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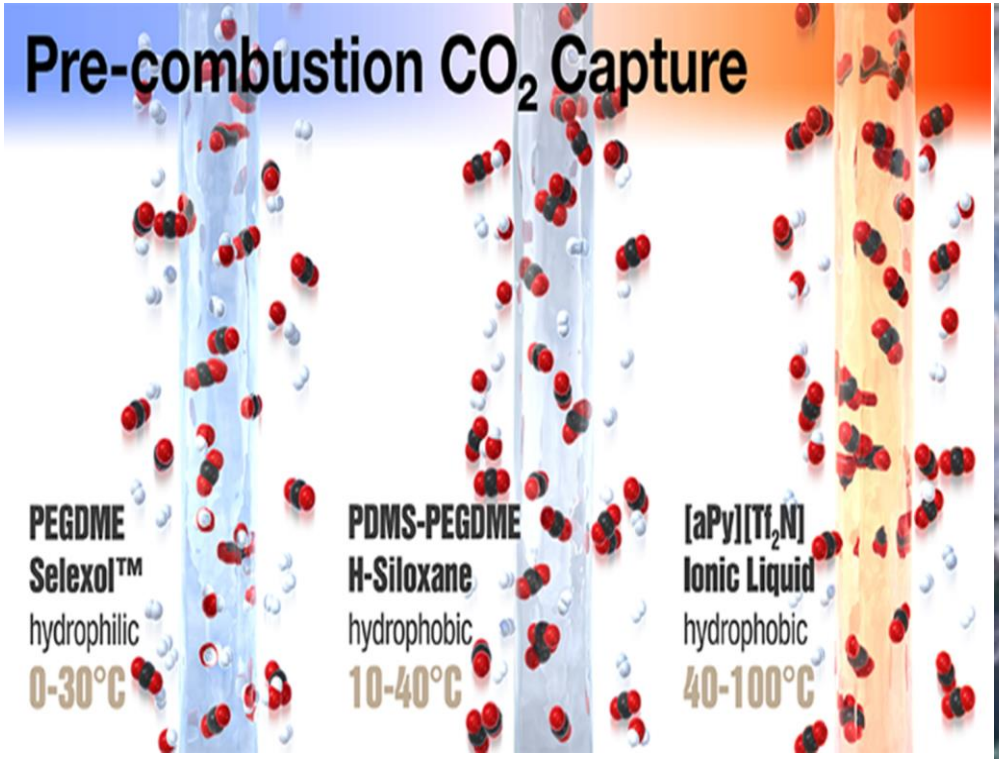


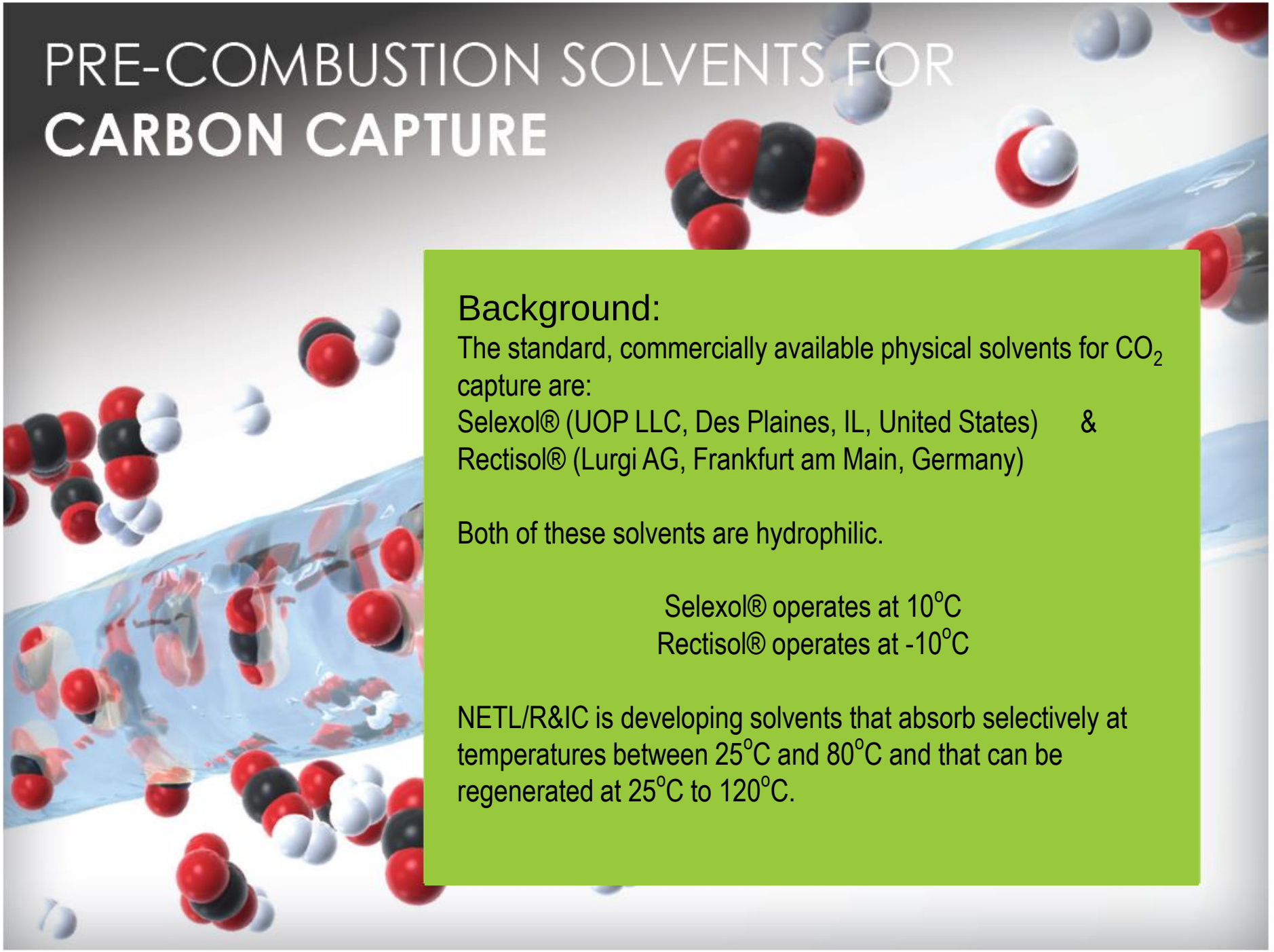
Experimental Materials Development and Bench-Scale System Design for Pre-combustion Solvents

Nicholas Siefert, TTC
David Hopkinson, TPL

August 21, 2017

U.S. DEPARTMENT OF ENERGY

PRE-COMBUSTION SOLVENTS FOR CARBON CAPTURE



Background:

The standard, commercially available physical solvents for CO_2 capture are:
Selexol® (UOP LLC, Des Plaines, IL, United States) & Rectisol® (Lurgi AG, Frankfurt am Main, Germany)

Both of these solvents are hydrophilic.

Selexol® operates at 10°C
Rectisol® operates at -10°C

NETL/R&IC is developing solvents that absorb selectively at temperatures between 25°C and 80°C and that can be regenerated at 25°C to 120°C.

Motivation: CO_2 Capture at Warm Temperatures & Take Advantage of Low Grade Heat

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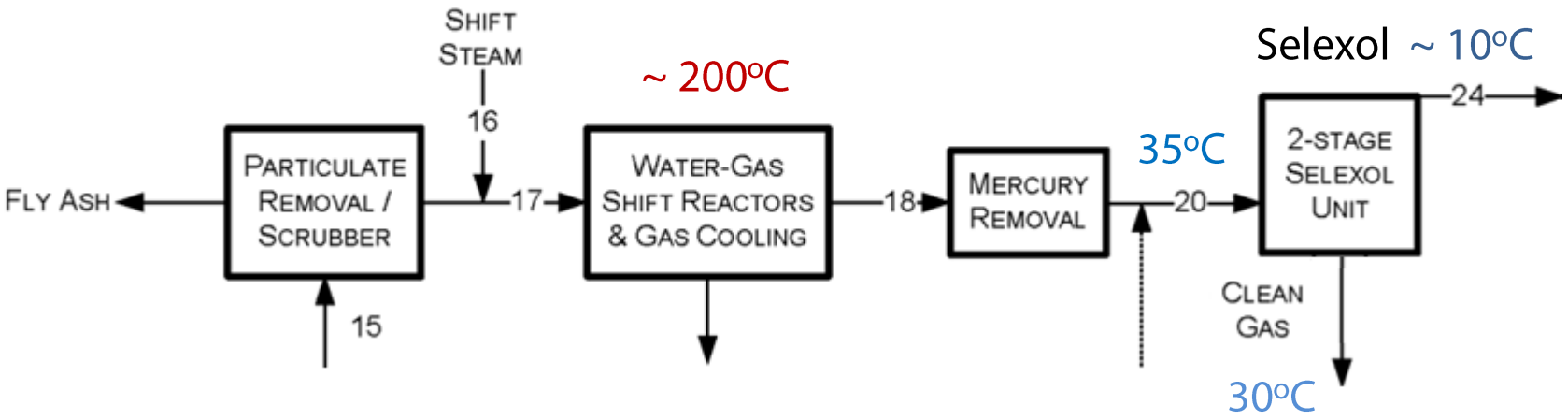
Exhibit 3-37 Case S1B and L1B Process Flow Diagram



- Current CO_2 capture process at IGCC-CCS requires chilling a hydrophilic solvent to below room temperature and does not take advantage of low-grade heat at the plant

Motivation: CO_2 Capture at Warm Temperatures & Take Advantage of Low Grade Heat

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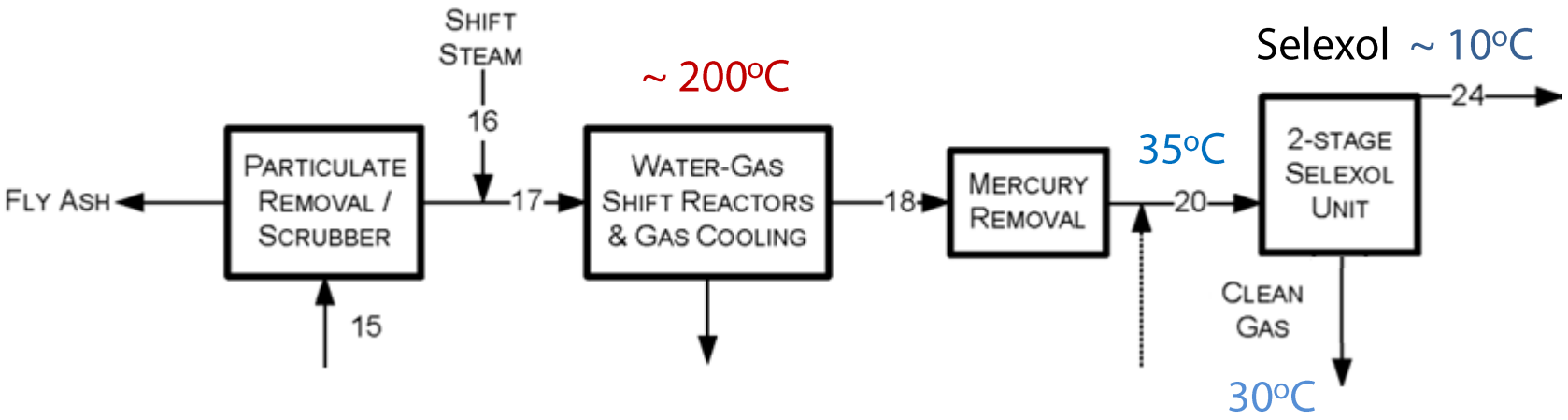
Exhibit 3-37 Case S1B and L1B Process Flow Diagram



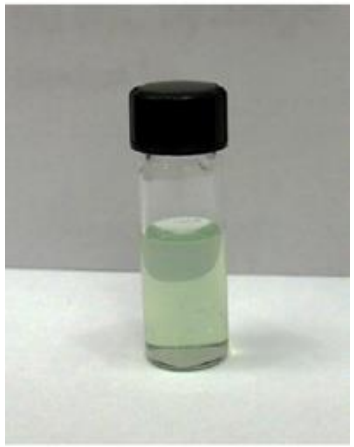
- Current CO_2 capture process at IGCC-CCS requires chilling a hydrophilic solvent to below room temperature and does not take advantage of low-grade heat at the plant

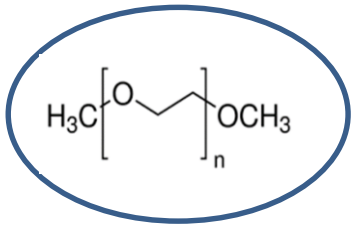
- Process efficiency can be improved up to ~2% with a warm gas separation process and there is the potential for significant capital cost reduction for the capture units

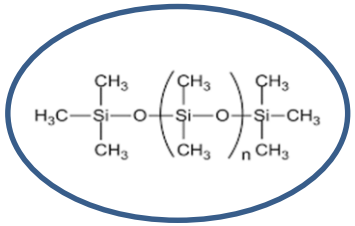
Pros & Cons of Selexol vs. Silicone Oils

	Selexol (PEGDME)	PDMS
Operating Temp.	Below room temperature	Above room temperature
Chemical Stability	Mid	High
Hydrophobicity	Low	High
Corrosion	Mid	Low
Cost of the Solvent	Low	Mid
CO_2 / H_2 Selectivity	High	Low

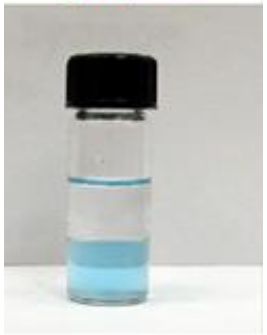
PEGDME
fully miscible with water;
Extremely hydrophilic







PDMS
immiscible with water, even at 120°C and 10,000 psi; separates quickly after shaking;
Extremely hydrophobic



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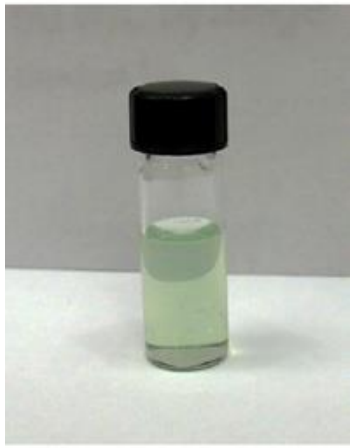
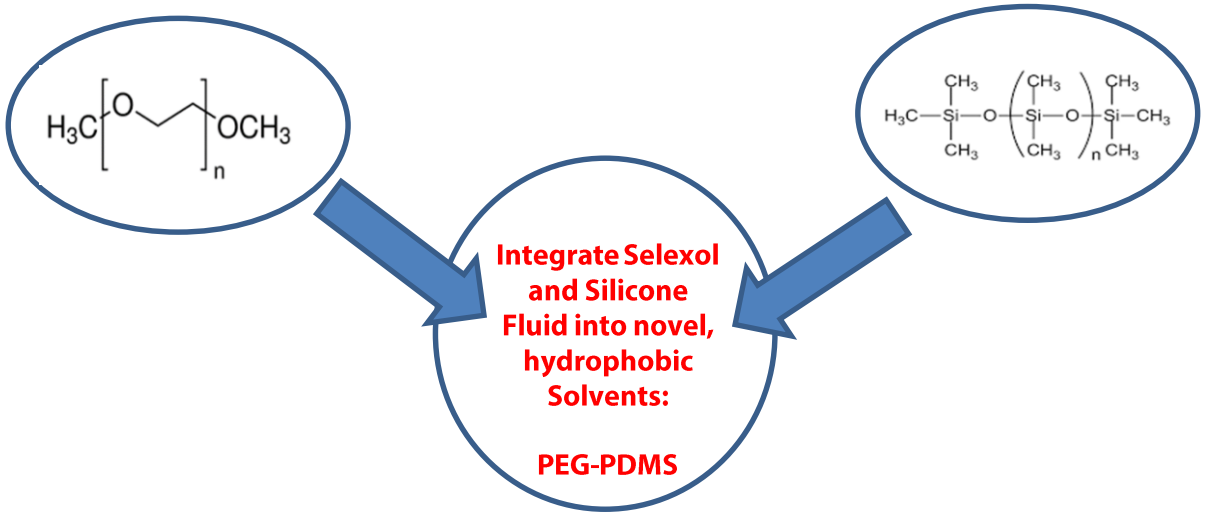
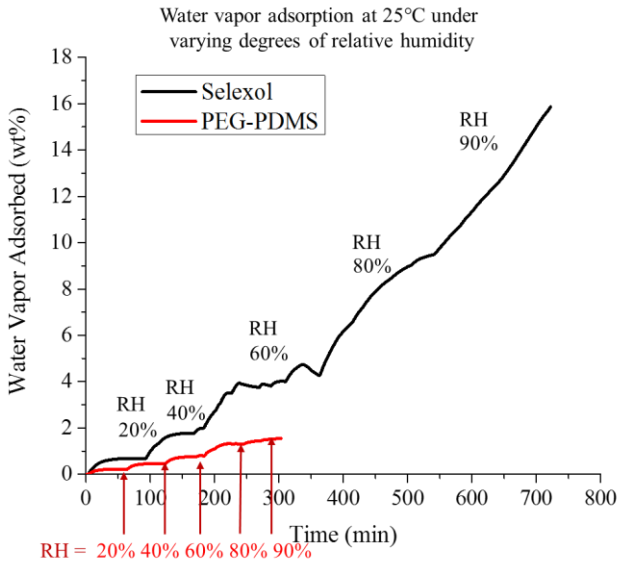




PDMS
immiscible with water, even at 120°C and 10,000 psi; separates quickly after shaking;
Extremely hydrophobic

PEG-PDMS Solvents: Best of Both

	PEG-PDMS Solvents
Operating Temperature	**Above room temperature**
Chemical Stability	**High**
Hydrophobicity	**Mid**
Corrosion	**Low**
Cost of the Solvent	**Mid**
CO_2 / H_2 Selectivity	**Mid/High**



PEG-PDMS-1

Hybrid structure: Improved CO_2/H_2 selectivity compared with PDMS while maintaining good CO_2 solubility in a *hydrophobic* solvent system

Water uptake measurements performed by Jeff Culp on the Hiden Microbalance

"High performance hydrophobic solvent, carbon dioxide capture" Patent US 20150114226 A1

Foaming issue has been addressed

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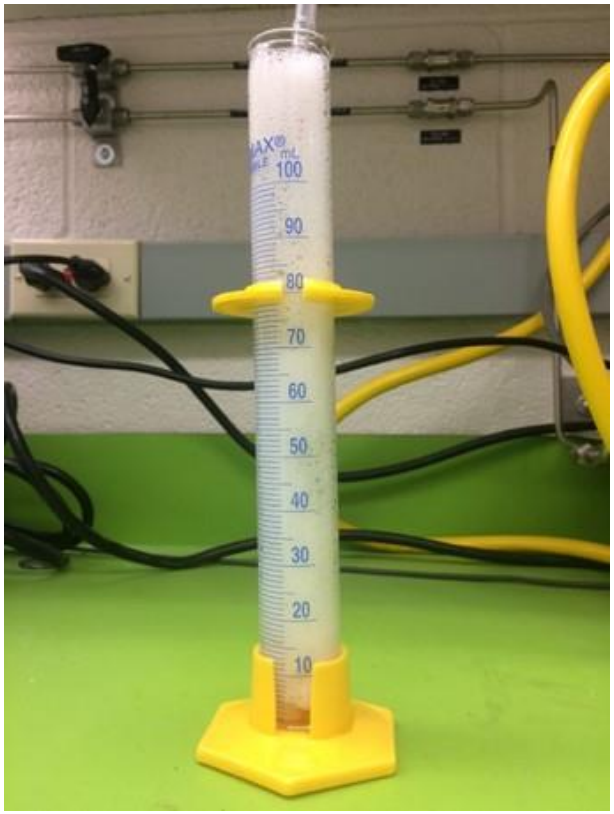
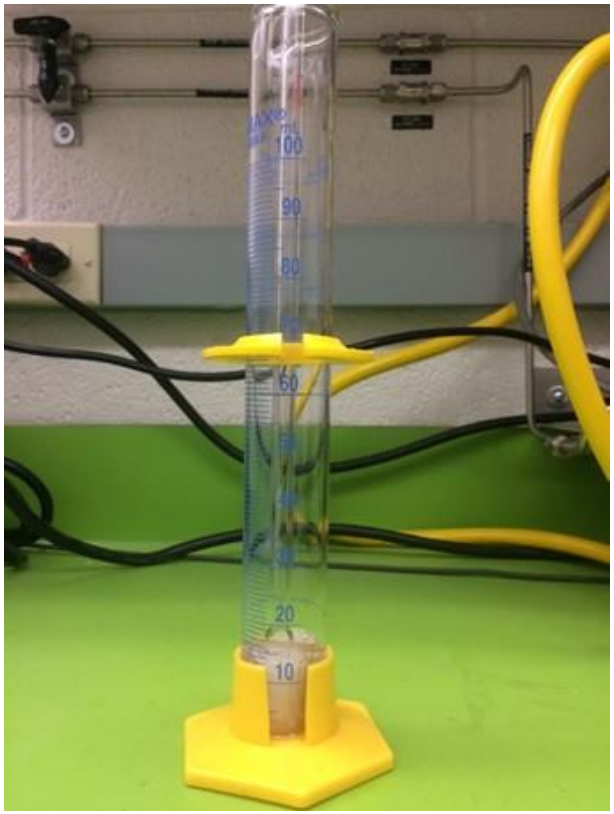
PEG-PDMS-1



Severe foaming

PEG-PDMS-3

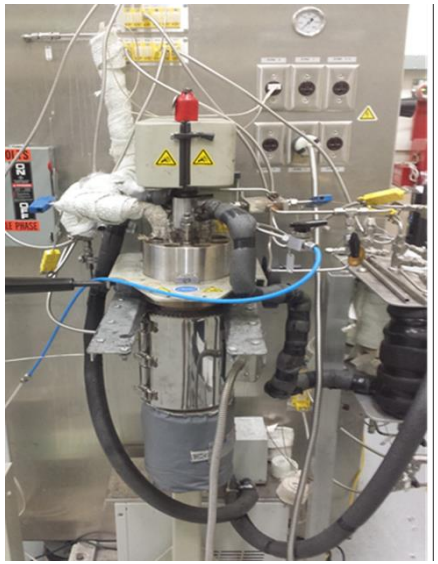


No foaming

Physical Properties

	MW, g/mol	Viscosity at 25°C, cP	Surface Tension at 25°C, N/m	CO_2/H_2 at 25°C	CO_2/H_2 at 40°C	Foam?
Selexol*	280	5.8	32	45	30.7	no
PEG-PDMS-1	427	3.9	22	38.5	27.4	yes
PEG-PDMS-2	427	5.3	22	-	-	yes
PEG-PDMS-3	617	12.2	22	**57.7**	**48.3**	**no**

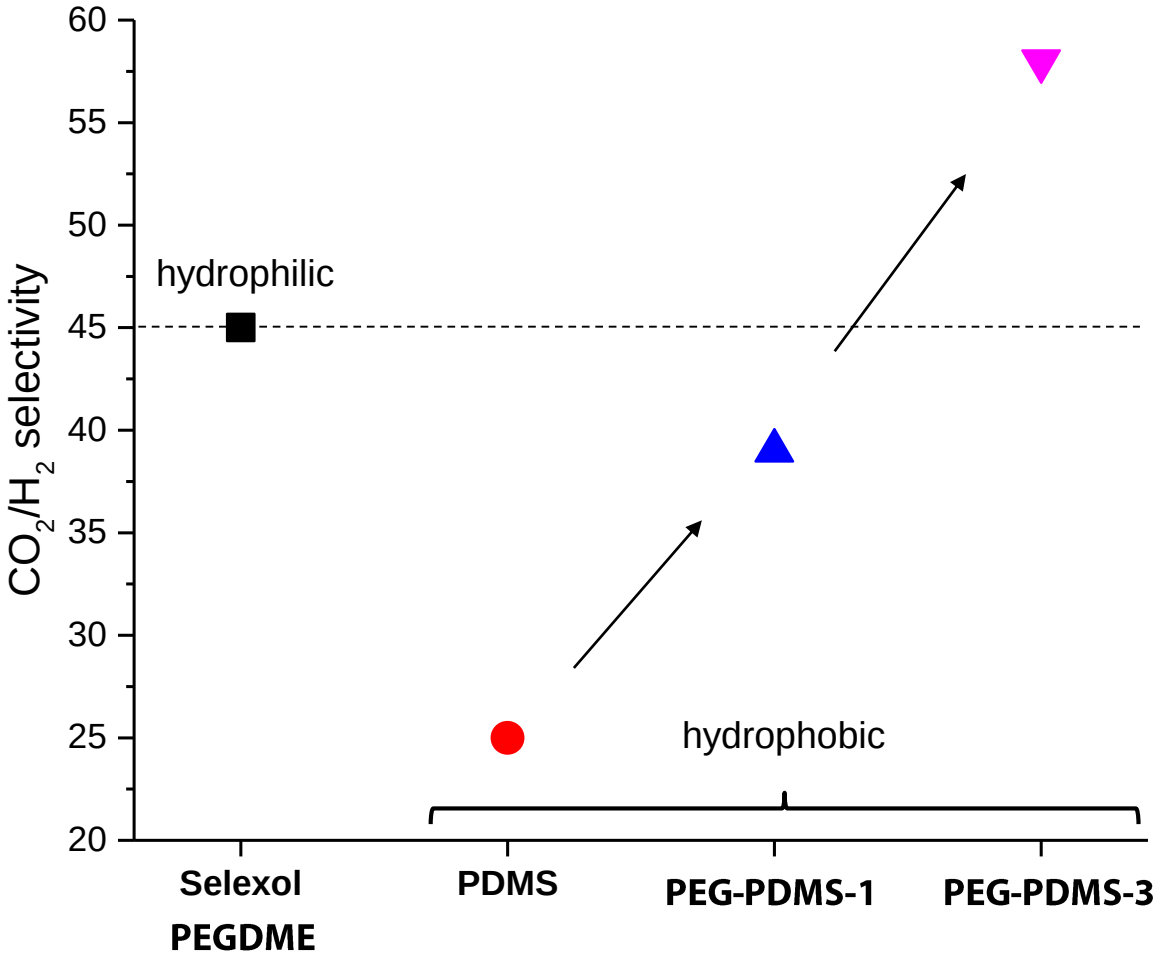
- First two versions of hybrid PDMS had favorable viscosities and CO_2 uptake, but lower CO_2/H_2 selectivity and tendency to foam limited their suitability
- Third version showed better selectivity than Selexol and reduced tendency to foam



* = dry Selexol-like polyethylene glycol dimethyl ether (PEGDME)
Note: CO_2/H_2 selectivity is a strong function of water content

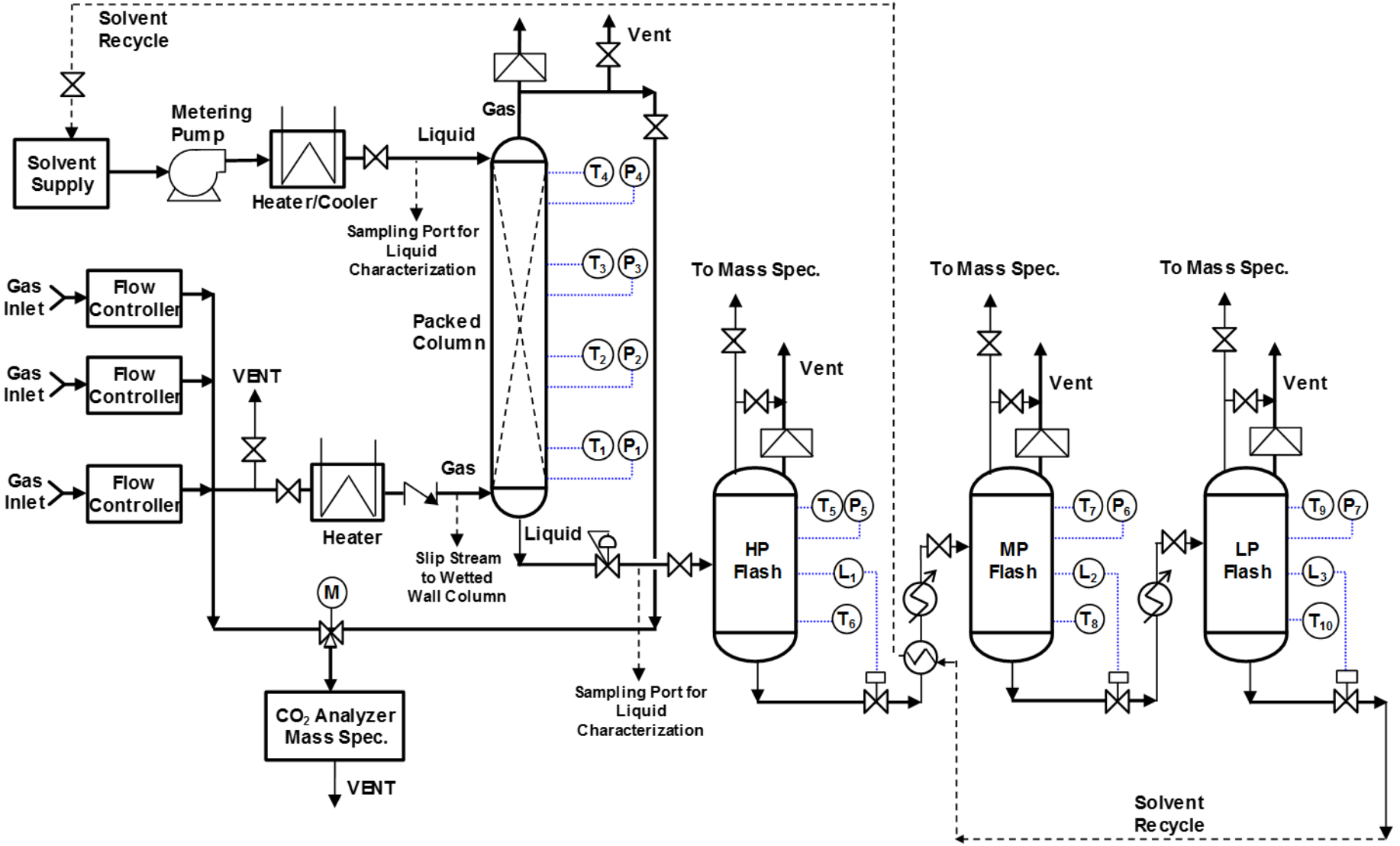
Hybrid PDMS Solvents

Progress of CO_2/H_2 selectivity in Hybrid PDMS Solvents



CO_2/H_2 selectivity measurements performed by Lei Hong on CSTR at NETL using dry solvents

R&IC's Pre-combustion Continuously Looping CO_2 Capture Facility



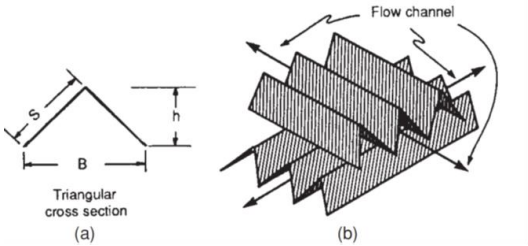
Absorber Design

Column

- ID: 12.7 cm (5″) H: 0.5, 1, 1.5 m

High efficiency packing

- MellaPak 250Y / 500Y



Liquid holdup

- Total available solvent 3 L
- Hold up 4% - 15%

Lean liquid flow

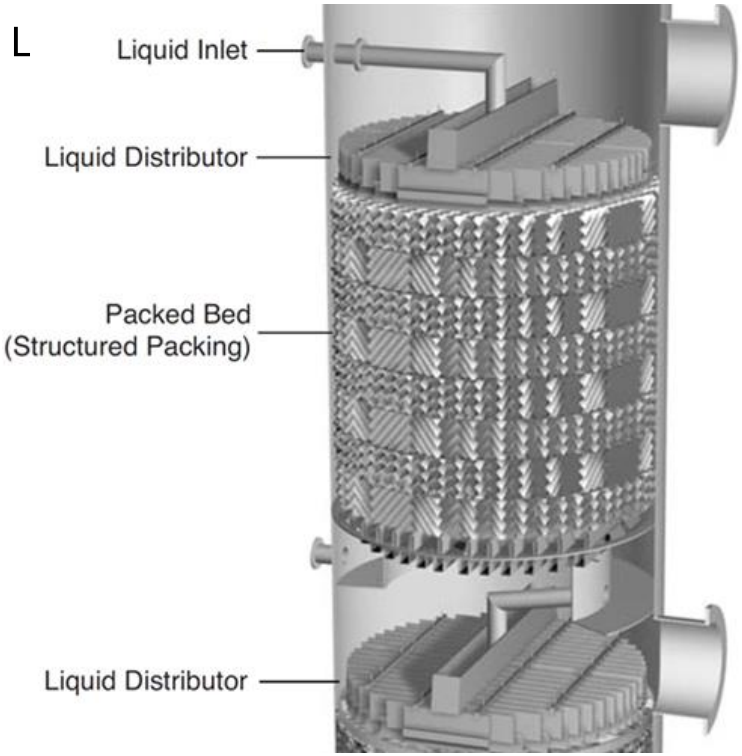
- 1.2 – 9 L/min
- Total resident time
  0.5 – 2 min

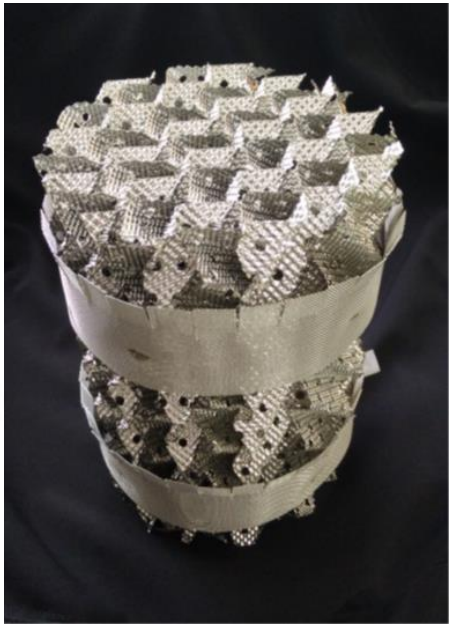
Pressure

- 50 bar

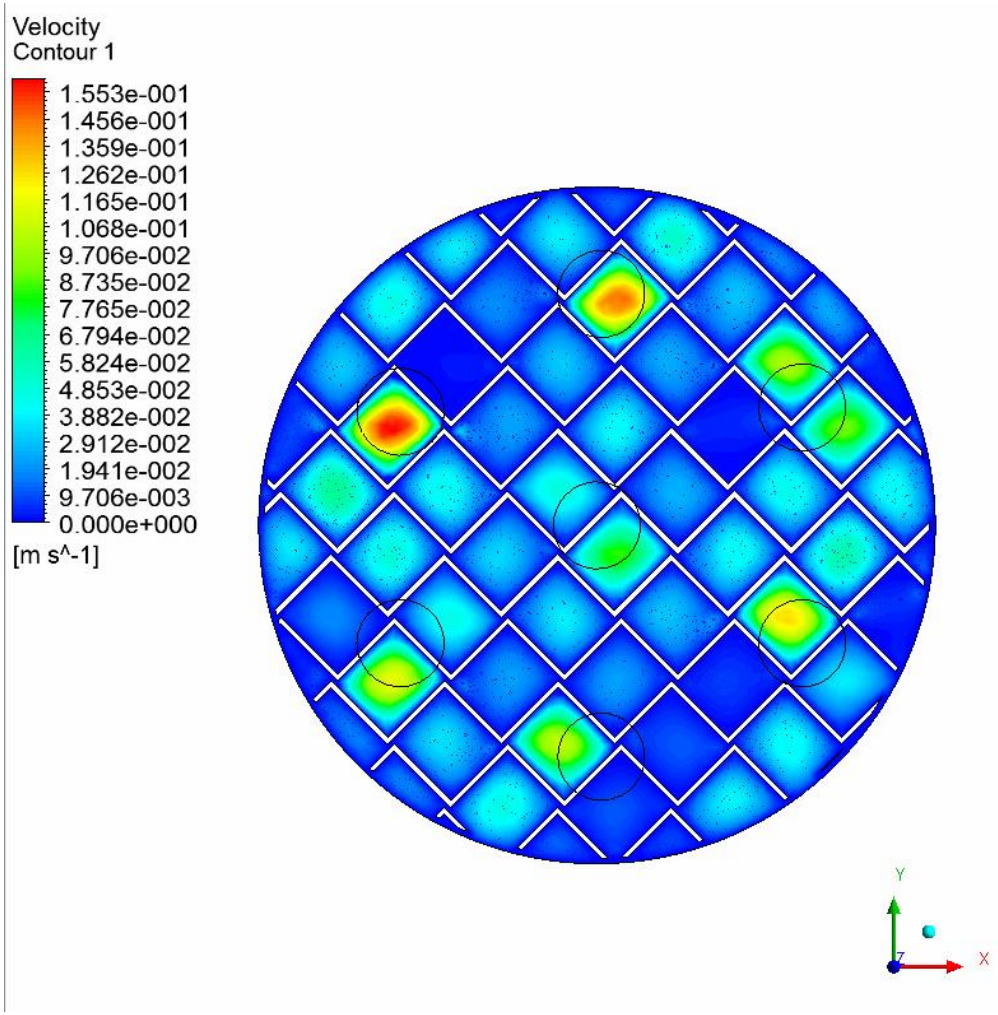
Temperature

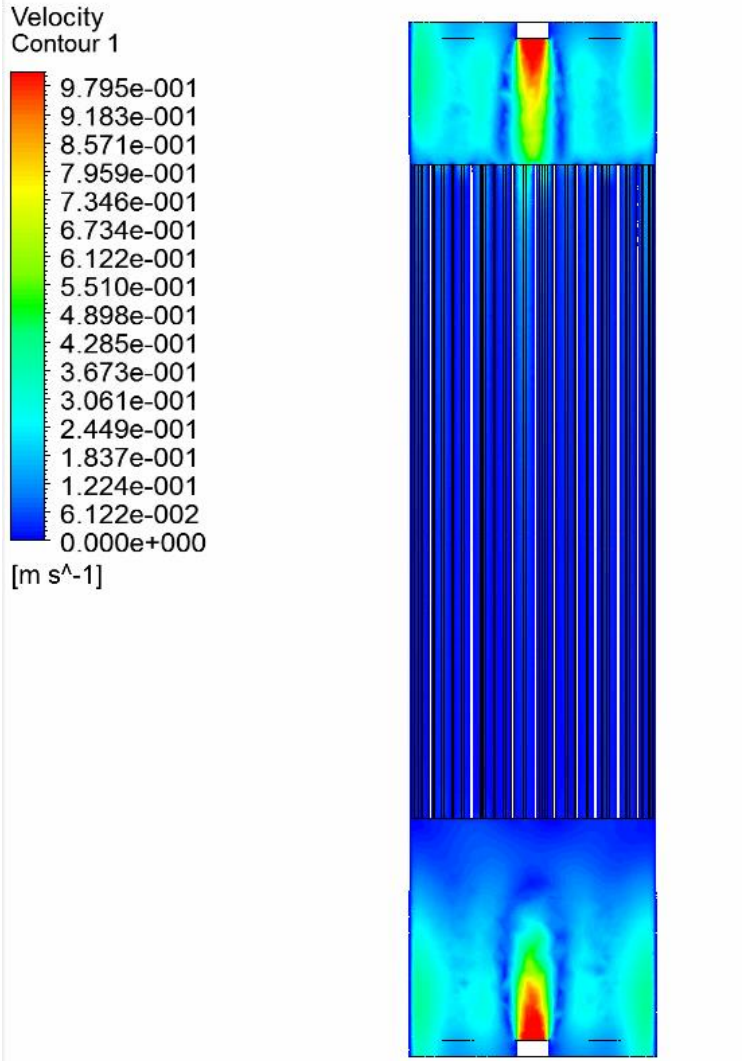
- 10°C – 50°C



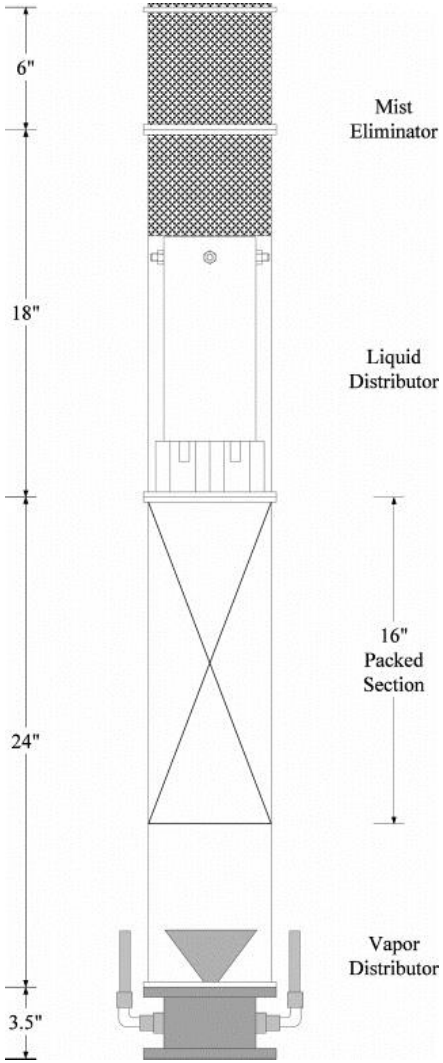


CFD Modeling

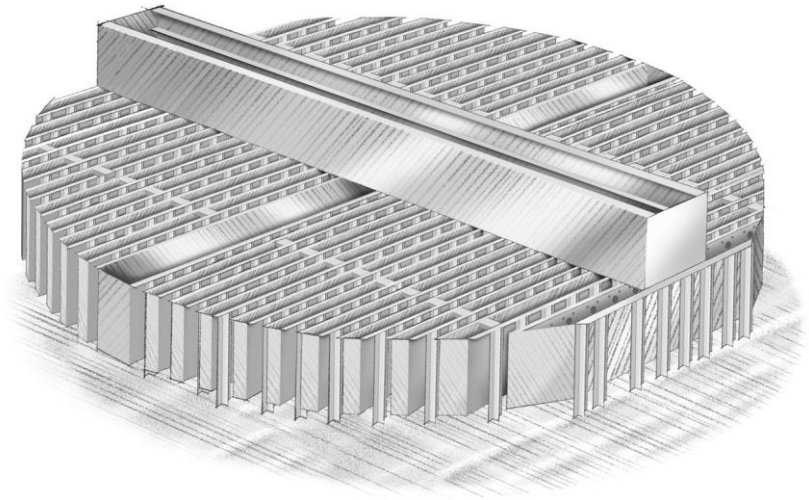




CFD Model Validation



- **Diameter: 14.61 cm (5.75 in)**
- **Mellapak 250Y (a_p = 250 m^2/m^3, ε = 0.987)**
- **Height of packing = 40.7 cm (16 in)**
- **Liquid flow rate = 5.4 – 48.9 m^3/m^2-h**
- **Koch-Glitsch Drip tube liquid distributor**



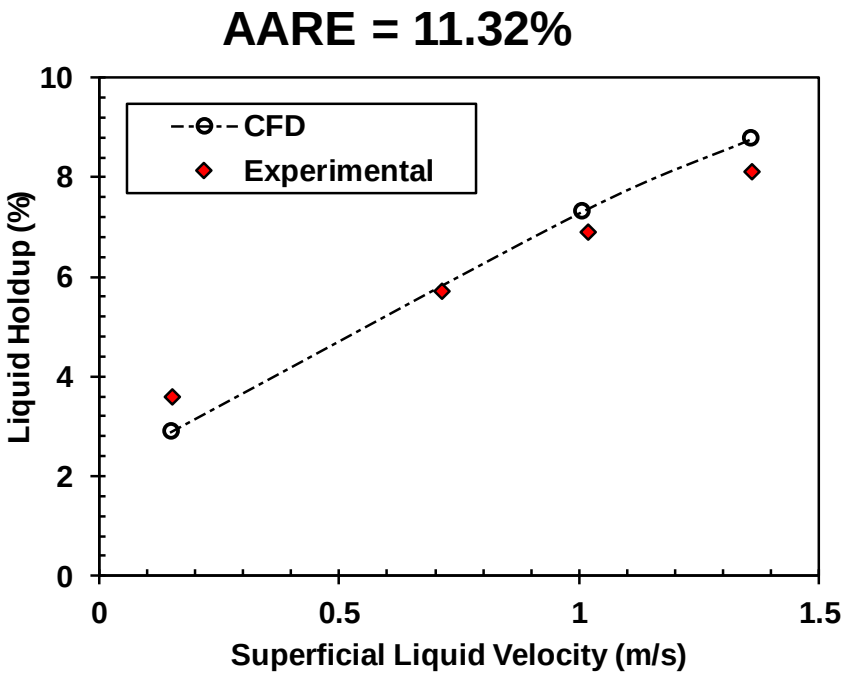
UT Austin Water Column

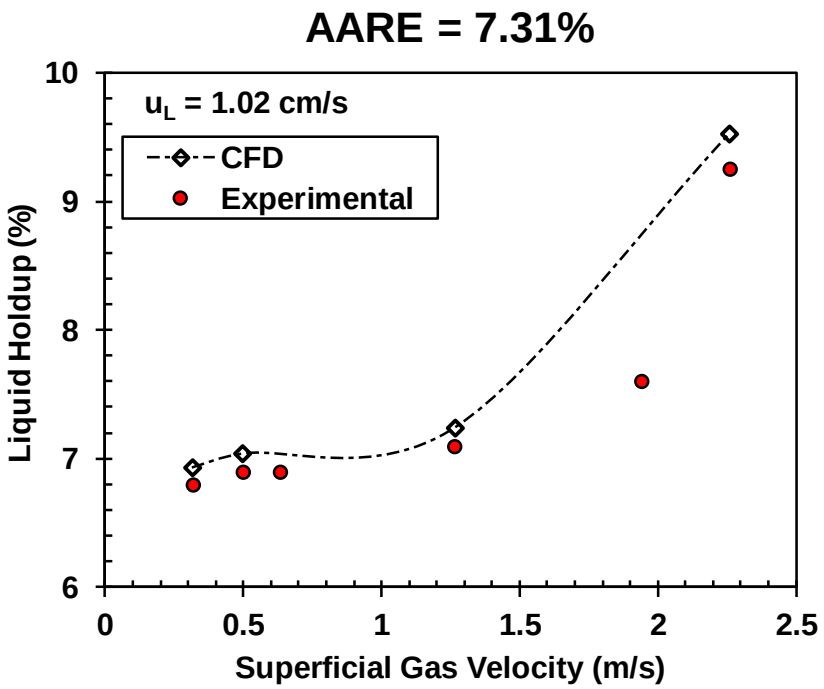
Green, Christian W., et al. "Novel application of X-ray computed tomography: Determination of gas/liquid contact area and liquid holdup in structured packing." *Industrial & engineering chemistry research* 46.17 (2007): 5734-5753.

CFD Model Validation – Liquid Holdup

Liquid holdup close to experimental values

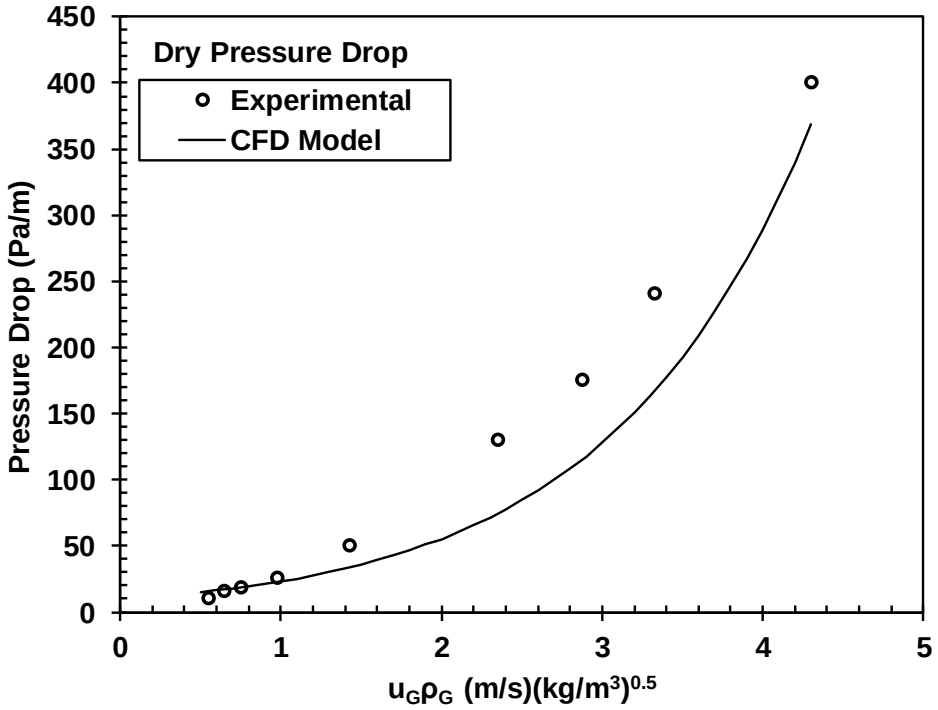
Working on improving CFD model

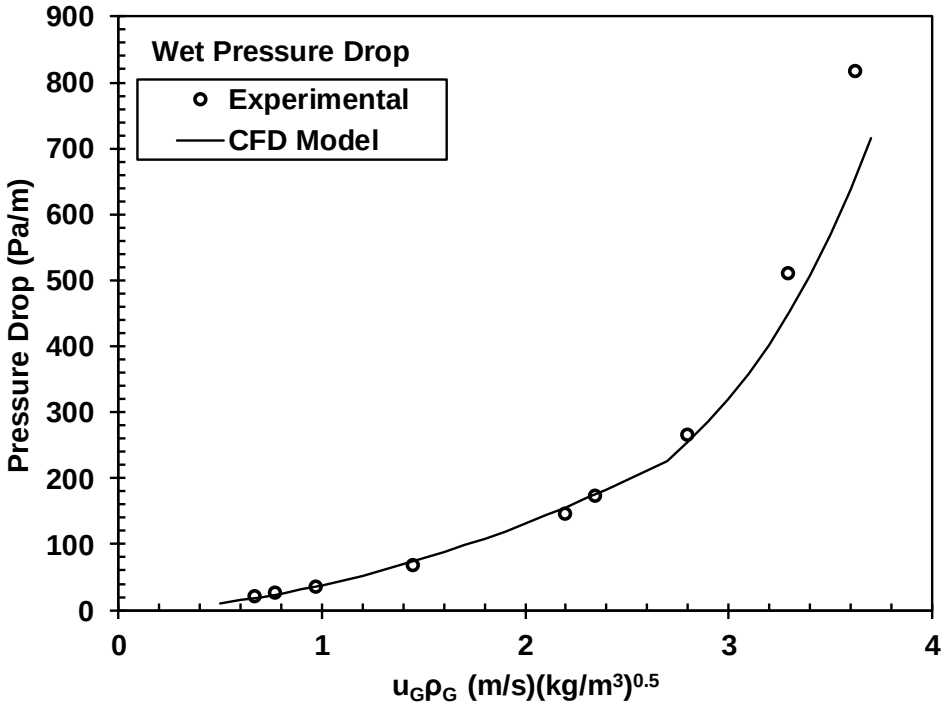




CFD Model Validation – Pressure Drop

Dry Pressure Drop: One Phase – Gas through empty packing
Wet Pressure Drop: Two Phase – Gas through wetted packing

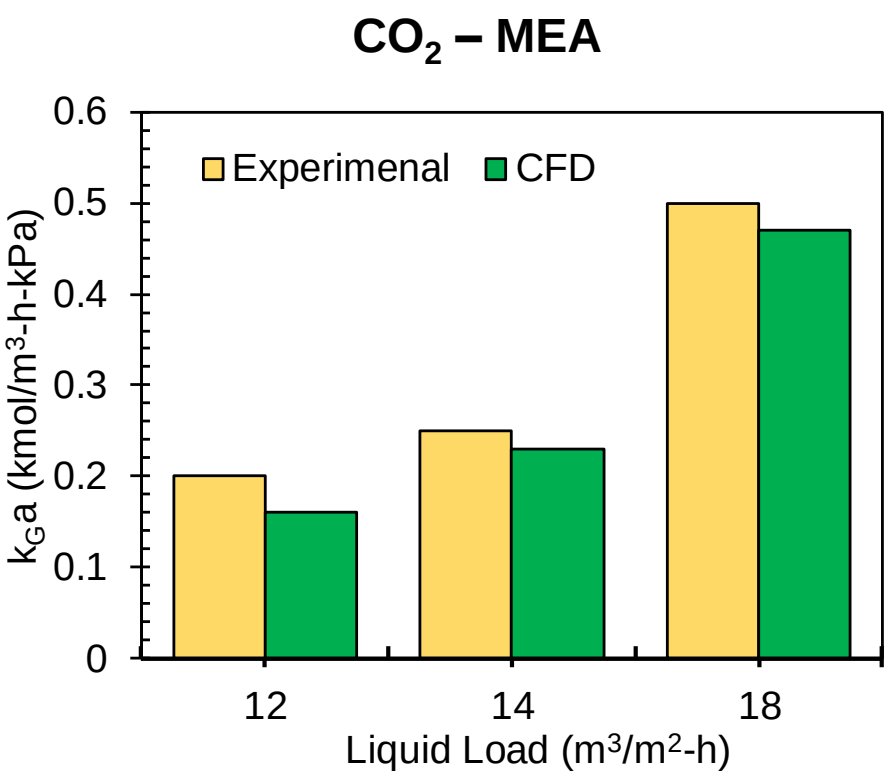


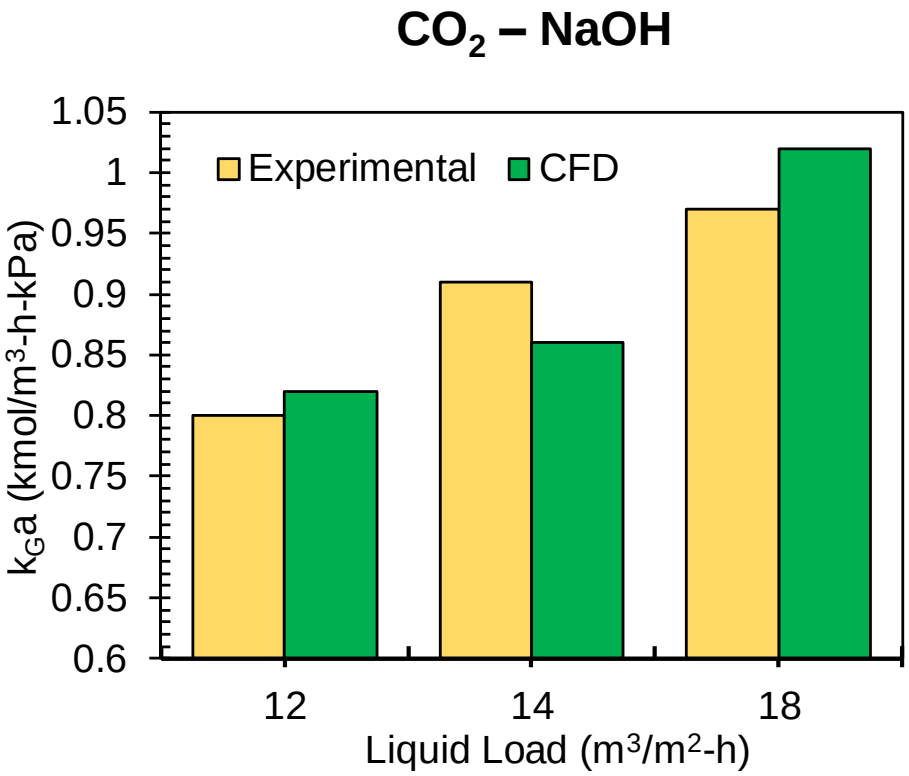


J. A. Rocha, J. L. Bravo, and J. R. Fair, "Distillation columns containing structured packings: a comprehensive model for their performance. 1. Hydraulic models," *Industrial and Engineering, Chemistry Research*, vol. 32, no. 4, pp. 641–651, 1993.

CFD Model Validation – Mass Transfer

Validating $k_G a$ using data from a 0.1 m diameter column





Aroonwilas, Adisorn, Amornvadee Veawab, and Paitoon Tontiwachwuthikul. "Behavior of the mass-transfer coefficient of structured packings in CO2 absorbers with chemical reactions." *Industrial & engineering chemistry research* 38.5 (1999): 2044-2050.

Column Design from CFD Modeling

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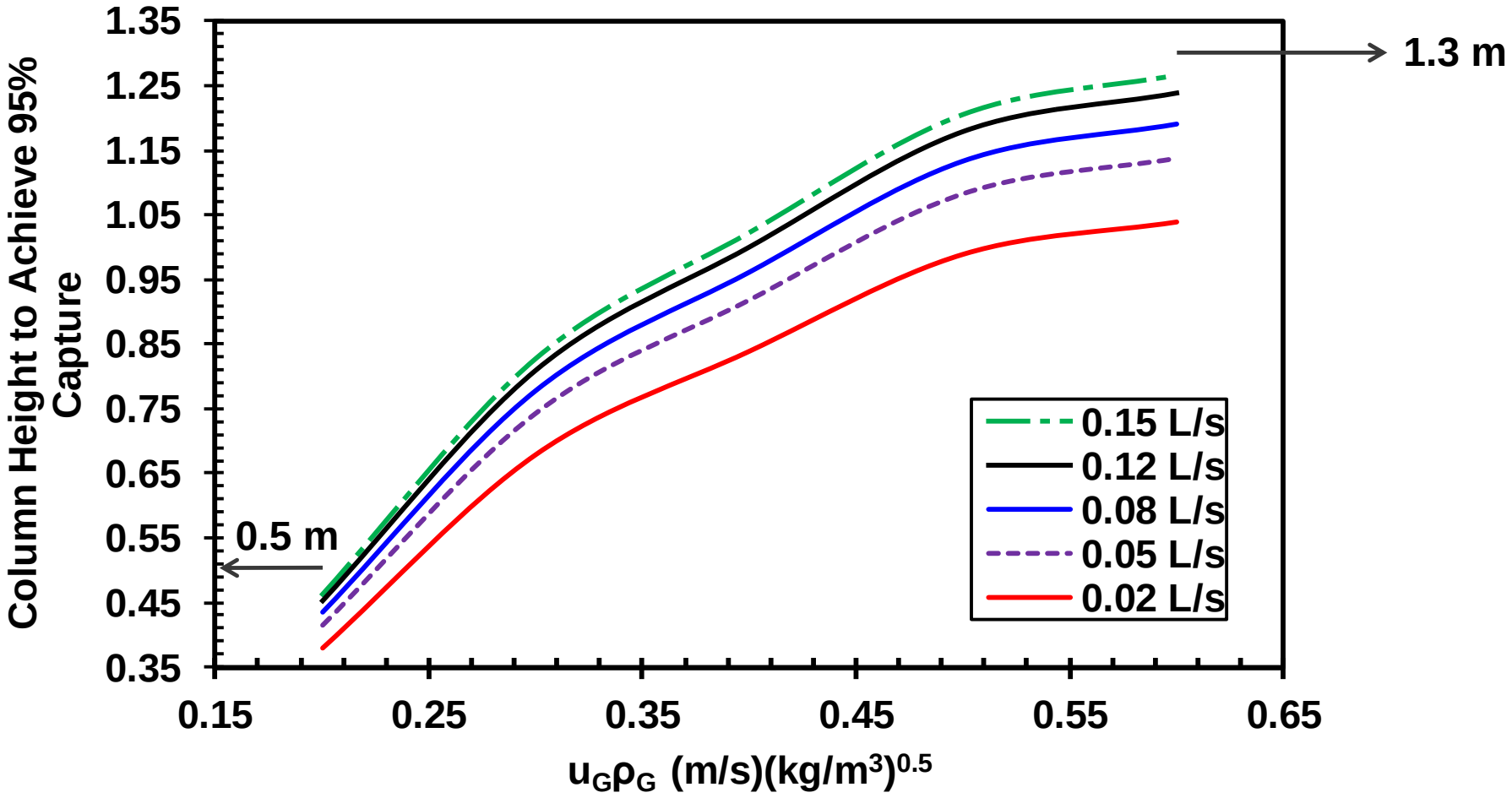
CFD results after validation using a PEGDME physical solvent



Integrated Computational Solvent Screening

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NIST database for pure compounds (~23000)
- Melting (T_m), boiling (T_b) temperatures, viscosity, surface tension, density (molar volume)

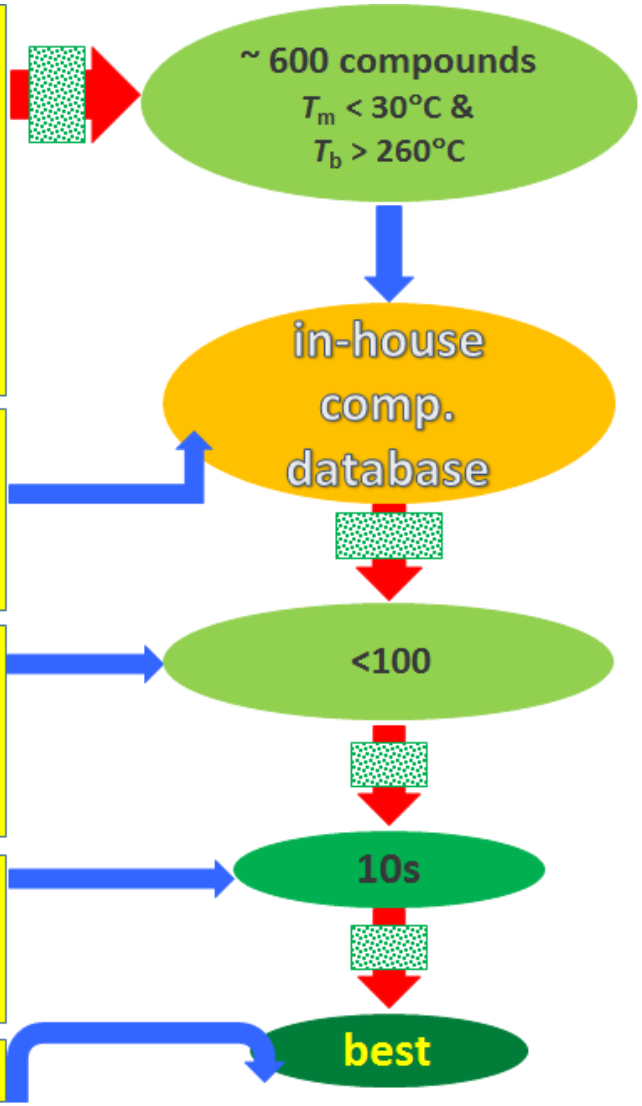
open literature
- Physical properties, such as flashing point
- Safety, health, environment
- Price

In-house computational database: quantum mechanics for gas – chemical function group interactions
- CO_2, CH_4, H_2, H_2O, H_2S, SO_2, O_2, N_2, etc.

In-house molecular simulation: MC
- Chief criteria: CO_2 solubility, CO_2/H_2 solubility selectivity, heat of absorption
- H_2O solubility (hydrophobicity/hydrophilicity)

In-house molecular simulation: MD
- Surface tension, heat capacity, viscosity, CO_2 diffusivity, density, vapor pressure, therm. conduct.

Experiment: Testing & new chemical synthesis



Conclusions

New PEG-PDMS solvents were synthesized and characterized

All have good CO_2 working capacity between 2 - 25 bar

All have low water uptake and low viscosities (<20 cP)

PEG-PDMS-3 had both high CO_2/H_2 selectivity and no foaming issues

A small pilot plant is currently being designed through the use of CFD modeling and validation

Construction of the unit will begin in 2018

Acknowledgements

- NETL/R&IC Solvents Teams
  - Omar Basha
  - Isaac Gamwo
  - Megan Macala
  - Robert Thompson
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  - Lei Hong
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- NETL Technical Support Staff
  - Mike Ciocco
  - Roger Francis
  - Rich Valdisera
  - John O'Connor
- NETL/R&IC Management
  - Randy Gemmen
  - Jim Fisher
  - Dave Berry
  - David Alman
- University of Pittsburgh
  - Badie Morsi
  - Hseen Baled

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Questions?

Thank you for your attention.

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