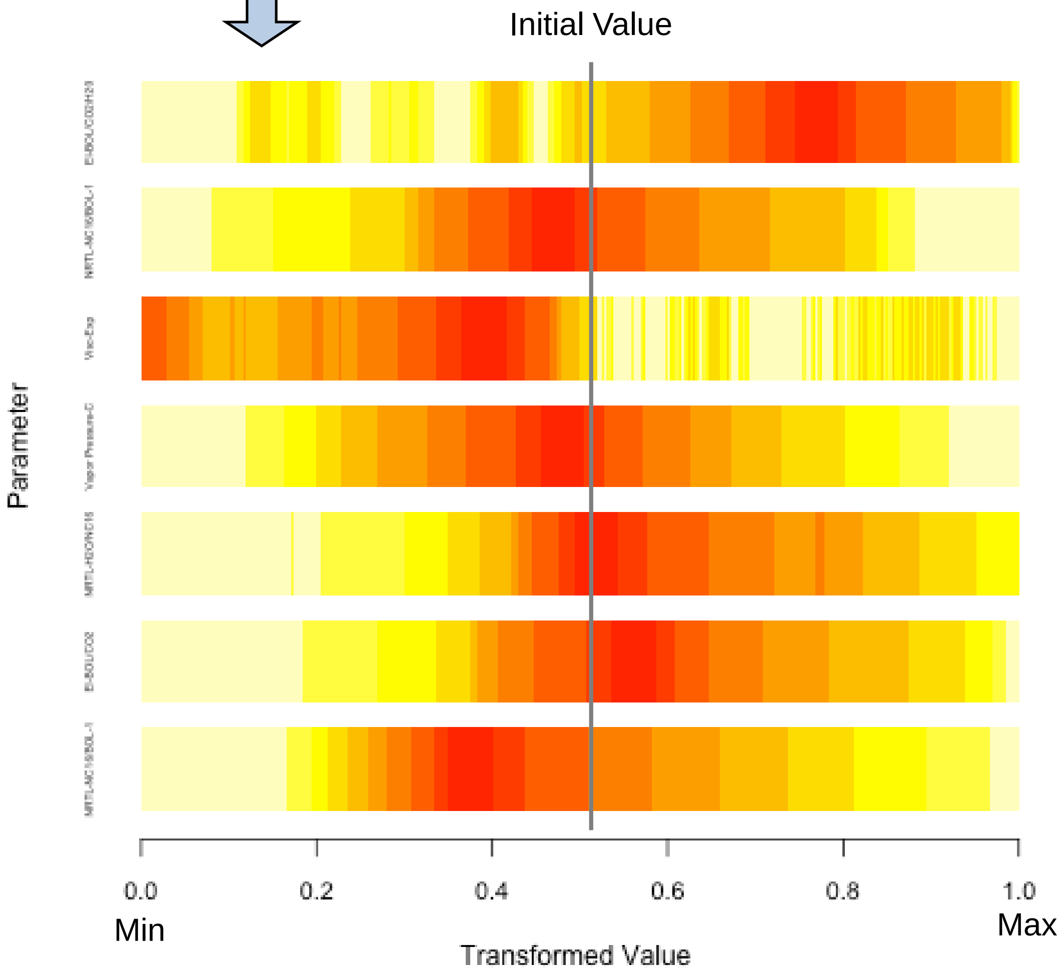
- **UQ Analysis is Done at Each Sub-Model as Well as Full-Scale Model**
  - Divided into Sub-Models such as Thermodynamics, Viscosity, Mass Transfer, Kinetics, etc.
- **UQ Requires Full Access to the Model**
  - When Subroutines are Used, Parameters Need to be Aspen-Accessible
- **Parameter Selection for CO_2BOLs***
  - >150 System-Specific Parameters Reduced to 41
- **What do you Want to Learn?**
  - Primary Objectives From UQ
    - Data Gaps
    - Uncertainty in Predictions of Carbon Capture or Energy Penalty
    - Accuracy of Model at Different Scales

***Further Details for CO_2BOLs Analysis at Tuesday Poster Session**

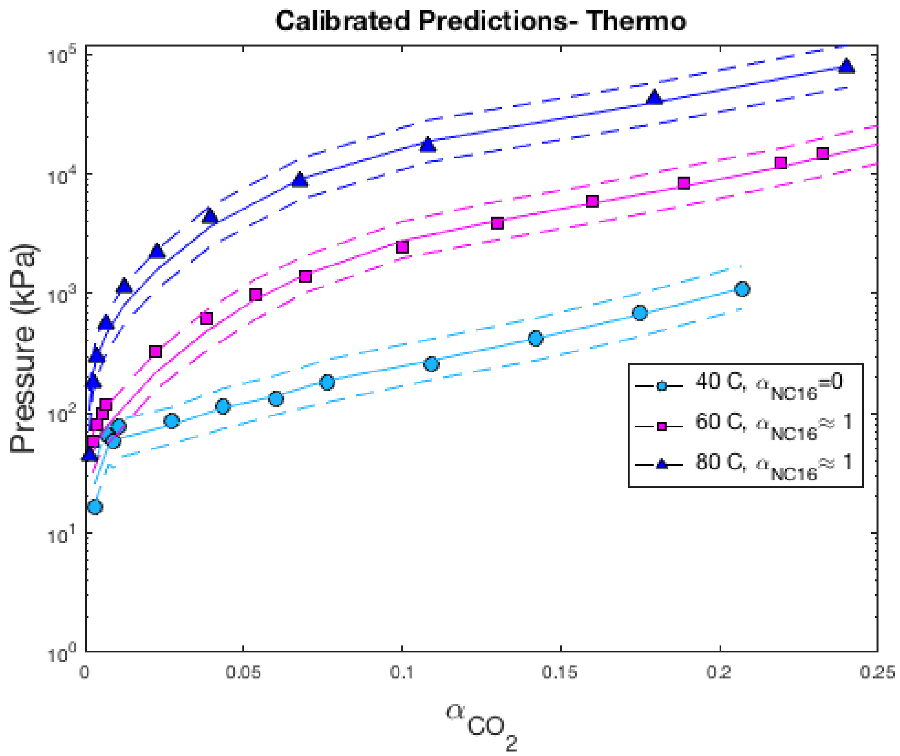
CO_2BOLs Thermodynamics Sub-model Results



- Begin With Parameter Distribution (Typically Uniform) and Determine New Distribution From Data
- Red Indicates High Likelihood of Parameter Value



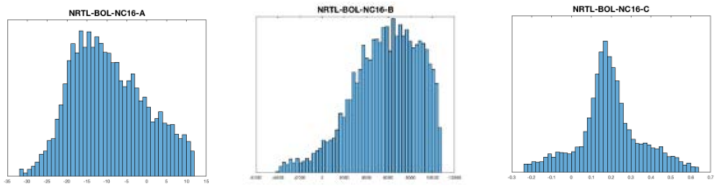
Predictions



Predictions (solid line) and 95% Uncertainty Bounds for Predictions (Dotted) Largely Covers PTx Data (Dots) for CO_2/BOL/NC16 System

Initial UQ Results for Full-Scale Model

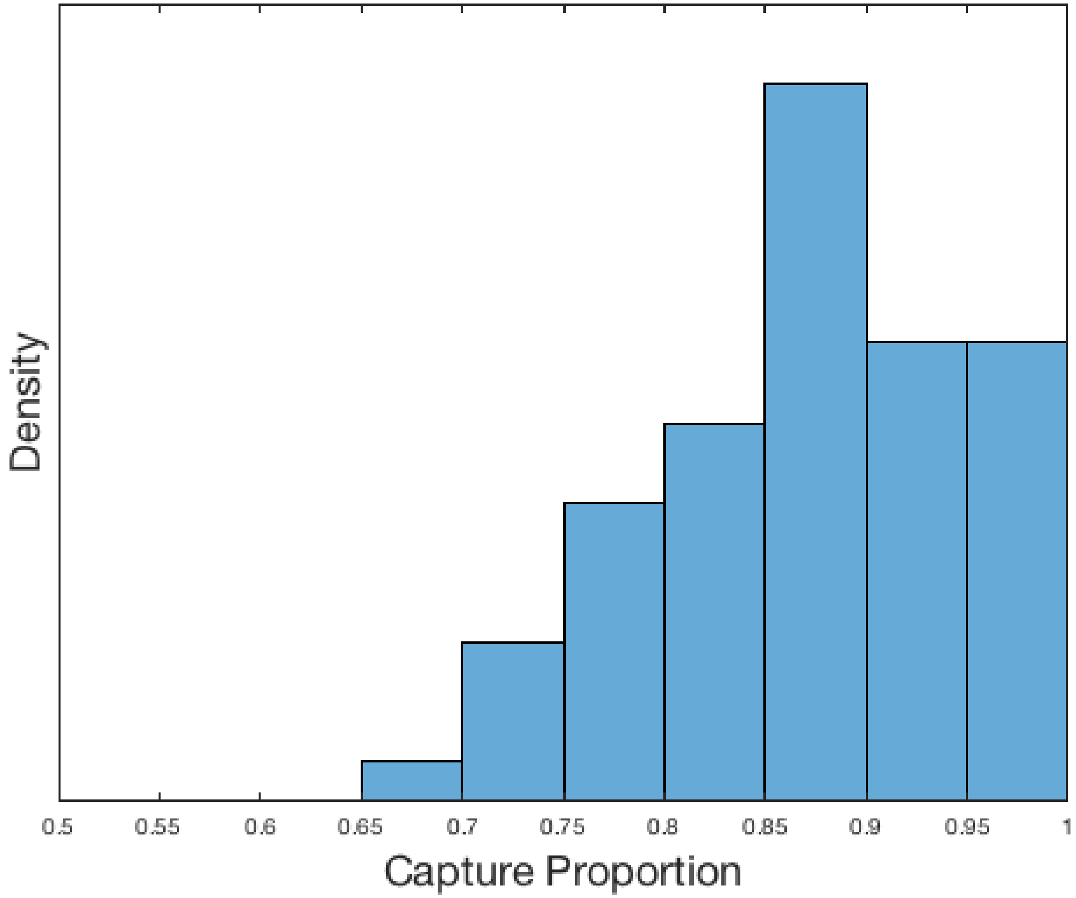
Sub-Model Posterior Parameter Distributions



Propagation of Sub-Model Results to Full-Scale Model

Full-scale Model

Full-Scale Model CO_2 Capture Predictions



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CFD Models for Solvent Absorption in Packed Column

Challenges:

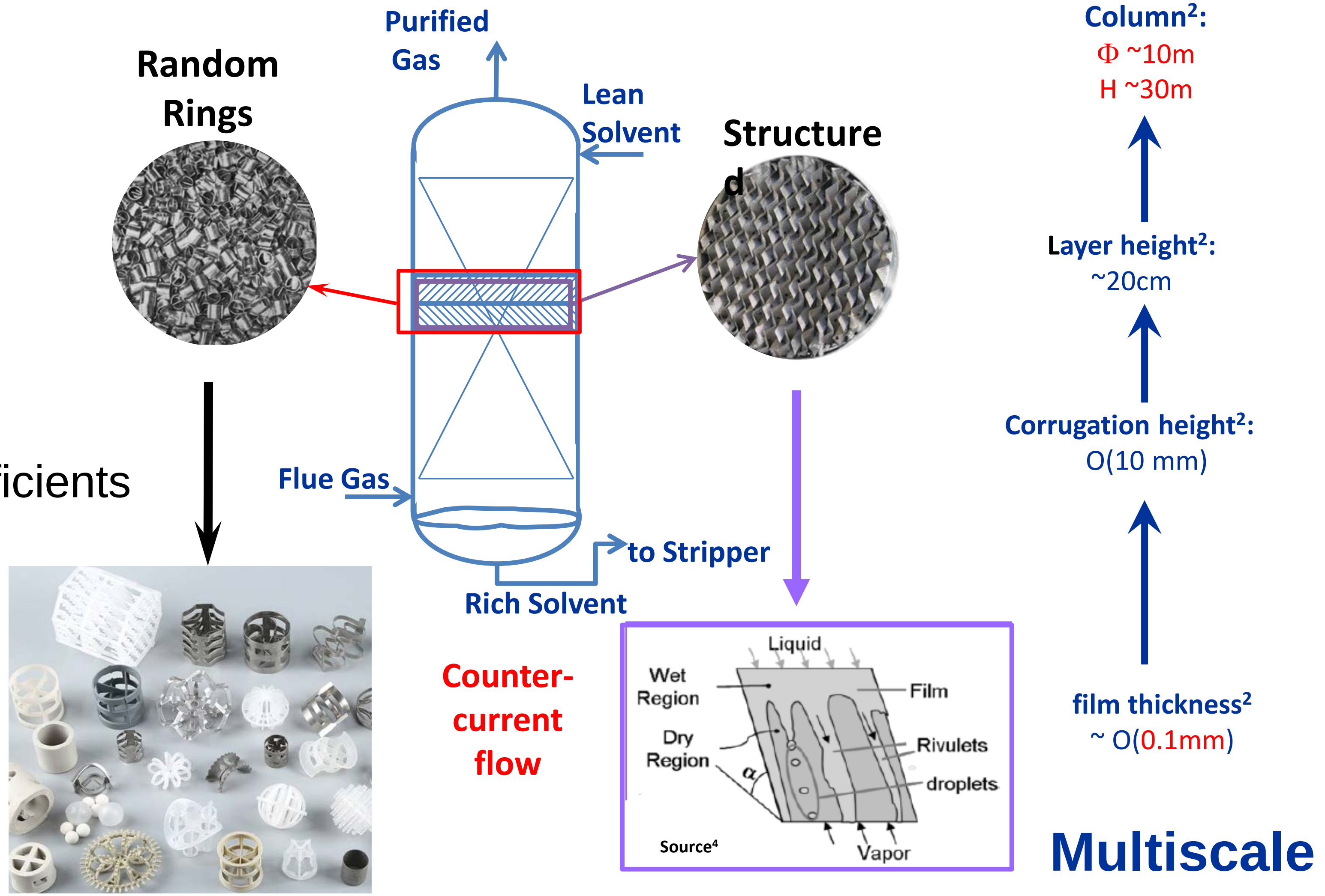
– Multiscale & Multiphysics
– Extremely complex geometry

Objectives: Using CFD to

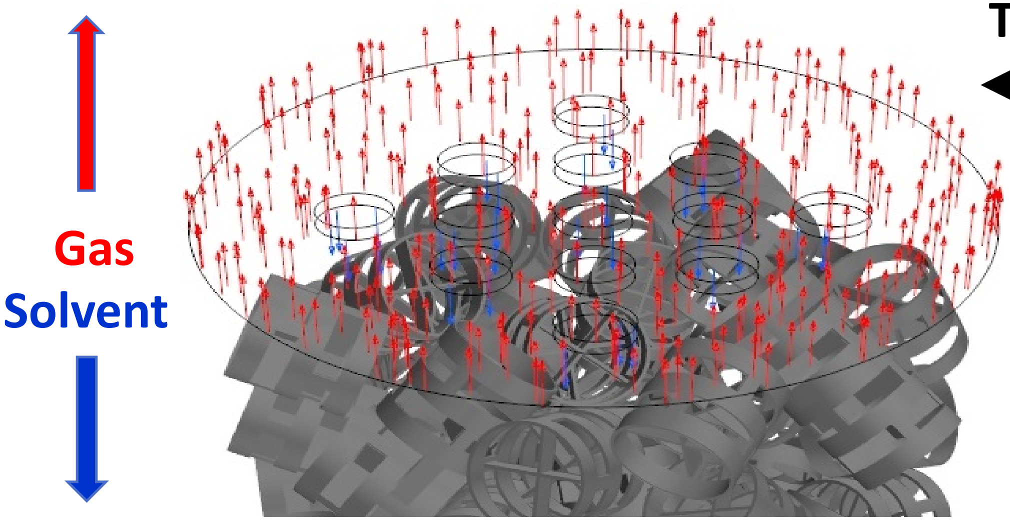
– Study the local hydrodynamics
– directly model the mass transfer coefficients
– directly model the mass transfer area

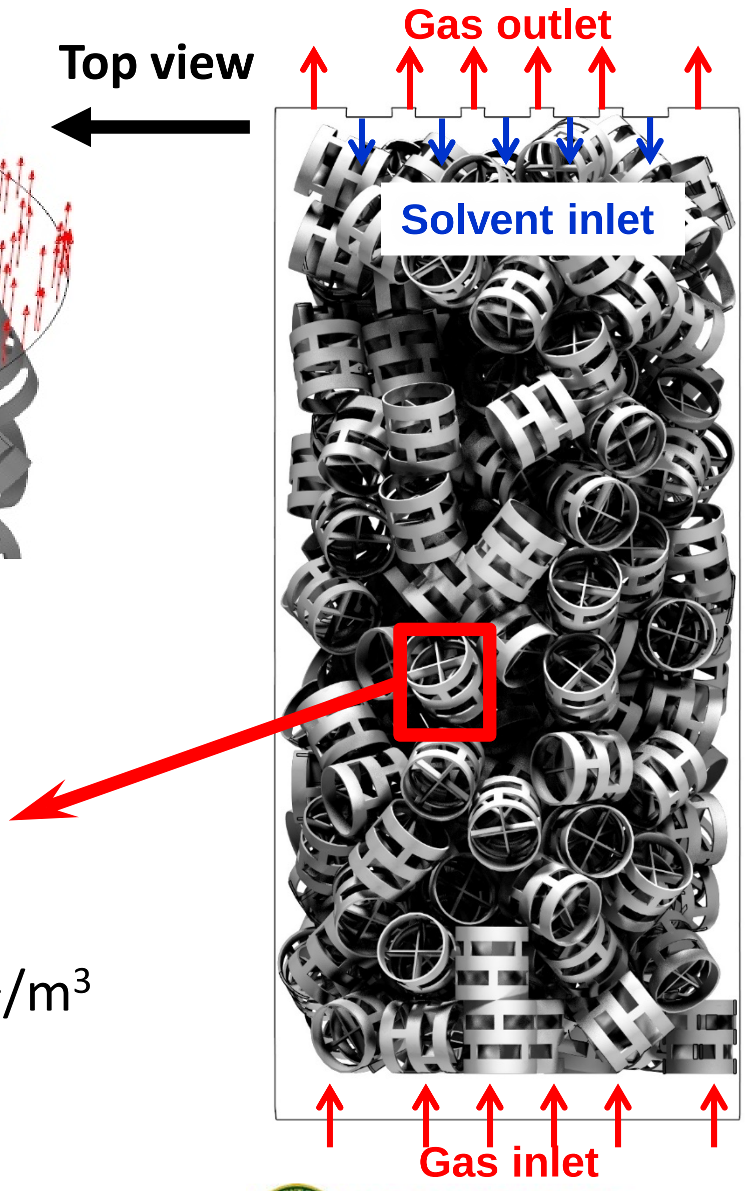
Methods:

- Multiphase flow using Volume of Fluid (VOF) method



Model Description: Countercurrent Flow in Random Packing





Packed column

- Column diameter: 100 mm
- Column height: 200 mm
- Number of Pall rings: 160

Boundary conditions

− 13 solvent dripping inlets (10 mm diameter)

− No slip ring surface

− Prescribed gas flow rate at outlet

Design of pall ring

- Diameter: 16 mm
- Height: 16 mm
- Thickness: 0.5 mm
- Specific Area: 282 m^2/m^3

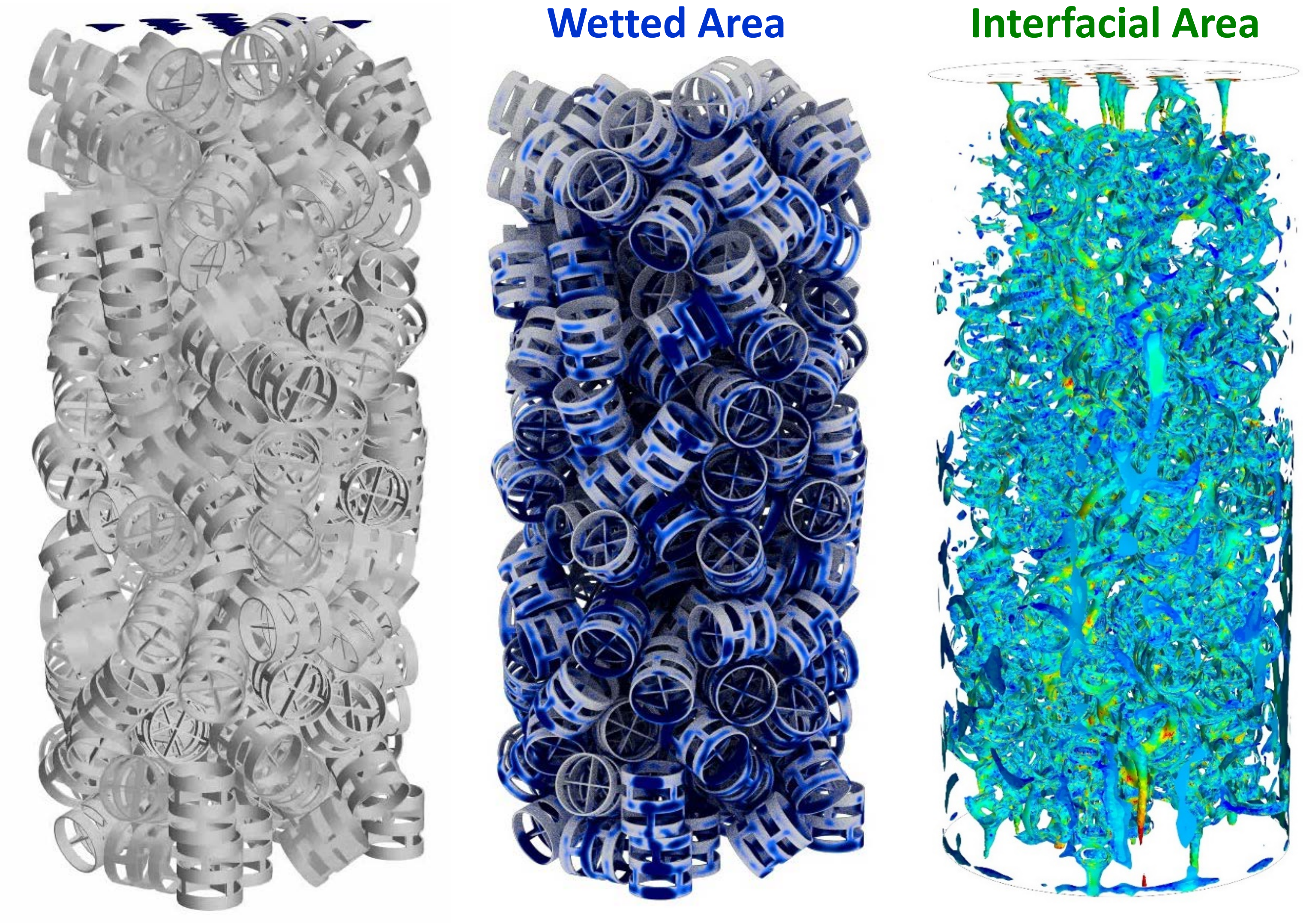
Model Validation: Hydrodynamics for Countercurrent Flow

Solvent Properties (30% MEA)

Physical Properties	
Density ρ (kg/m^3)	1000
Viscosity μ (cP)	2.46
$D_{CO_2}[l]$ (m^2/s)	1.0×10^{-9}
$D_{CO_2}[g]$ (m^2/s)	1.0×10^{-5}
Reaction Rate	5.96
Henry's constant (Dimensionless)	1.228
Surface Tension (N/m)	0.065
Contact angle (°)	40

Computational cost

- 96 cores on PNNL PIC HPC
- 7 CPU hours for every 1s solution



Liquid Load: 40 m^3/m^{2}h   Gas Load: 0.27 Pa$^{1/2}$

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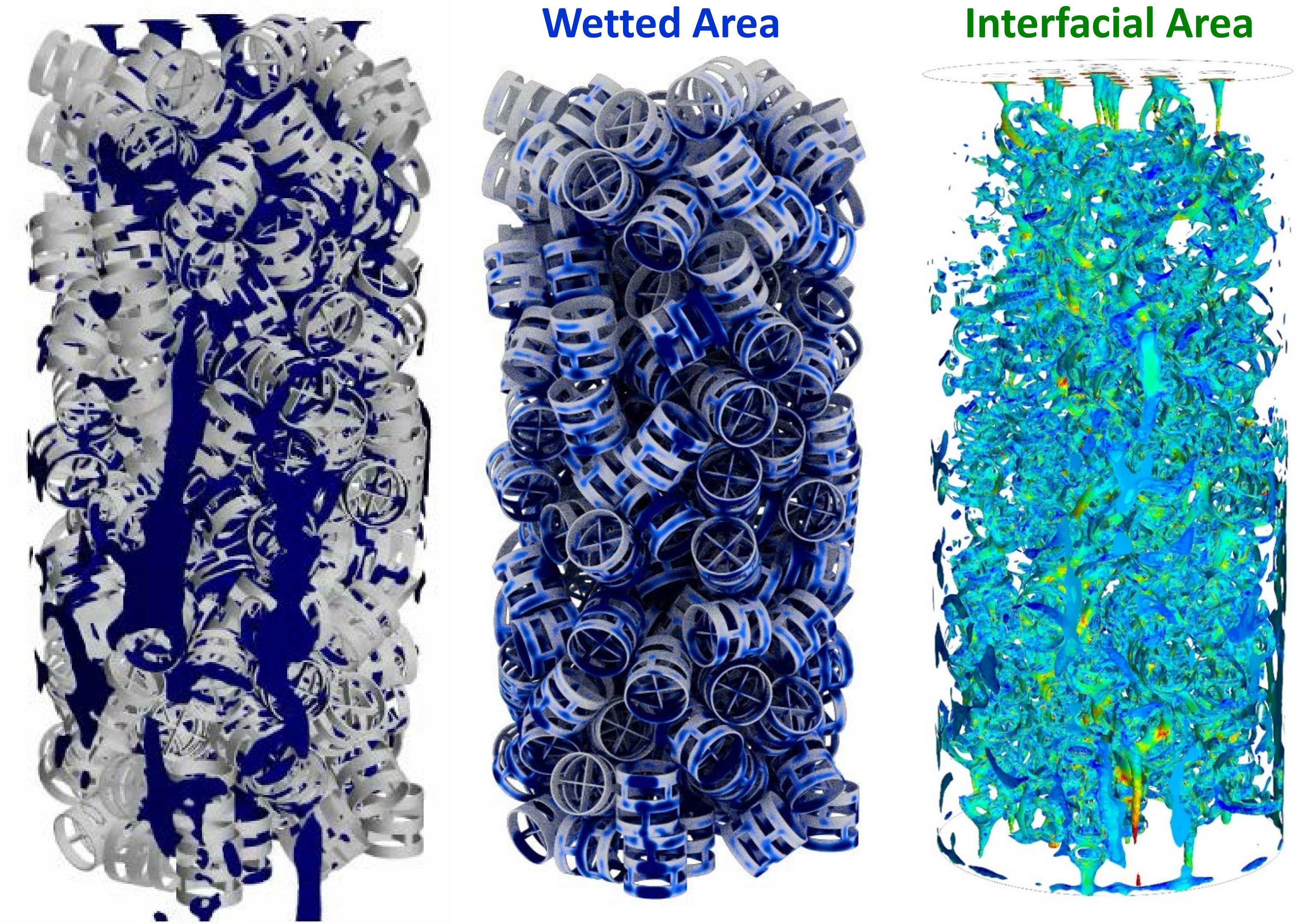

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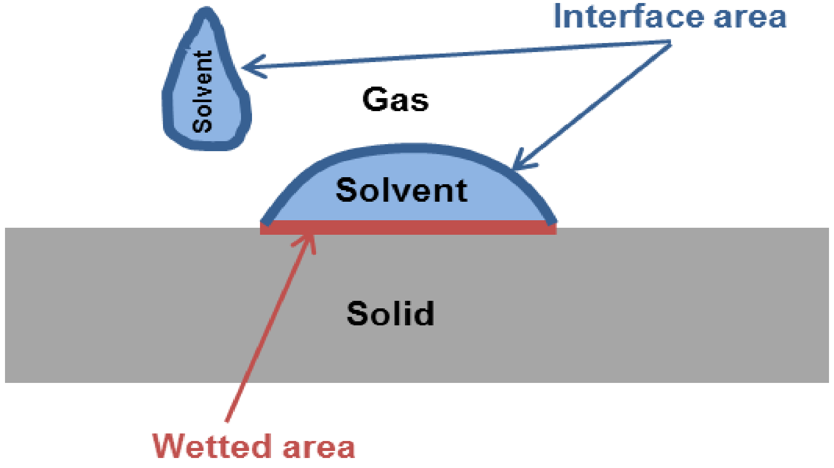
Model Validation: Mass Transfer Areas

Distinguish three areas

- Interface area (CFD)
- Wetted area (CFD)
- Effective mass transfer area (Exp.)



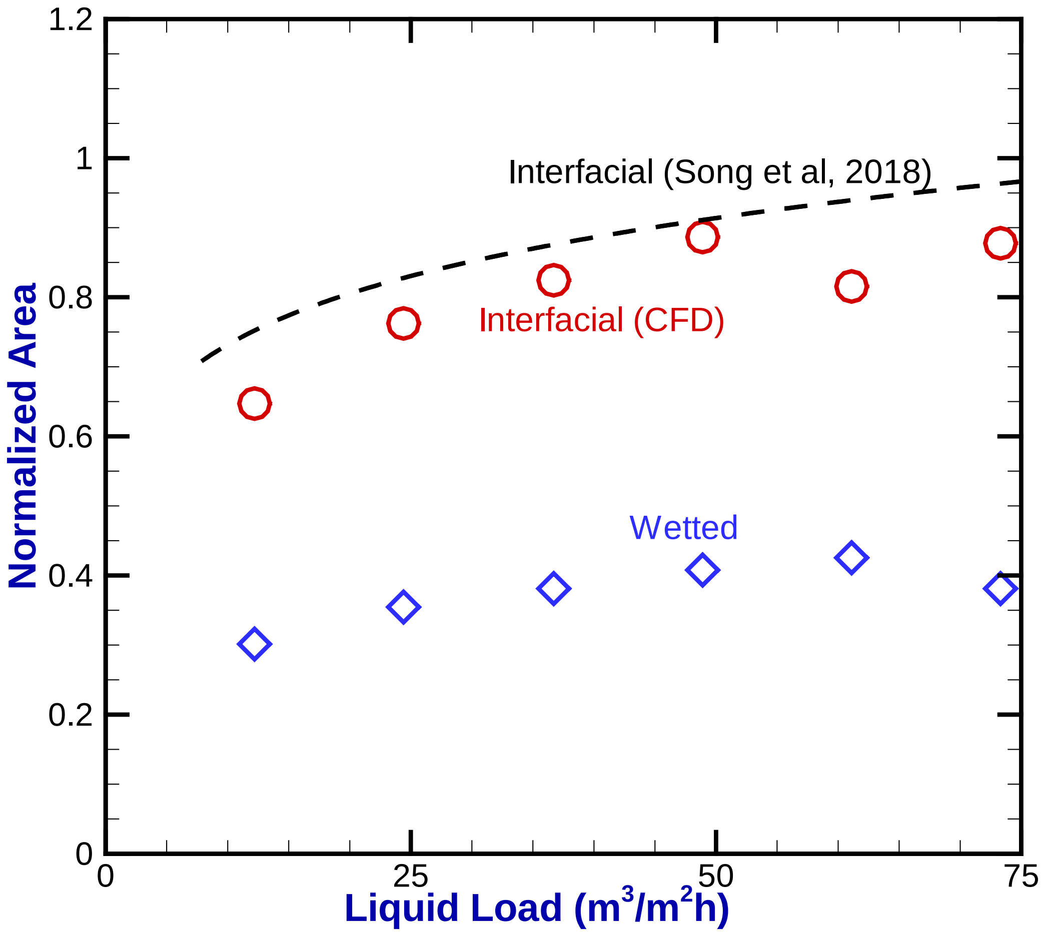
All areas are normalized by the packing Specific Area;

Correlation from column experiment (dash line):

$$A = 1.16\eta(\boldsymbol{u}_L g^{1/2} a_P^{-3/2} \rho_L/\sigma)^{0.138}$$

Song et al. (Ind. Eng. Chem. Res. 2018, 57, 718−729)

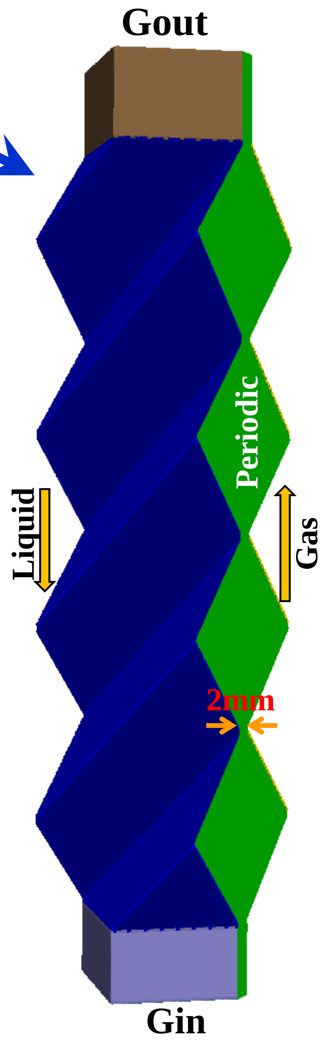
For given size of Pall Ring (16mm):
effective area ≈ Interfacial area > wetted area



Comparison with Experiment

Application to Structured Packed Column

Mellapak 250.Y



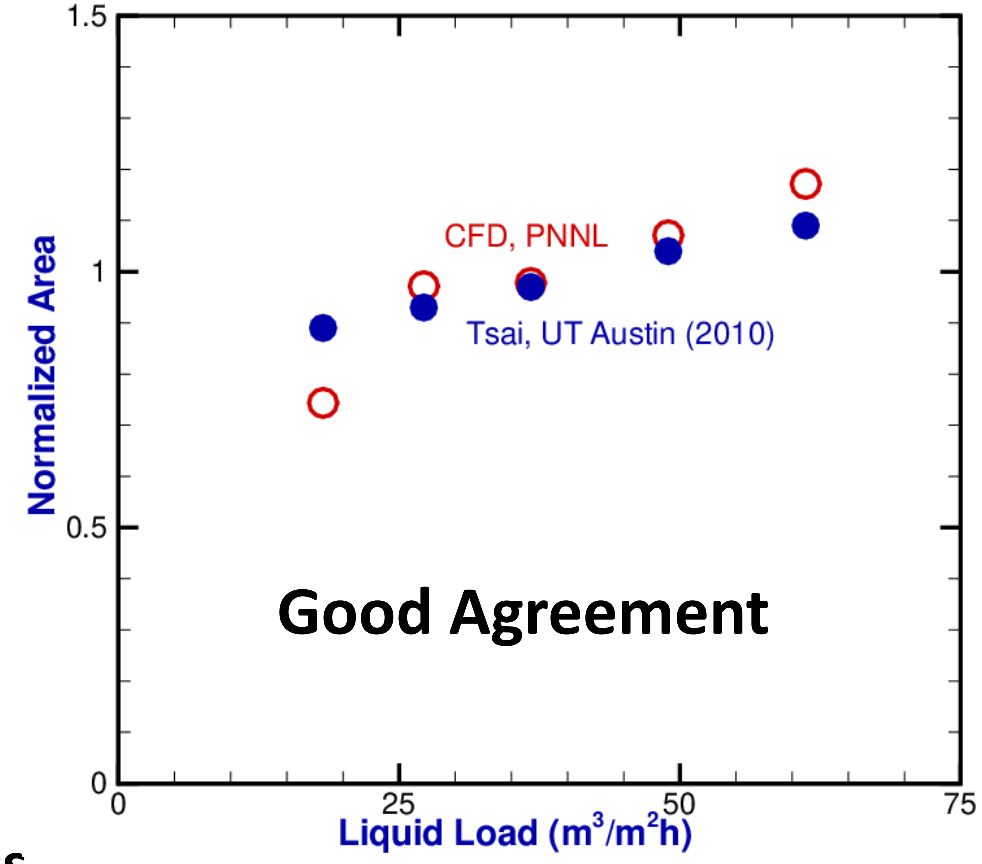
Model **Hydrodynamics**

Solvent (0.1M NaOH)

Physical Properties	
Density ρ (kg/m^3)	998
Viscosity μ (cP)	0.89
$D_{CO_2}[l]$ (m^2/s)	1.0×10^{-9}
$D_{CO_2}[g]$ (m^2/s)	1.0×10^{-5}
Surface Tension (N/m)	0.072

Effective area

$$a_e = \frac{u_g}{k_g' ZRT} ln\left(\frac{C_{CO_2, in}}{C_{CO_2, out}}\right)$$



Good Agreement

Application to CO2BOL in Packed Column

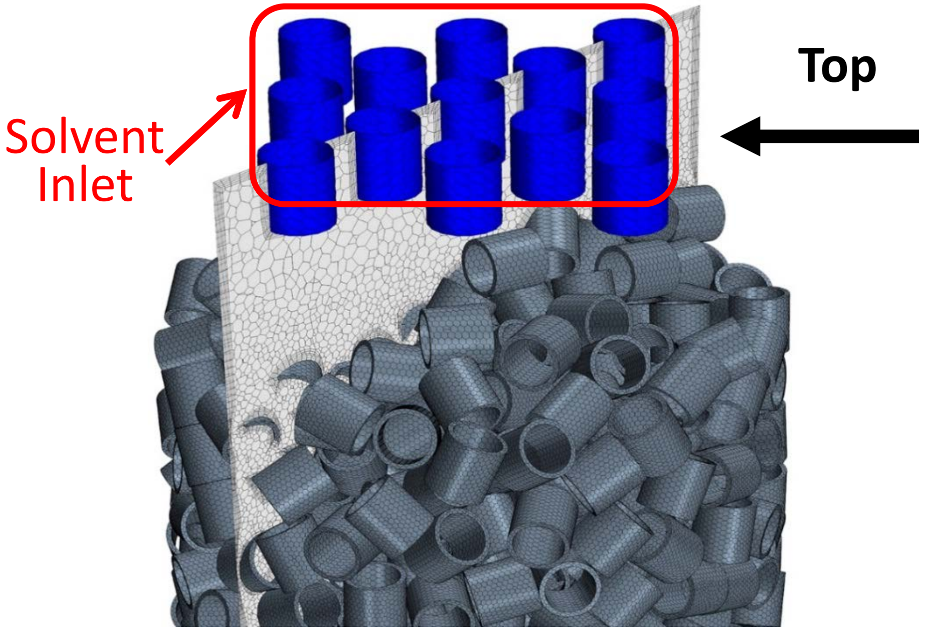
Design of Column

- Column Diameter: 63 mm
- Column Height: 200 mm
- Number of packed rings: 2366

CO2BOL-2 water-lean solvent:

- Density: 1015 kg/m^3
- Viscosity: 10.6 cP
- Surface tension: ~0.028 N/m ?
- Contact angle: ~10^o ?

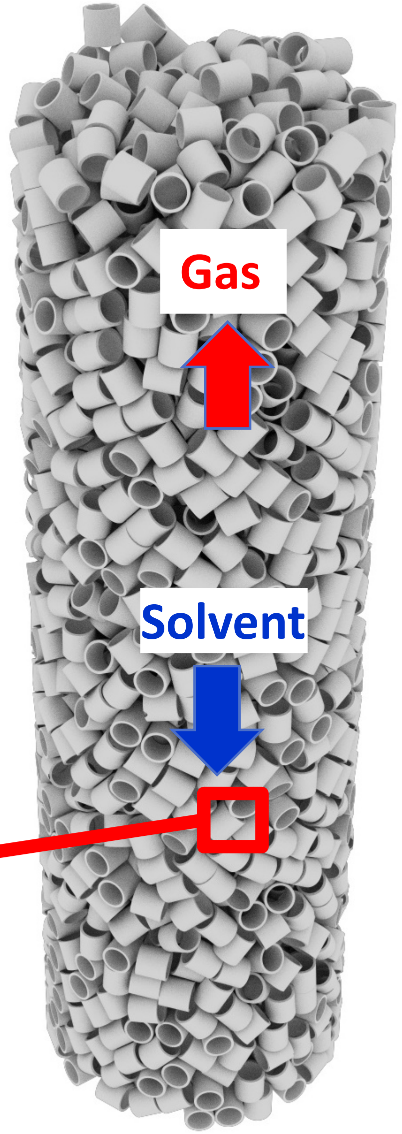
DOCCSS



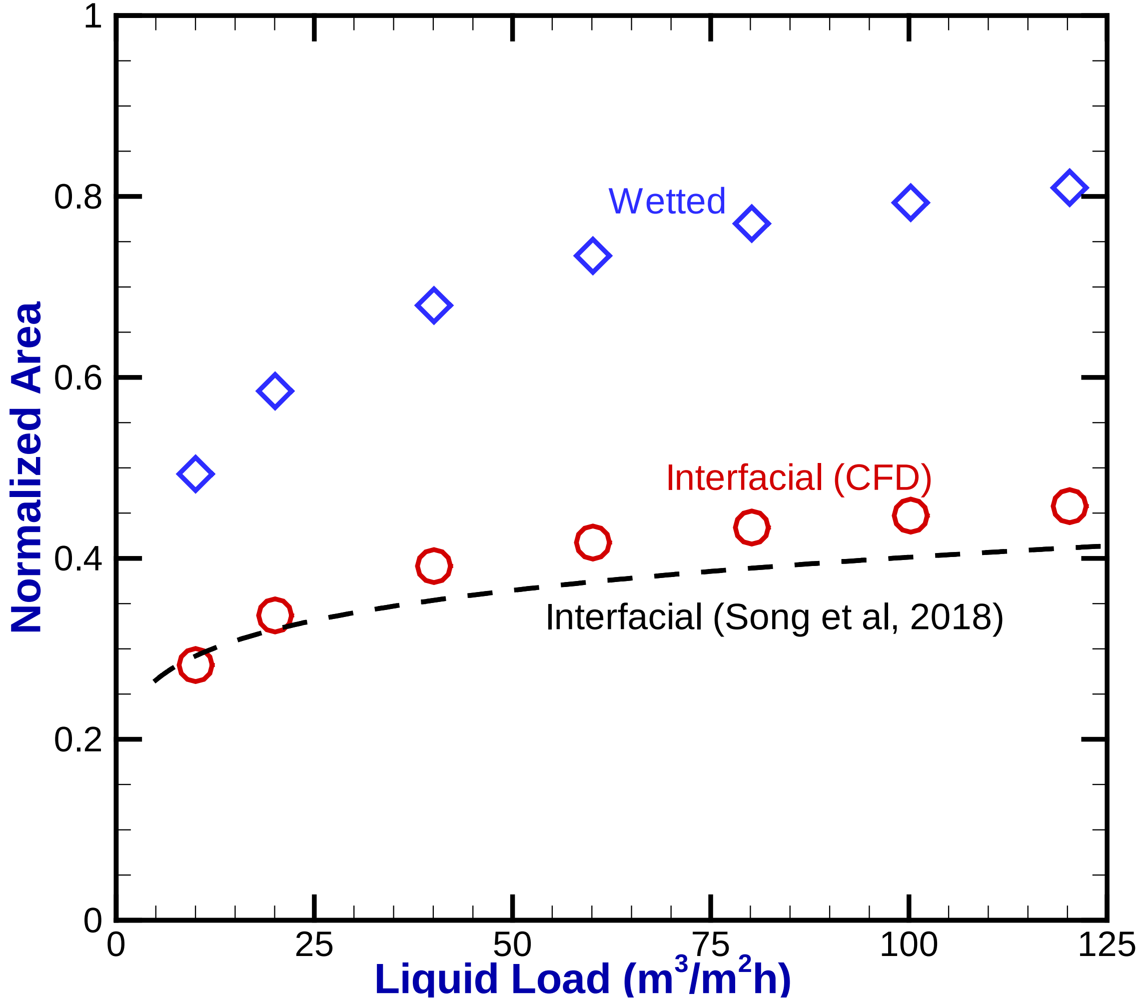
Raschig Ring Design

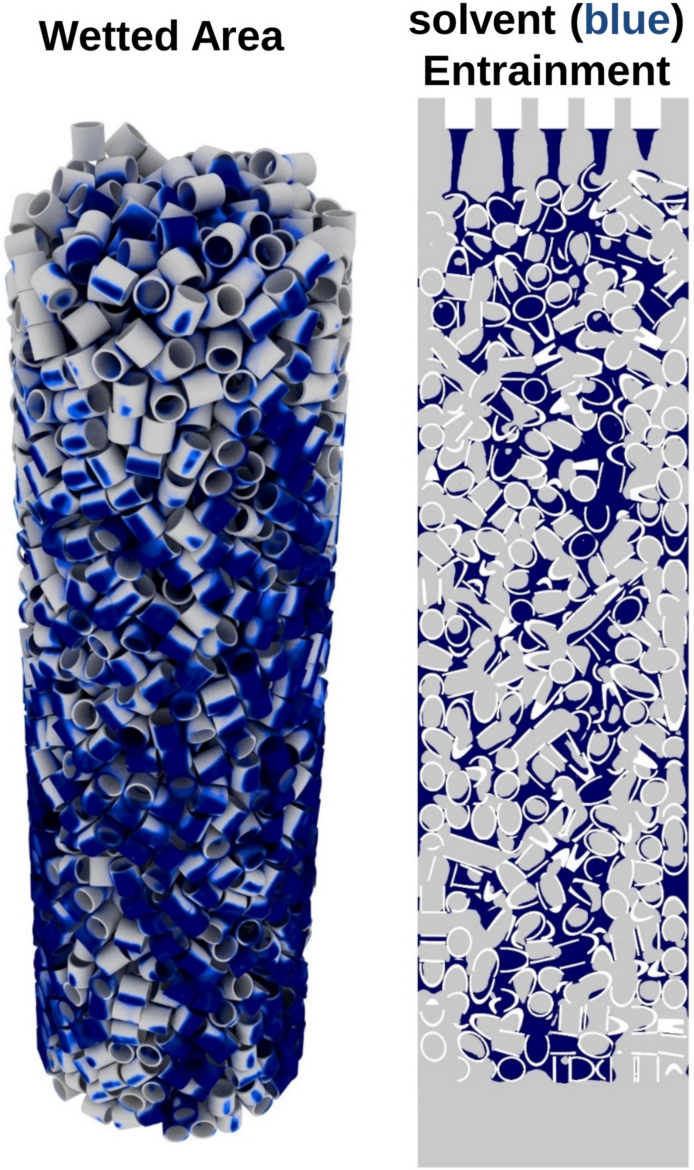
- Diameter: 6 mm
- Height: 6 mm
- Thickness: 0.5 mm
- Specific Area: 827 m^2/m^3

CFD Model



Application to CO2BOL in Packed Column





For small size of raschig ring (6mm):

effective area≈Interfacial area < wetted area

- Multiphase flow simulations for random/structure packings
- Validation with experiments (Song et. al. (2017))
- Interface/wetted areas directly from CFD
  - Small rings ➡ large wetted area $\neq$ mass transfer area
- Affordable for a full-size bench-scale column
- Applications to CO2BOL or other solvents
- More detailed results in poster presentation (Tuesday)

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Estimate Energy Use for Any Solvent by Rigorous Thermo

- Energy use by:
  1. $Q_{Reboiler} + W_{compression}$

Or 2. $W_{min} + W_{lost}$

- W_{min} by rigorous thermo
- W_{lost} by
  - standard estimate
  - Or by ΔG (EstΔG)

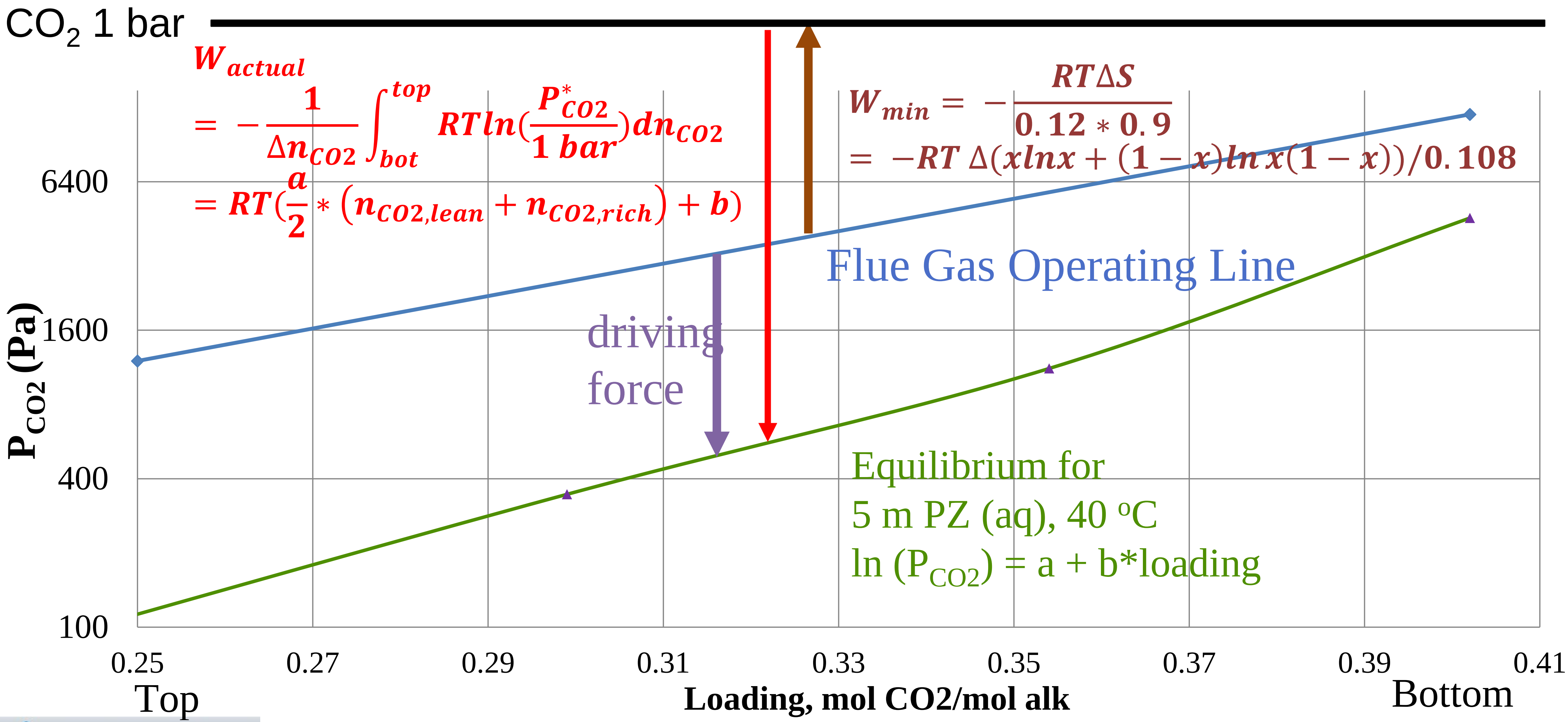
Useful to

1. Estimate energy for new solvent
2. Define operating conditions for new solvent
3. Qualify estimates of energy use by other methods
4. Evaluate potential of solvent classes such as water lean

Lost work in absorber = $W_{actual} - W_{min}$

$$W_{actual} = -\frac{1}{\Delta n_{CO2}} \int_{bot}^{top} RT\ln\left(\frac{P^*_{CO2}}{1\ bar}\right) dn_{CO2} = RT\left(\frac{a}{2} * \left(n_{CO2,lean} + n_{CO2,rich}\right) + b\right)$$

$$W_{min} = -\frac{RT\Delta S}{0.12 * 0.9} = -RT\ \Delta(x\ln x + (1-x)\ln x(1-x))/0.108$$



Heat Exchanger lost work by EstΔG (Carnot)

- Simplify by assuming $\Delta T_{approach} = \Delta T_{LM}$, constant

- $W_{lost} = \sum\left(1 - \frac{T_C}{T_H}\right) Q \;\; = -\frac{\dot{m}C_p}{\dot{n}_{CO2}} \int_{in}^{out} \frac{\Delta T_{LM}}{T_{lean}} dT = \frac{\dot{m}C_p}{\dot{n}_{CO2}} \Delta T_{LM} ln \frac{T_{in,lean}}{T_{out,lean}}$
- Total Cost = W$ $*$ Wlost + Area$*Q/$\Delta T_{LM}$
- $\Delta T_{LM,opt}$:CAPEX:OPEX $\propto \mu^{0.175} k^{-0.325} C_p{}^{0.825} \Delta T_{crx}^{0.5}$
- $\Delta C_{norm} = \Delta C_{solv} \left(\frac{\mu}{\mu_{5\,m\,PZ}}\right)^{-0.175} \left(\frac{k}{k_{5\,m\,PZ}}\right)^{0.325} \left(\frac{C_p}{C_{p,5mPZ}}\right)^{-0.825}$
  - Greater ΔC_{norm} = lower HX cost and lower W_{lost}

HX energy cost: normalized capacity

	μ	k	C_p	ΔC_{cyc}	ΔT_{opt}	$\Delta C_{k,Cp,\mu}$	$\Delta C_{k,Cp,\mu}$
	cP	W/mK	J/gK	$\frac{mol\ CO_2}{kg\ solvent}$		w/o ΔT_{crx}	with ΔT_{crx}
5 m PZ(aq)	4	0.41	3.6	0.95	5	0.95	
7 m MEA (1water/3NMP)	16	0.28	2.8	0.85	7.5	0.72	
1 CO2BOL/1 C16	20	0.14	2.2	0.72	7	0.58	0.68
1 CO2BOL/2 C16	20	0.14	2.4	0.59	7.1	0.44	0.61

Lost work (kJ/mol CO_2 removed)

Solvent	5 m PZ	8 m PZ	Water lean
Stripper	AFS	Simple	Simple
Absorber	5.5	5.5	5.5
P^*_{CO2} at 40°C lean/rich (kPa)	0.1/5	0.1/5	0.1/5
Heat exchanger	4.1	4.2	4.5
$\Delta T_{LM,opt}$	5	5.8	7.2
Condenser	0.8	5.8	(0.8)
Compressor	2.3	2.3	2.5
Stripper P (bar)	6.5	6.5	1.8
Reboiler	1.2	1.7	1.2
Trim cooler, stripper, et al.	1.6	1.6	(1.6)
Total $W_{eq} = W_{lost} + W_{min}$	33.7	39.3	34.3

1. Water lean cases use CO2BOL properties

Conclusions

- W_{eq} & Q_{reb} for water lean solvent may compete with 2X aqueous
  - If normalized capacity is similar
  - If $W_{lost,condenser}$ is low as expected with little water
- Normalized capacity determines heat exchanger CAPEX & OPEX
  - CO_2 solubility, μ, k_{cond}, & C_p all matter

$$\Delta C_{norm} = \Delta C_{solv}\left(\frac{\mu}{\mu_{ref}}\right)^{-0.175}\left(\frac{k}{k_{ref}}\right)^{0.325}\left(\frac{C_p}{C_{ref}}\right)^{-0.825}$$

  - Representative water lean solvents have lower ΔC_{norm} than 2X aqueous amine

CCSI² Carbon Capture Simulation for Industry Impact

Acknowledgments

Carbon Capture Simulation for Industry Impact (CCSI^2)

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