



NATIONAL ENERGY TECHNOLOGY LABORATORY

Pre-combustion CO₂ Capture

PEGDME
Selexol™
hydrophilic
0-30°C

PDMS-PEGDME
H-Siloxane
hydrophobic
10-40°C

[aPy][Tf₂N]
Ionic Liquid
hydrophobic
40-100°C



A High Performance Physical Solvent for Pre-Combustion CO₂ Capture

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David Hopkinson, TPL
2018 CO₂ Capture Technology Review



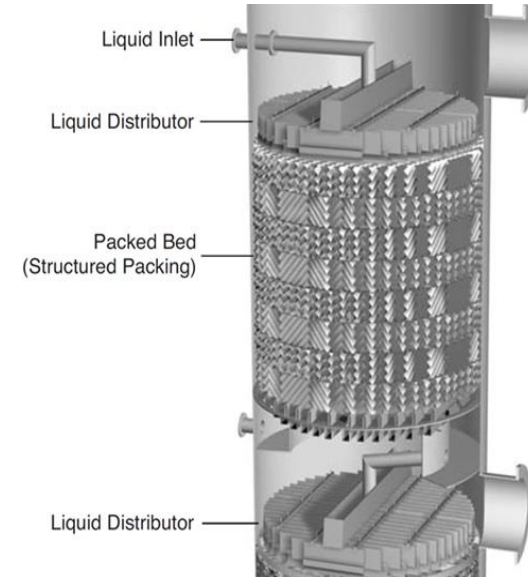
U.S. DEPARTMENT OF ENERGY
ENERGY

Applications for Physical Solvents

Commercial Applications

Tailored markets

- Pre-combustion CO₂ capture at IGCC-CCS
- Generation of H₂ from reformed natural gas
- Generation of H₂ at petroleum refineries
- Adjust CO/H₂ ratio for coal & biomass to liquids
- Remove CO₂ from syngas for ammonia/fertilizer



PRE-COMBUSTION SOLVENTS FOR CARBON CAPTURE



Problem:

Commercially operated physical solvents for CO₂ /H₂ separation operate at below room temperature. Hence, they incur a significant electrical cost to chill and can't be regenerated using waste heat.

These solvents are hydrophilic and have high vapor pressure.

Selexol® operates at 10°C (Kemper County, MS)

Rectisol® operates at -10°C (Great Plains, ND)

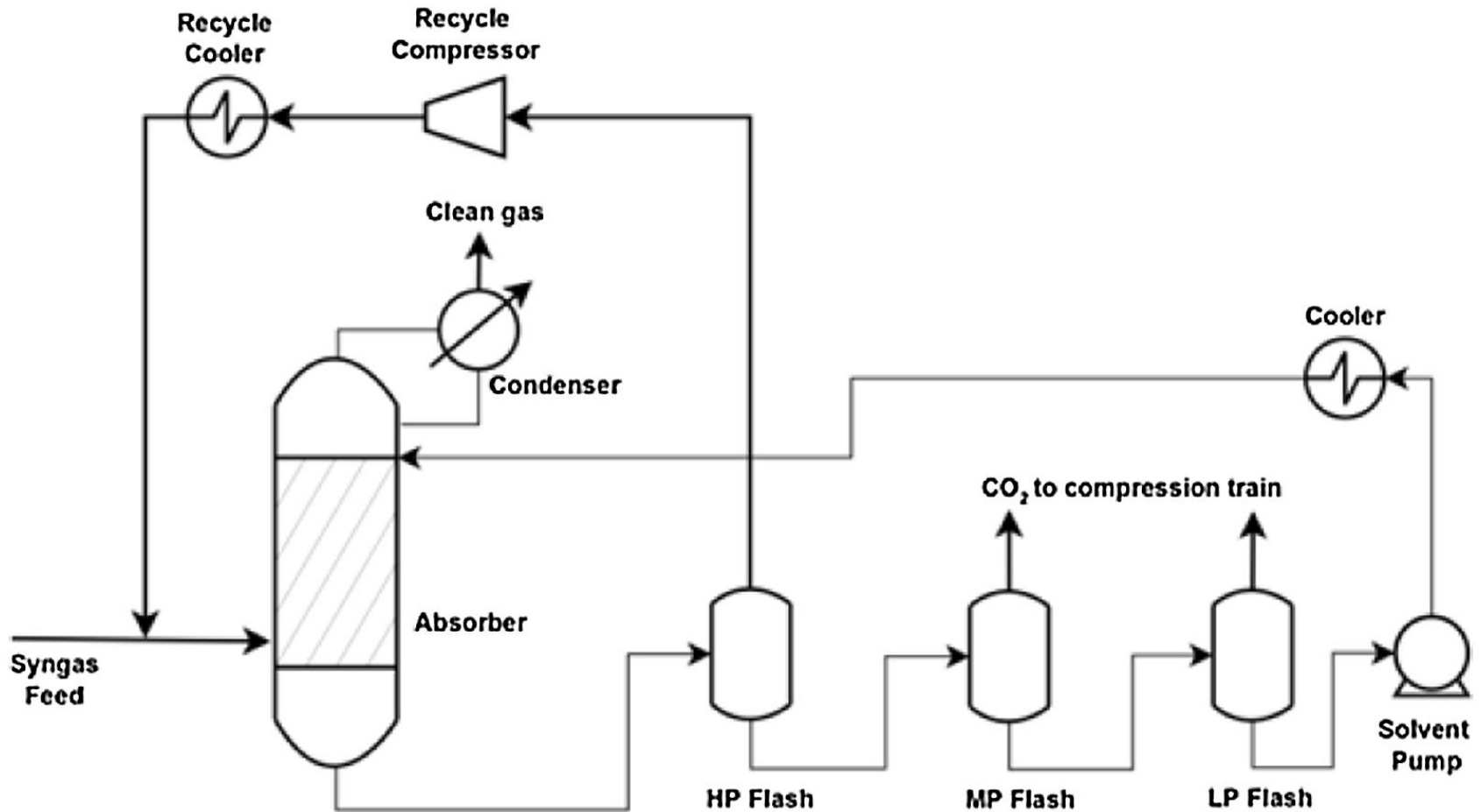
Selexol® (UOP / Dow Chemical) &

Rectisol® (Air Liquide Global E&C Solutions GmbH / Linde AG)

Solution:

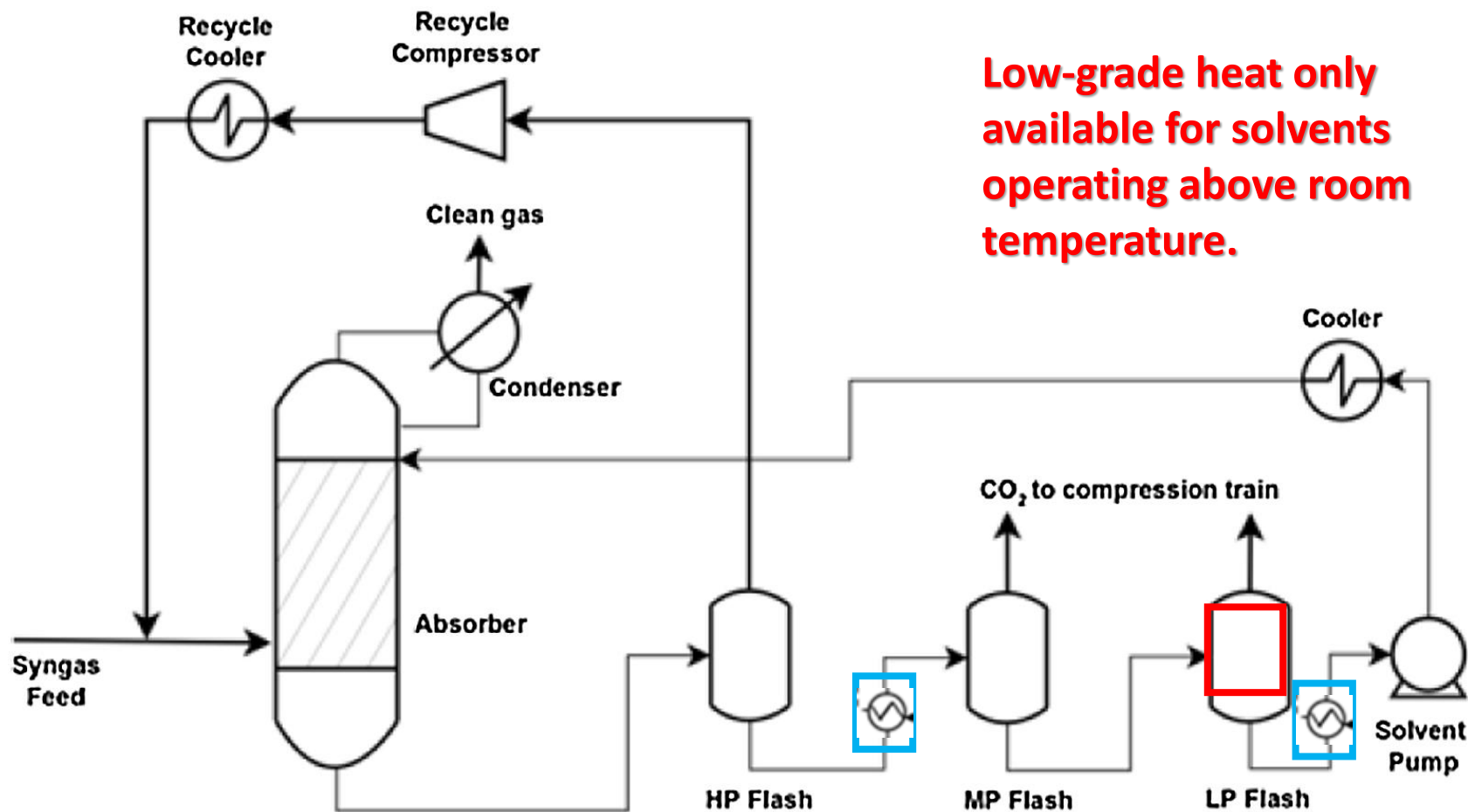
- Find new physical solvents that selectively absorb CO₂ between at temperatures between 25°C and 100°C
- Find solvents that also can be regenerated using waste heat

Baseline Selexol Process Flow Diagram



- In NETL baseline, Selexol® solvent loops at a temperature of 10°C

Potential Process Using Low-Grade Heat



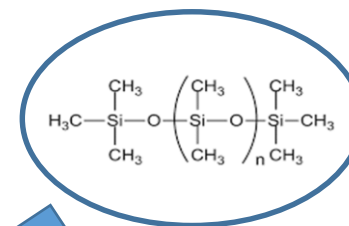
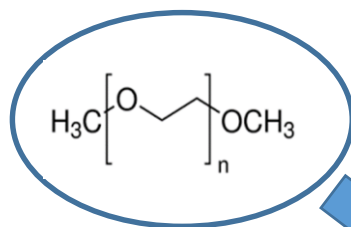
Low-grade heat only available for solvents operating above room temperature.

Pro's & Con's of Selexol vs. Silicone Oils

	Processes based on Selexol or Similar Hydrophilic PEG Solvents	Processes based on PDMS or Similar Hydrophobic Solvents
Operating Temperature	Below room temperature	Above room temperature
Chemical Stability	Mid	High
Corrosion	Mid	Low
Cost of the Solvent	Low	Mid
CO ₂ / H ₂ Selectivity	High	Low

PEGDME

fully miscible with water;
Extremely hydrophilic



Integrate Selexol and silicone fluid into novel, hydrophobic solvents: Hybrid PDMS (HPDMS)

PDMS

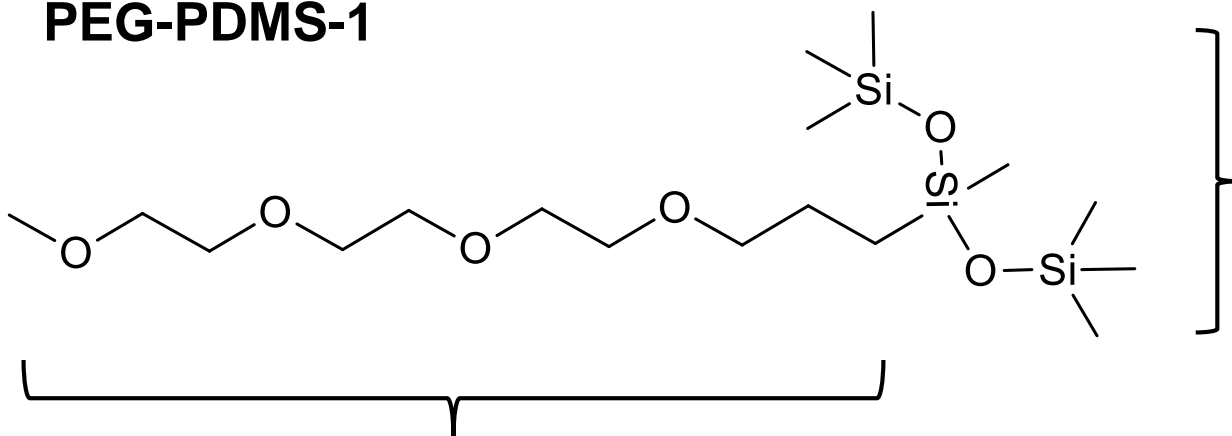
immiscible with water, even at 120C and 10000 psi; separates quickly after shaking;
Extremely hydrophobic



PEG-PDMS solvent#1

Attempt to incorporate best of both systems

PEG-PDMS-1



Siloxane functionality
resembling PDMS:
hydrophobicity and
improved gas selectivity

PEG functionality resembling Selexol:
to maintain good CO₂ uptake capacity

Hybrid structure - improve CO₂/H₂
selectivity, while maintaining good CO₂
solubility in a *hydrophobic* solvent system

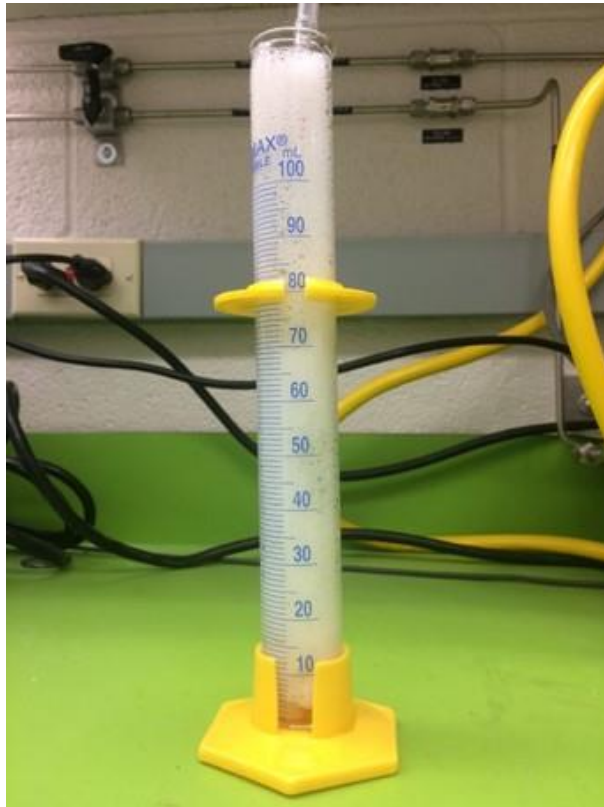


"High performance hydrophobic solvent, carbon dioxide capture"

[Patent 9,643,123 \(issued May 9, 2017\)](#)

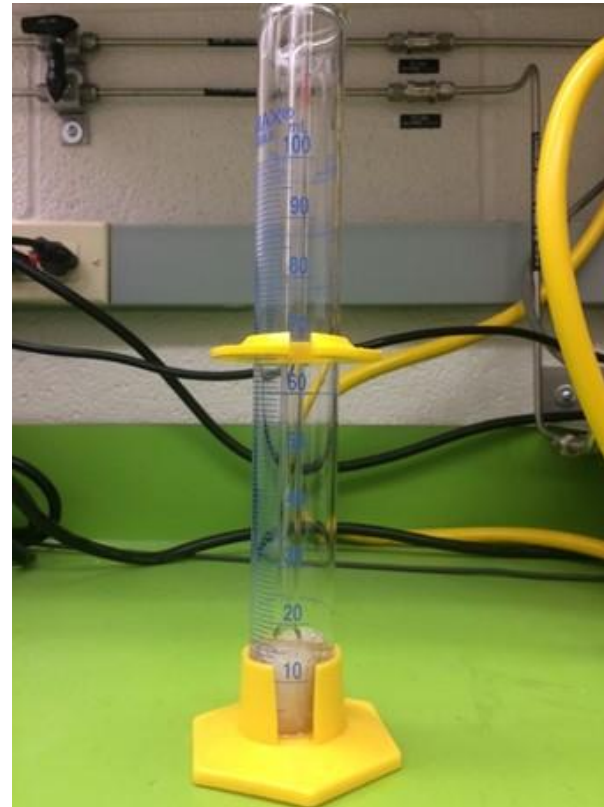
Foaming issue has been addressed

PEG-PDMS-1



Severe foaming

PEG-PDMS-3



No foaming

Physical Properties

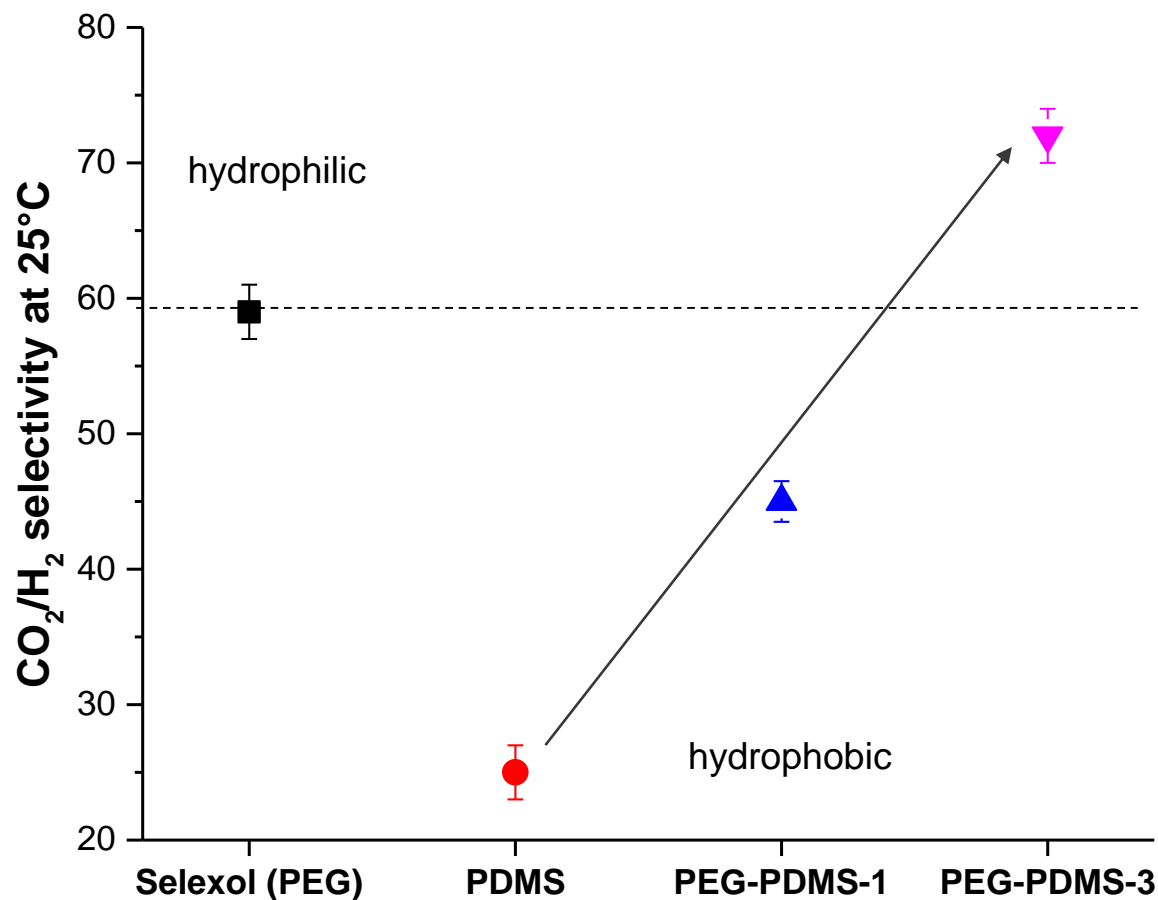
	MW, g/mol	density, g/mL at 25°C	viscosity, cP at (X°C)	CO ₂ /H ₂ at 25°C	CO ₂ /H ₂ at 40°C	foam?
Selexol*	280	1.03	10.6 (10°C)	59 ± 2	40 ± 2	no
PEG-PDMS-1	427	0.935	3.9 (30°C)	45 ± 1	33 ± 1	yes
PEG-PDMS-3	620	0.987	8.1 (40°C)	72 ± 2	60 ± 1	no

- PEG-PDMS-3 is the best overall performing precombustion physical solvent known in the literature for CO₂ capture
- Synthesis procedure is simple and scalable, and raw feedstocks are moderately priced
- Allows for CO₂ capture at above room temperature and allows for waste heat to be used to regenerate the solvent
- = Selexol surrogate tested at NETL/RIC CSTR
Univar (Bunola, PA)



PEG-PDMS Solvents

progress of crucial characteristics



* =Selexol surrogate (sold by Univar) tested at NETL/RIC's CSTR

Low Moisture Uptake

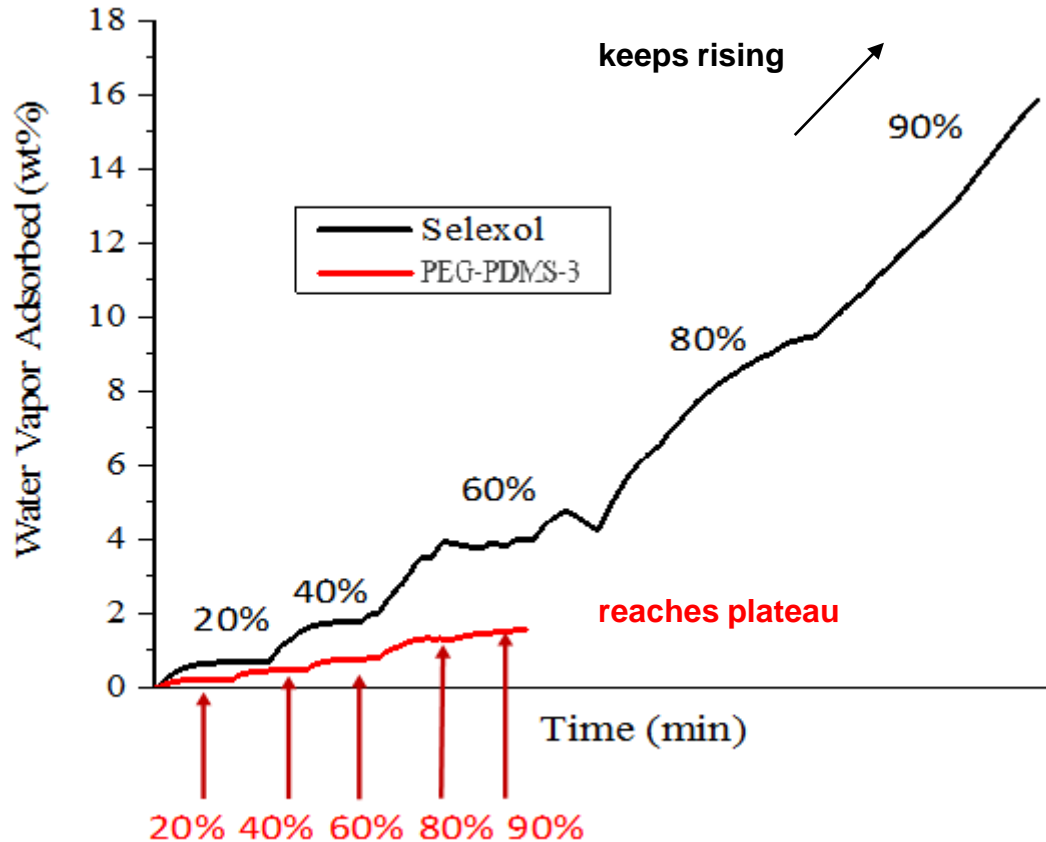
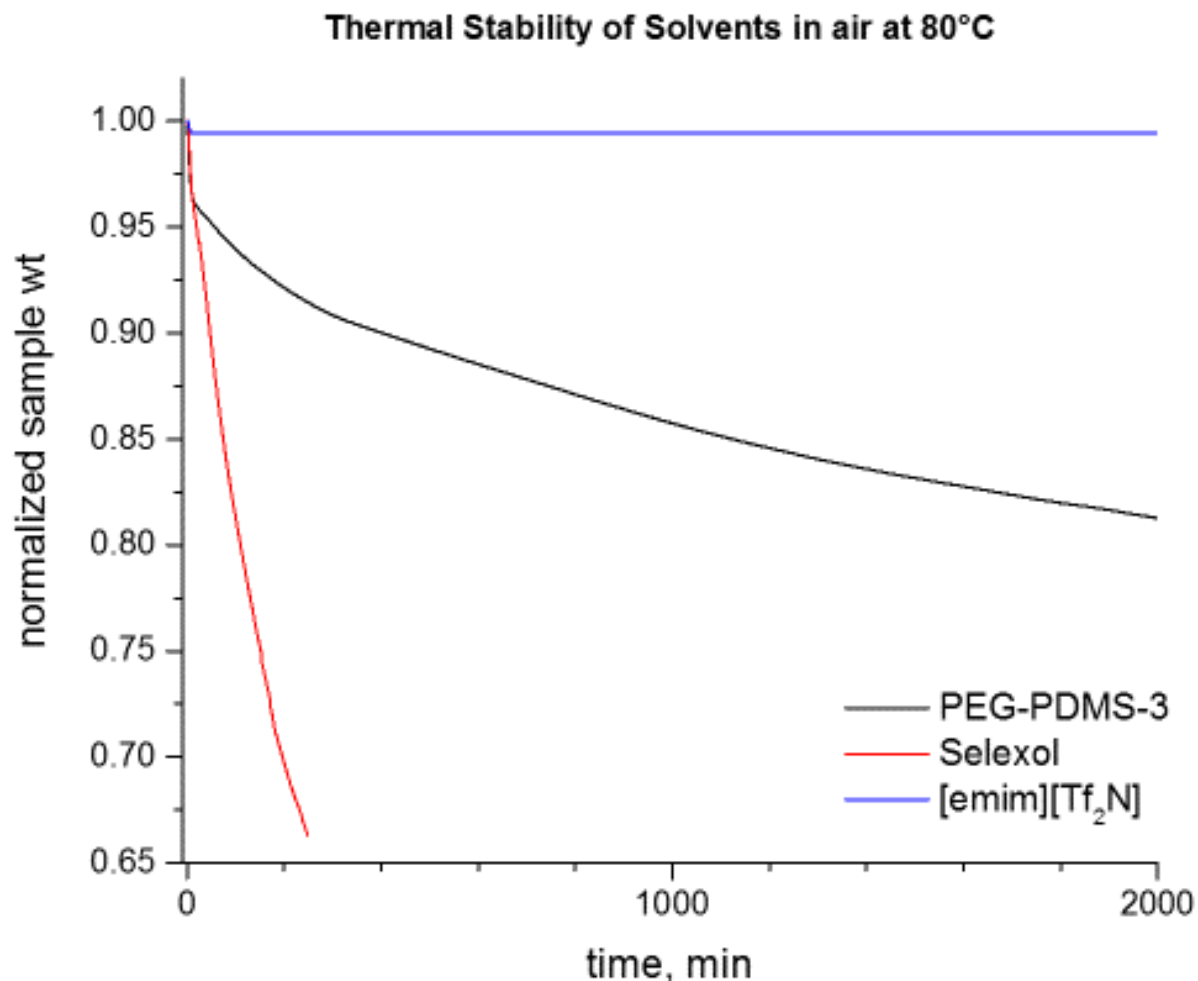


Figure 2: Comparison of water vapor absorption for PEG-PDMS-3 and Selexol surrogate (Univar.) Sample temperature at 25°C. Feed gas is a blend of wet and dry N₂. The percent of wet N₂ in the feed stream at different points in the curves is indicated by the numbers on the plot. Data was collected on the Hiden IGA. Note: Selexol surrogate does not approach saturation under high humidity conditions

- **PEG-PDMS-3 absorbs significantly less water vapor than Selexol***

Low Evaporation Rate for PEG-PDMS-3



- Vapor pressure of PEG-PDMS-3 is significantly below Selexol*

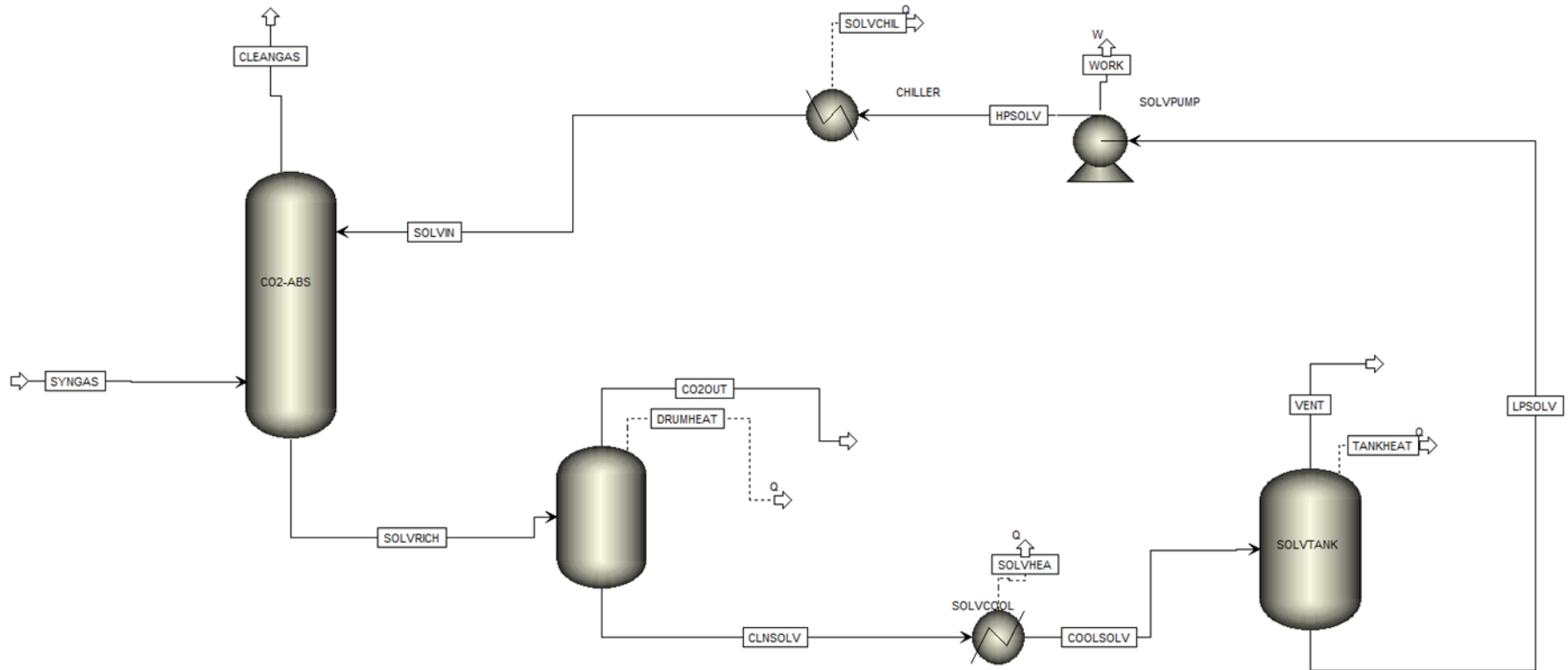
Future Testing of PEG-PDMS-3 at UND EERC Gasifier

- Goal: Test both PEG-PDMS-3 and Selexol® under real syngas generated at either a fluidized or entrained flow gasifier
- Test scale = 60 liters of solvent
- Absorption at 10-40°C
- Regeneration at 10-80°C



Gasifier Name	Type	Scale	Feed Rate, lb/hr	Syngas Production, scfm	System Pressure, psi	Gasifier Nominal Temperature, °F	Warm-Gas Cleanup Capability
CFBR	Fluidized bed	Bench	4	8 on air 1.5-2 on O ₂	150	1525 (metal reactor)	Full stream
TRDU	Transport reactor	Pilot	200-500	400 on air 250 on O ₂	120	2000 refractory-lined	Slipstream, 5%
EFG	Entrained flow	Bench	4-16	16-20	300	2730 refractory-, ceramic-lined	Full stream
HPFBG	Fluidized bed	Bench	4-20	30-40	600-1000	1600 to 1800 depending on operating pressure (metal reactor)	Full stream

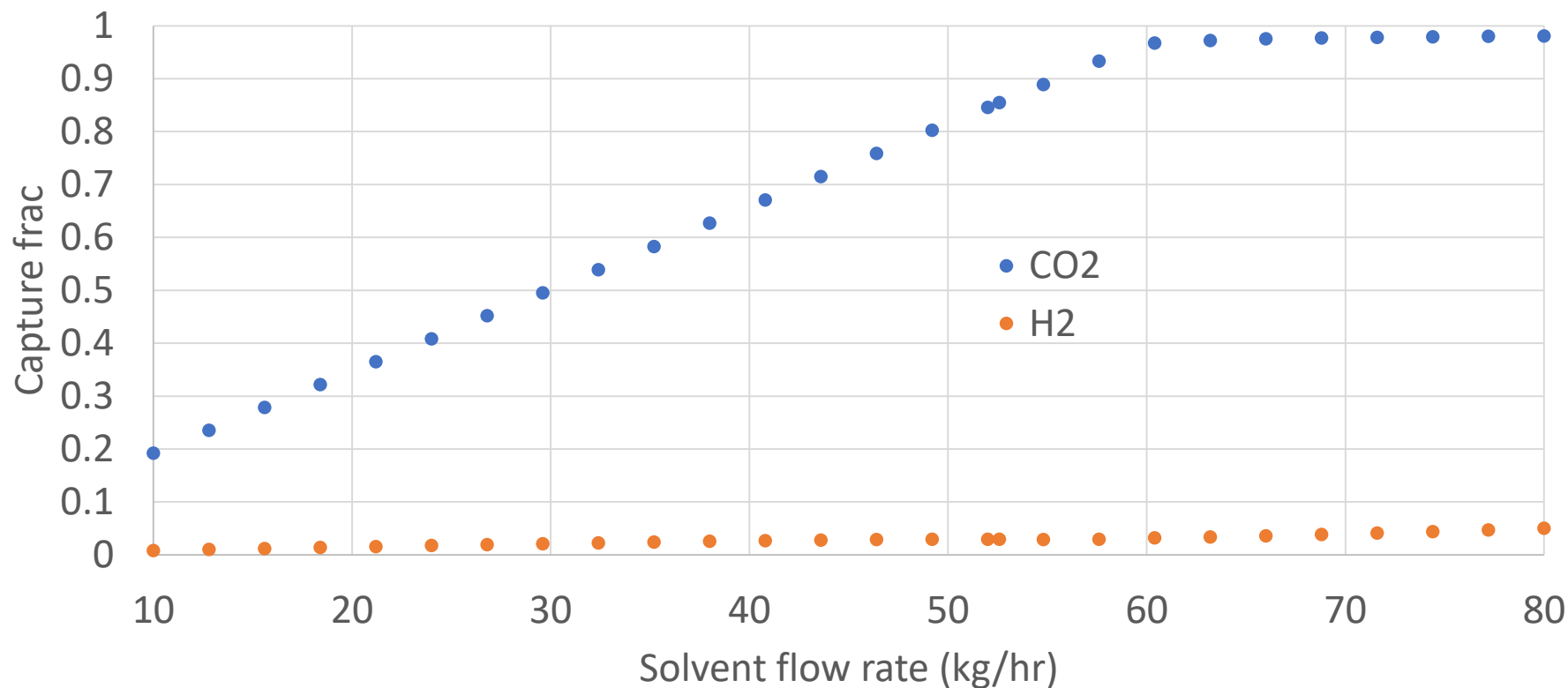
Aspen Plus Modeling of UND EERC



- Absorption column at UND EERC was modeled as a RadFrac Rate Based Separator in Aspen Plus. Kinetics were estimated using experimental data from the facility.

Aspen Plus Results for UND EERC Conditions

PEG-PDMS-3 H₂ and CO₂ capture fraction at 40°C, 50 bar

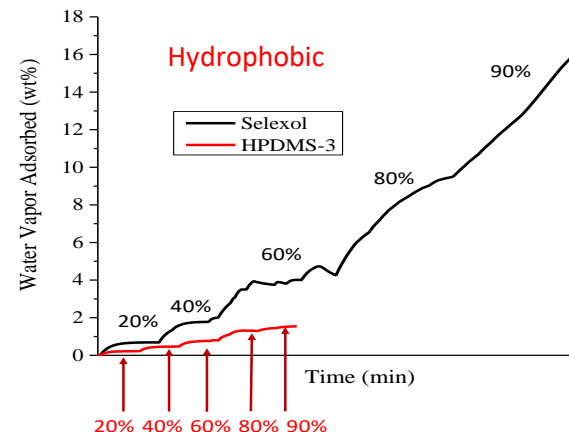
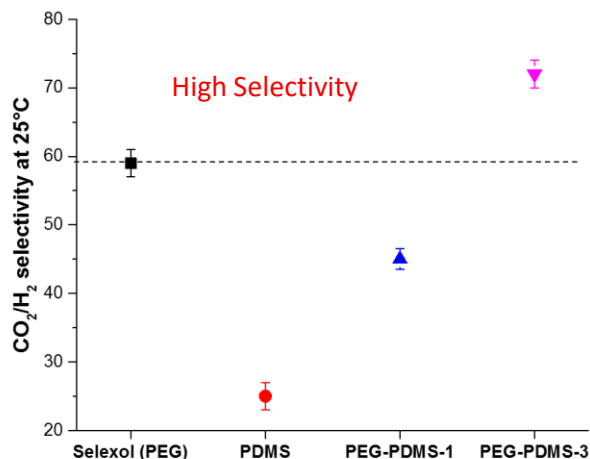


- Predictions for CO₂ and H₂ uptake into PEG-PDMS-3 as a function of solvent flow rate

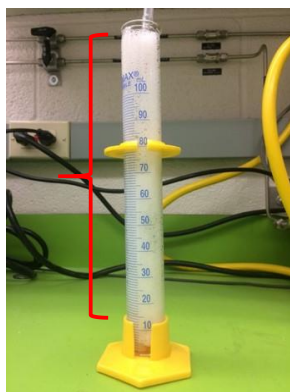
Conclusions

PEG-PDMS-3

- Higher CO₂/H₂ selectivity than Selexol*
- Hydrophobic
- No foaming
- Low vapor pressure
- Low evaporation



PEG-PDMS-1



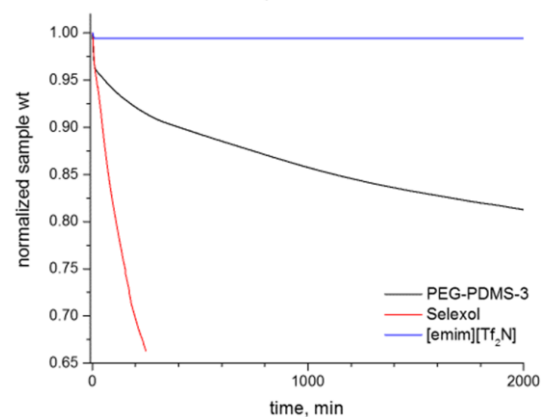
severe foaming

PEG-PDMS-3



no foaming

Thermal Stability of Solvents in air at 80°C



Lower Vapor Pressure = Lower Evaporation

Acknowledgements



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