Hydrophobic, Physical Solvents for Pre-combustion CO_2 Capture: Experiments and System Analysis

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Task Technical Coordinator

Solvents—Maturation

CO_2 Capture Technology Conference 6/25/2015

Team Members: Sweta Agarwal, Hunaid Nulwala, Elliot Roth, Victor Kusuma, Fan Shi, Wei Shi, Jeff Culp, Sarah Narburgh, David Miller, and Dave Hopkinson

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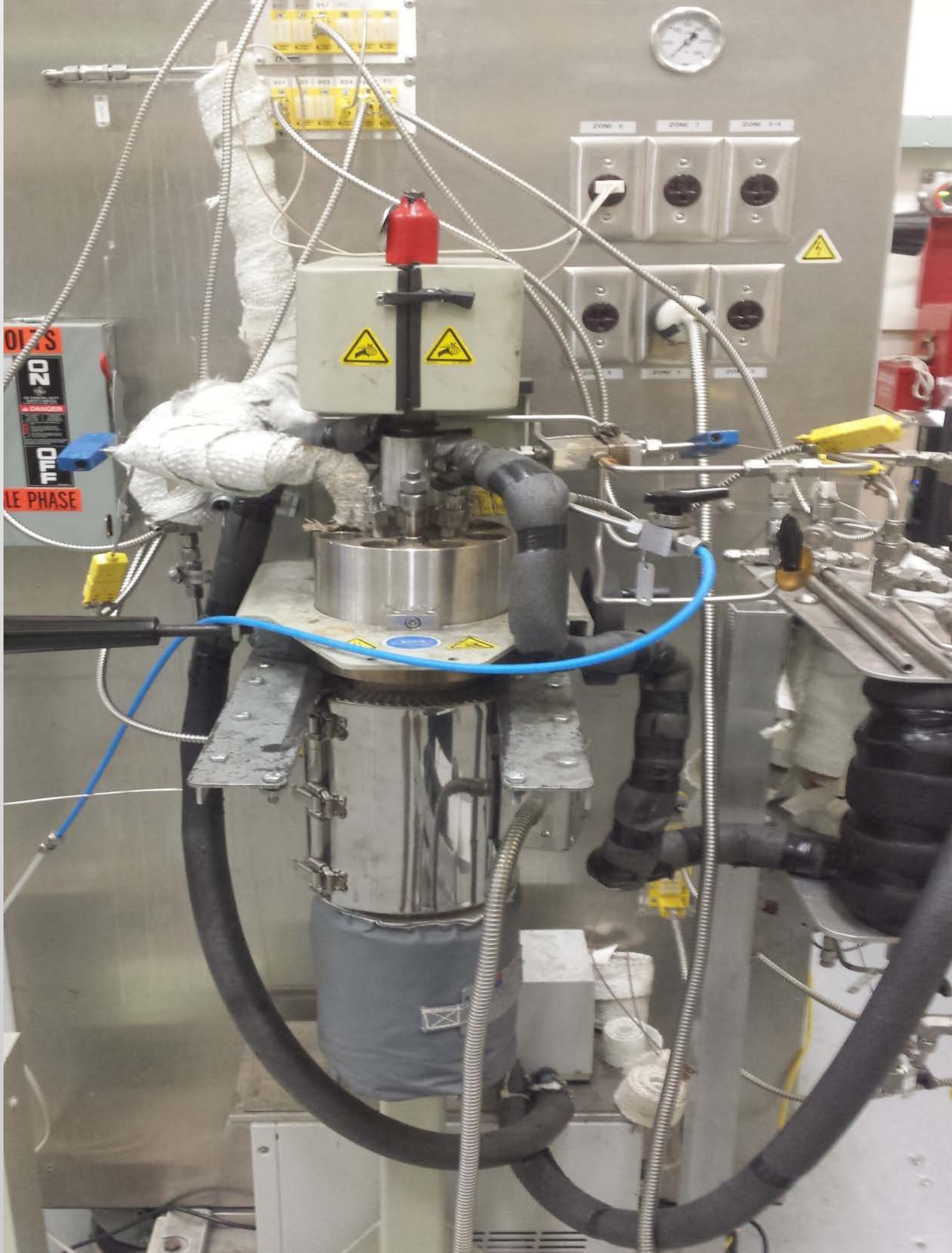
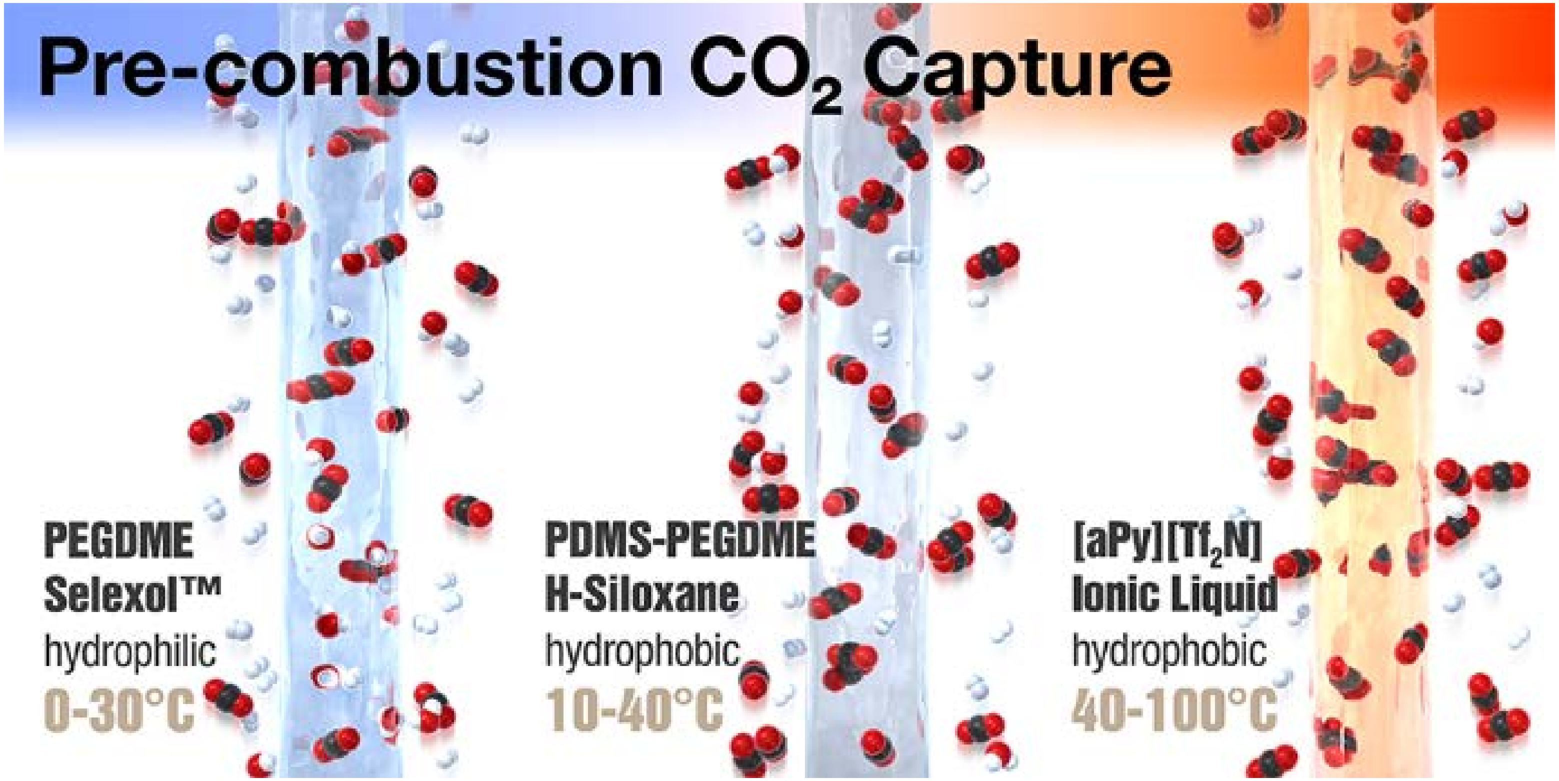


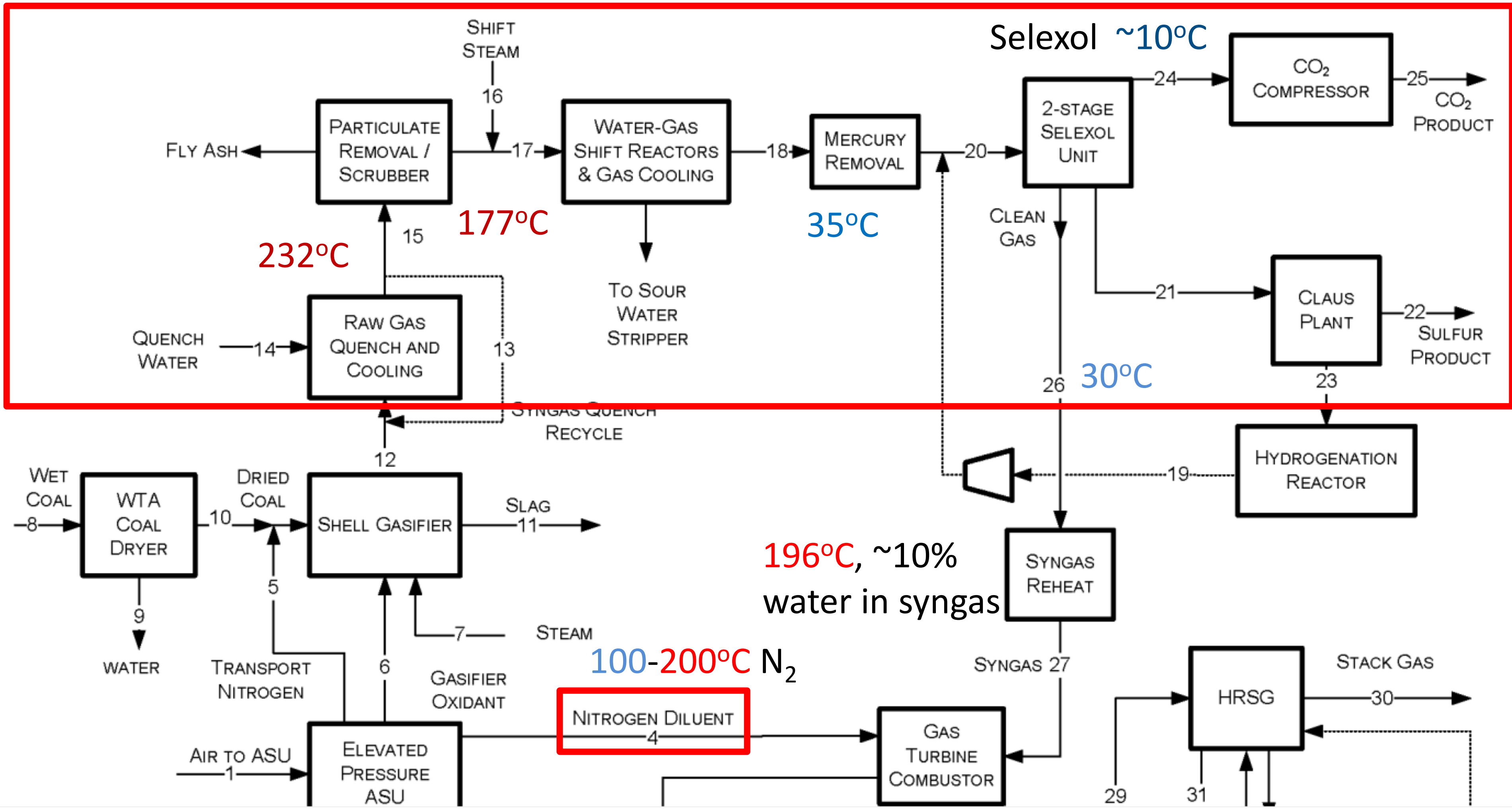
Outline

- Overall goal of project: Why Hydrophobic Solvent?
- Experimental Data & Computational Simulations
- System & Exergy Analysis



Process Flow Diagram: IGCC w/ CO_2 Capture

Exhibit 3-37 Case S1B and L1B Process Flow Diagram

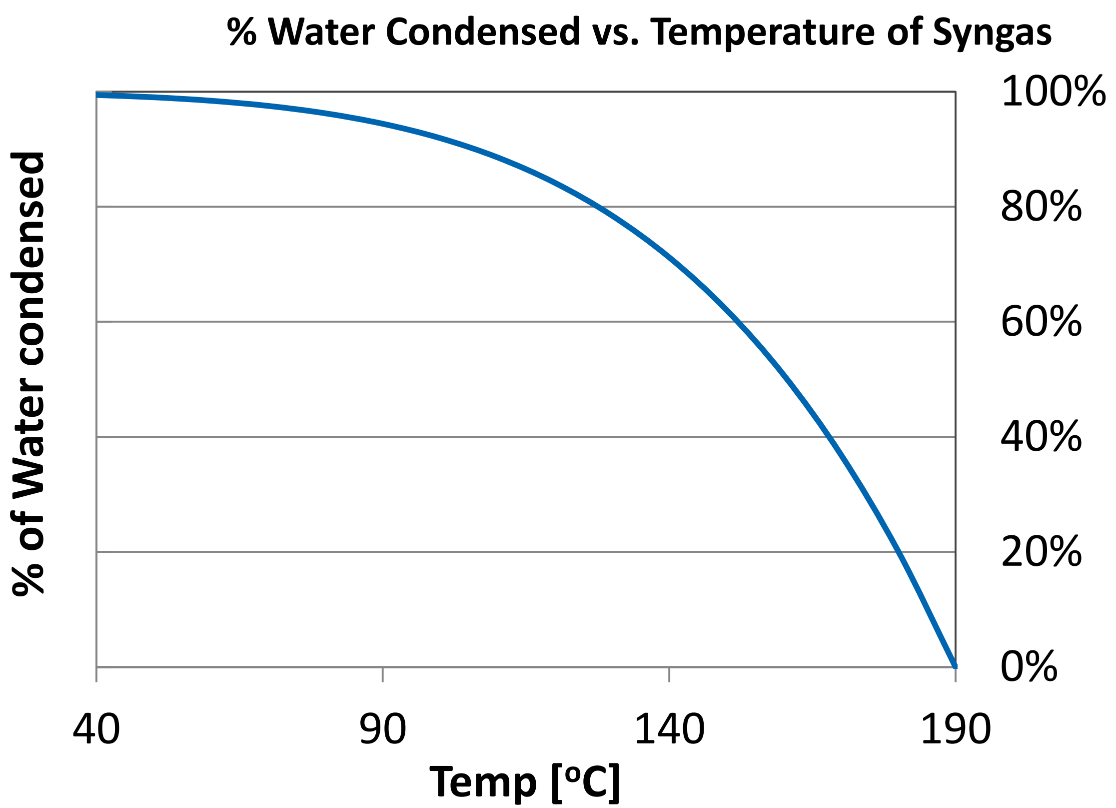


http://www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/Coal/LR_IGCC_FR_20110511.pdf

NETL

Background: Why Selexol operates < 40°C

- Higher CO_2 and H_2S selectivity against H_2 at lower temperature
- <u>Constraint</u>: Selexol will absorb any remaining water in syngas



Commercially Available Physical Solvents for AGR

Table 1 – Properties of Physical Solvents

Solvent	**DEPG**	**PC**	**NMP**	**MeOH**
Process Name	Selexol or Coastal AGR	Fluor Solvent	Purisol	Rectisol
Viscosity at 25°C (cP)	5.8	3.0	1.65	0.6
Specific Gravity at 25°C (kg/m^3)	1030	1195	1027	785
Molecular Weight	280	102	99	32
Vapor Pressure at 25°C (mmHg)	0.00073	0.085	0.40	125
Freezing Point (°C)	-28	-48	-24	-92
Boiling Point at 760 mm Hg (°C)	275	240	202	65
Thermal Conductivity (Btu/hr*ft*°F)	0.11	0.12	0.095	0.122
Maximum Operating Temperature (°C)	175	65	-	-
Specific Heat 25°C	0.49	0.339	0.40	0.566
CO_2 Solubility (ft^3/U.S. gal) at 25°C	0.485	0.455	0.477	0.425

Table 2 – Solubilities of Gases in Physical Solvents Relative to CO_2

Selectivity	**DEPG** at 25°C	**PC** at 25°C	**NMP** at 25°C	**MeOH** at -25°C
CO_2/H_2	77	128	156	185
CO_2/N_2	50	119	NA	83
CO_2/CH_4	15	26	14	20
H_2S/CO_2	8.8	3.3	10.2	7.1

These AGR solvents are not designed for warm gas CO_2 removal. Too hydrophilic and/or volatile for high temperature operation

High Molecular Weight PDMS - Background

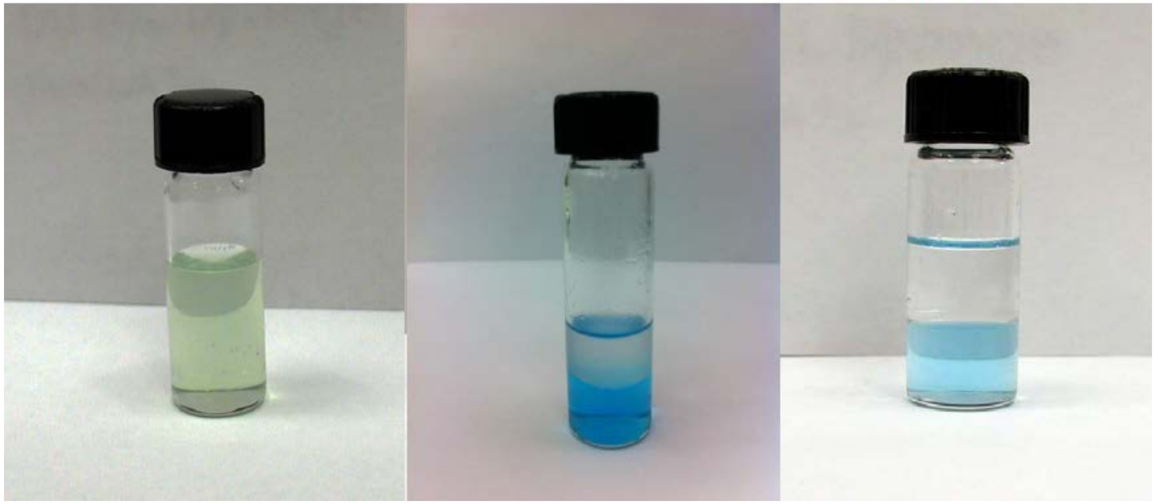
- **Objective:** **Lower the cost of capturing CO_2 from syngas**
- **Approach:** **Develop hydrophobic solvents for separation of CO_2 from warm syngas**

PEGDME
fully miscible with water;
Extremely hydrophilic

PDMS-PEGDME hybrid
absorbs <<1wt% water,
Very hydrophobic

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

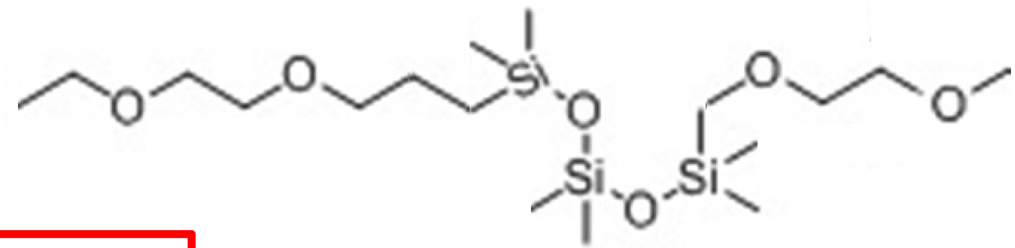
High CO_2 Uptake and CO_2/H_2 Selectivity

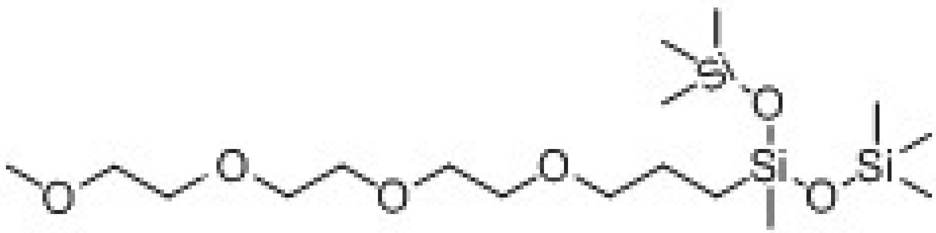


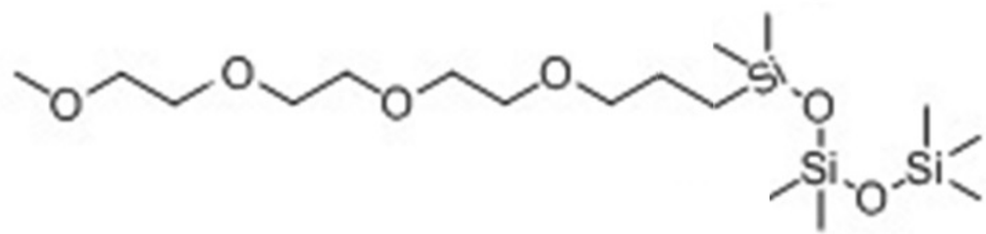
Low CO_2 Uptake and CO_2/H_2 Selectivity

The Solubility of Water in the Solvents

Options for Hybrid PEG-PDMS

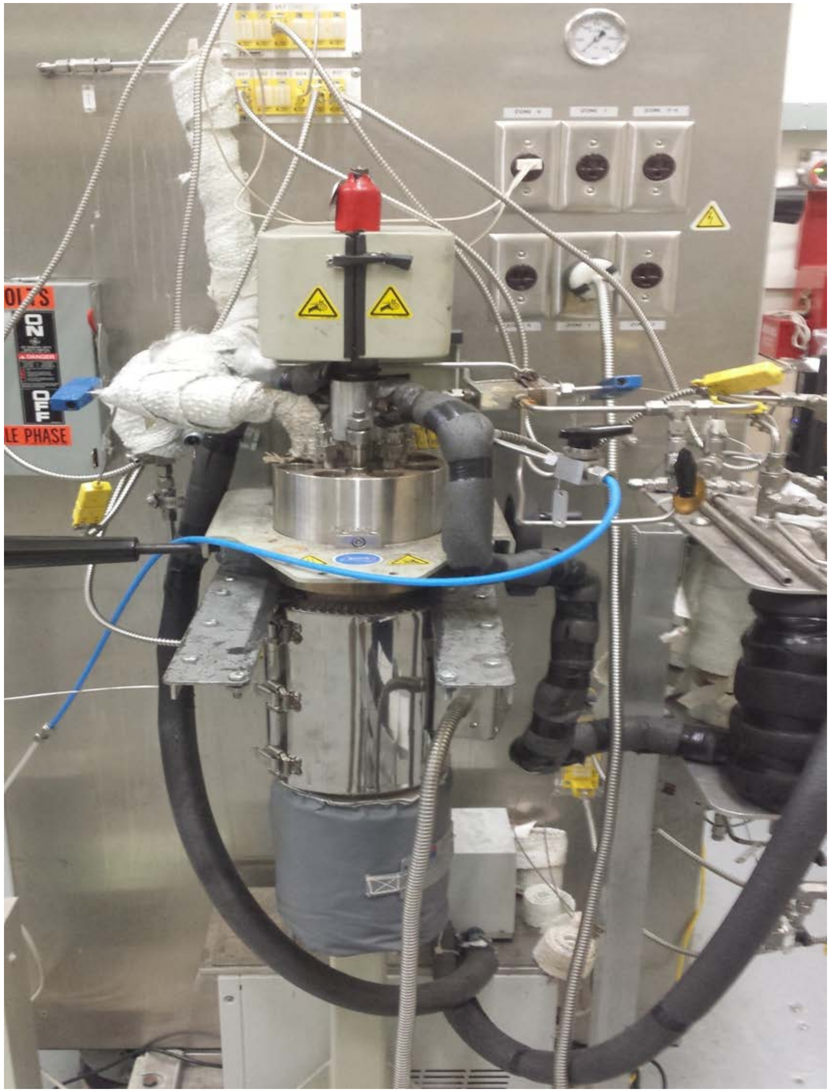


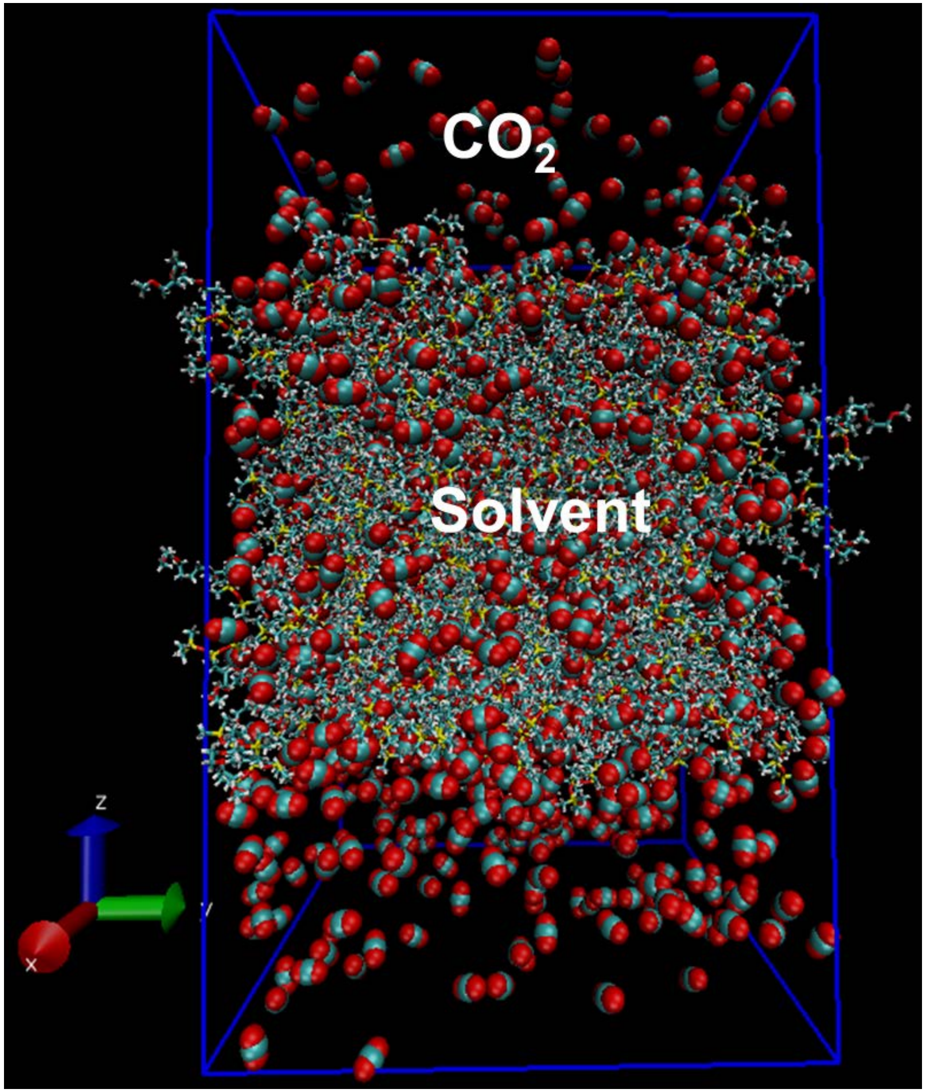




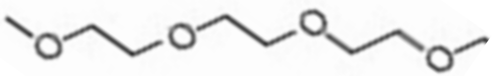
- Synthesized and Fully characterized by NETL/ORD
- To be synthesized and fully characterized by NETL/ORD

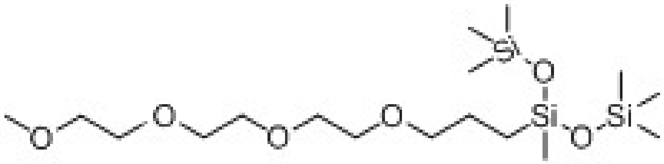
Experimental and Computational Results





Selexol vs. Hybrid @25°C





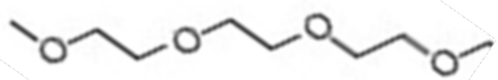
Selexol

- Hydrophilic
- MW = 280
- Viscosity = 5.8 cP, Pr = 63
- Specific heat = 2.06 kJ/kg·K
- Density = 1030 kg/m^3
- Thermal cond = 0.19 W/m·K
- Surface tension ~ 32 mN/m
- Vapor Pressure = 0.0007 mmHg
- CO_2/H_2 selectivity ~ 100

Hybrid PDMS-PEGDME

- Hydrophobic
- MW = 427
- Viscosity = 4.8 cP, Pr = 71
- Specific heat = 1.77 kJ/kg·K
- Density = 936 kg/m^3
- Thermal cond = 0.12 W/m·K
- Surface tension = 22.1 mN/m
- Vapor Pressure << 0.0007 mmHg
- CO_2/H_2 selectivity ~ 50

Selexol vs. Allyl Pyridinium Tf_2N @25°C



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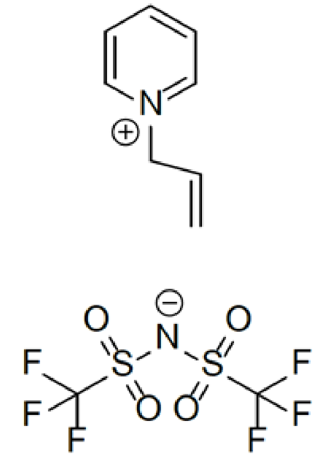
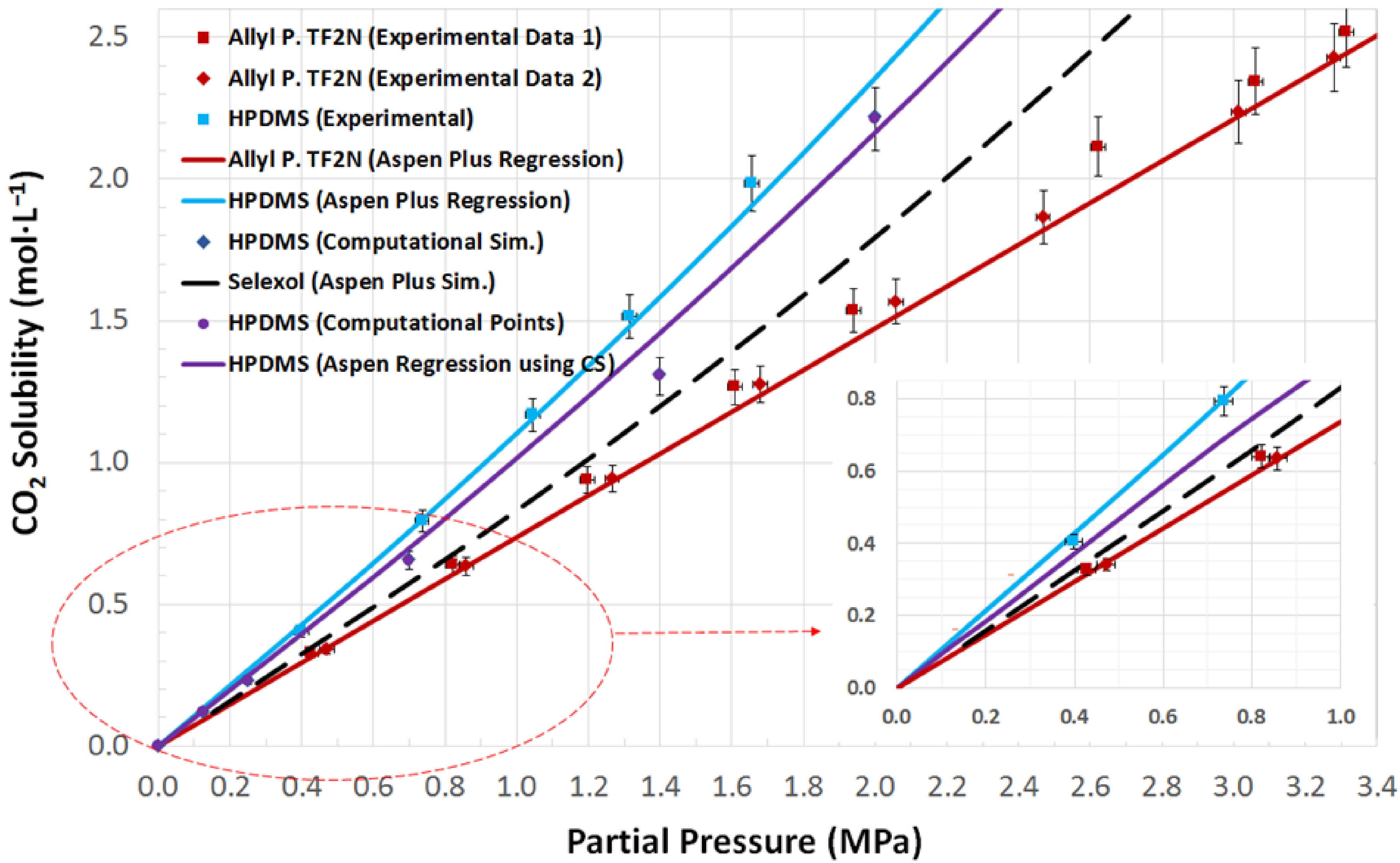


[aPy][Tf2N]

- Hydrophobic
- MW = 399
- Viscosity ~25 cP, Pr ~ 200
- Specific heat = 1.11 kJ/kg·K
- Density = 1515 kg/m^3
- Thermal cond = TBD*
- Surface tension = 35.2 mN/m
- Vapor Pressure <<< 0.0007 mmHg
- CO_2/H_2 selectivity ~ 100

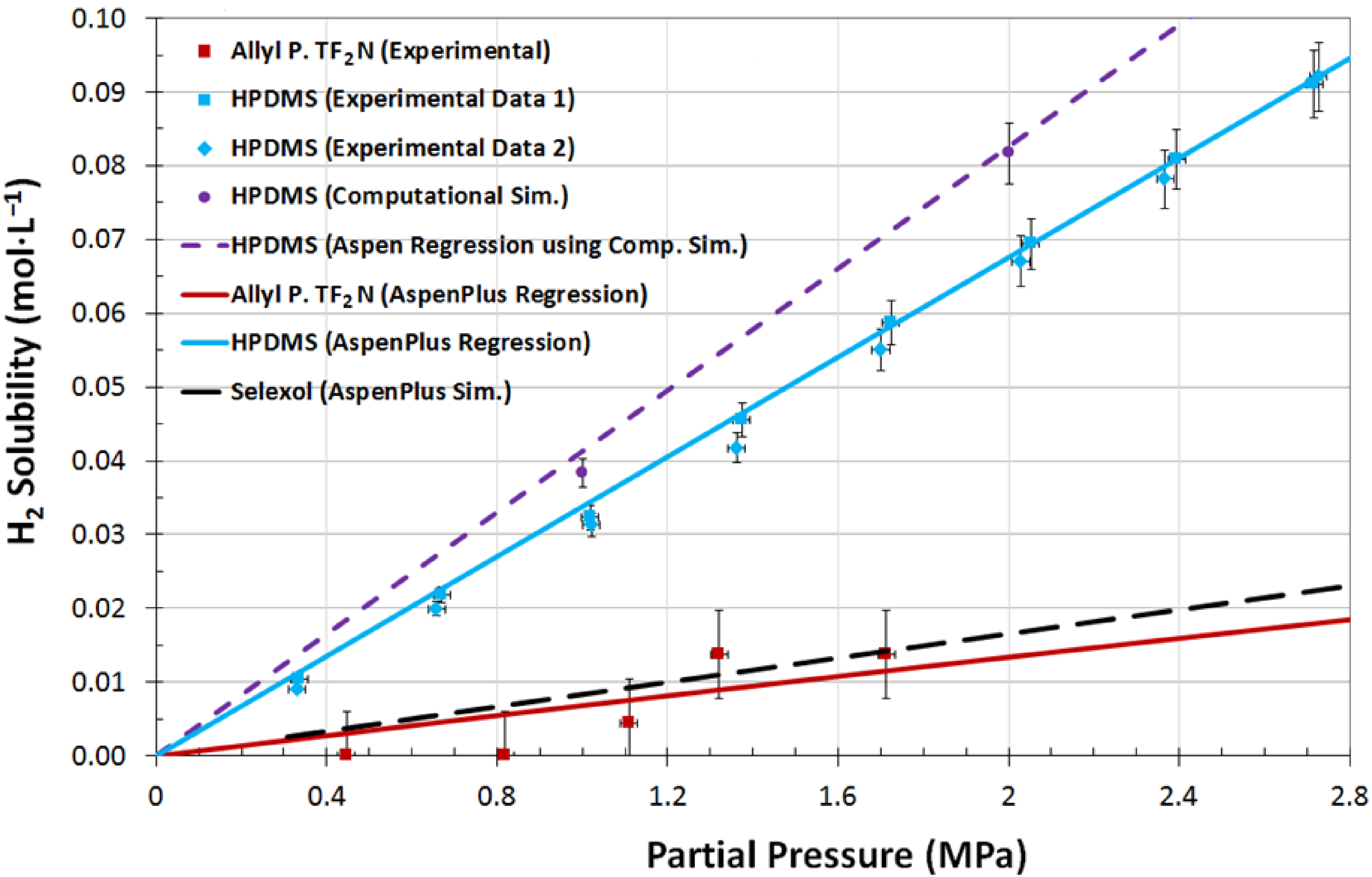
*GroupMethod estimates for thermal conductivity = 0.11 – 0.14 W/m·K

CO_2 solubility in physical solvents at 40˚C



CO_2 solubility = mol of CO_2 absorbed per liter of neat solvent

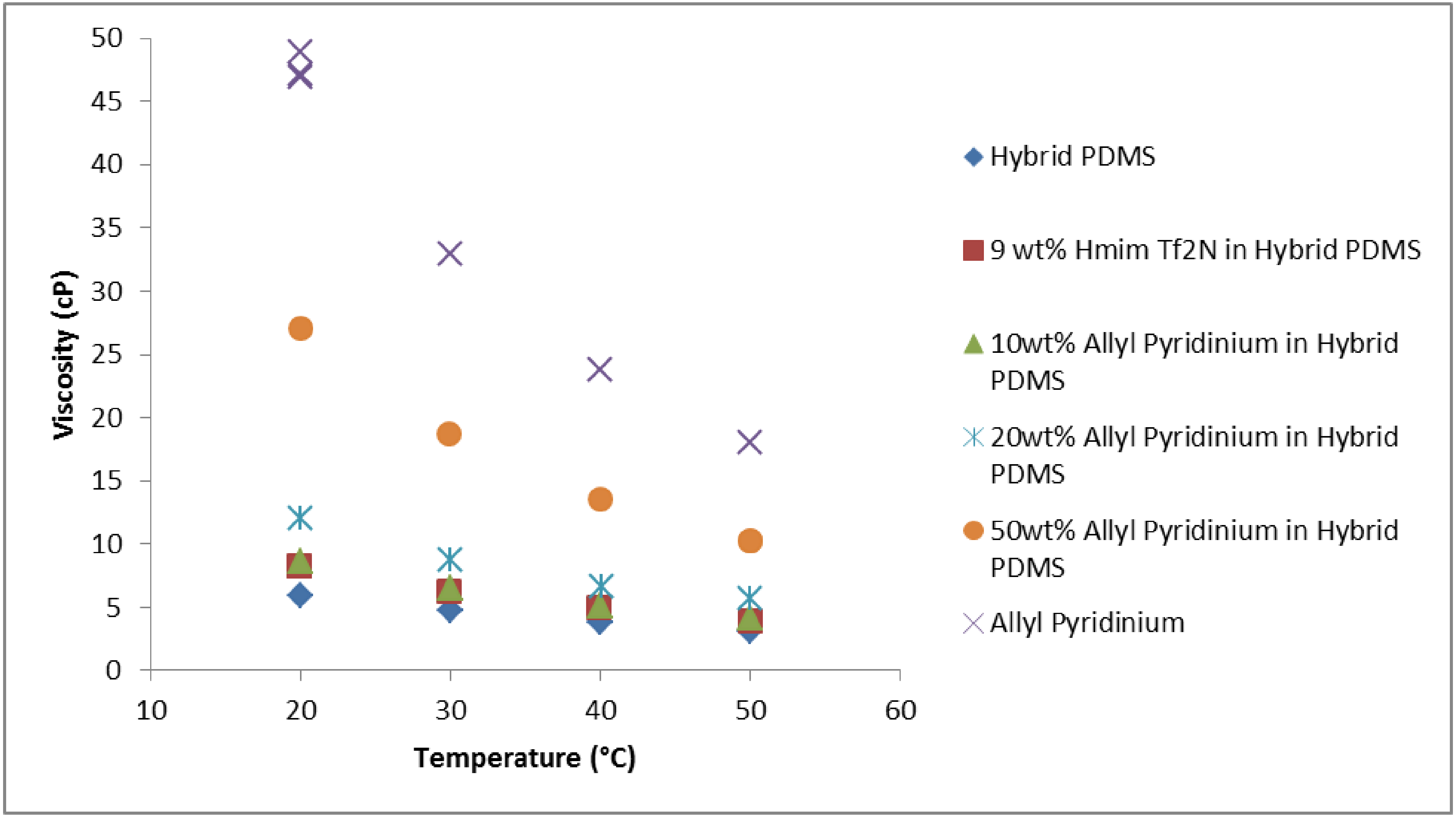
H_2 solubility in physical solvents at 40˚C



H_2 solubility = mol of H_2 absorbed per liter of neat solvent

Adding Ionic Liquid to HPDMS will increase Viscosity:

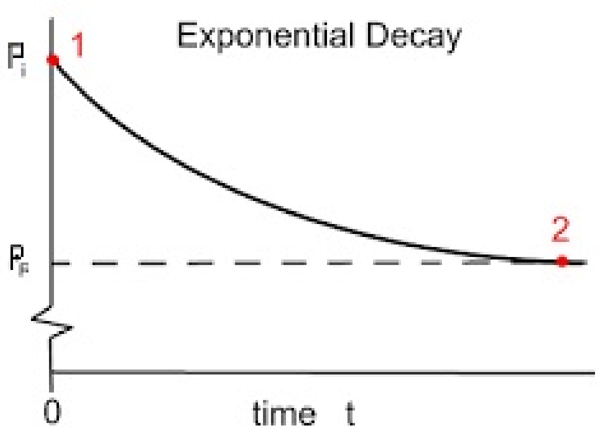
Allows for a Tunable Hydrophobic Solvent Mixture depending on Application



Measurements by Dr. Elliot Roth

Stirred Reactor Kinetics – k_l

Constant Stir Speed = 600 RPM		CO_2	H_2
100% HPDMS	25°C	$7.5 \cdot 10^{-4}\ s^{-1}$	$2.8 \cdot 10^{-3}\ s^{-1}$
	40°C	$1.1 \cdot 10^{-3}\ s^{-1}$	$3.4 \cdot 10^{-3}\ s^{-1}$
100% [aPy][Tf_2N]	25°C	~$2 \cdot 10^{-4}\ s^{-1}$	~$6 \cdot 10^{-4}\ s^{-1}$
	40°C		~$9 \cdot 10^{-4}\ s^{-1}$
90% HPDMS / 10% [aPy][Tf_2N]	25°C	$6.0 \cdot 10^{-4}\ s^{-1}$	$1.4 \cdot 10^{-3}\ s^{-1}$

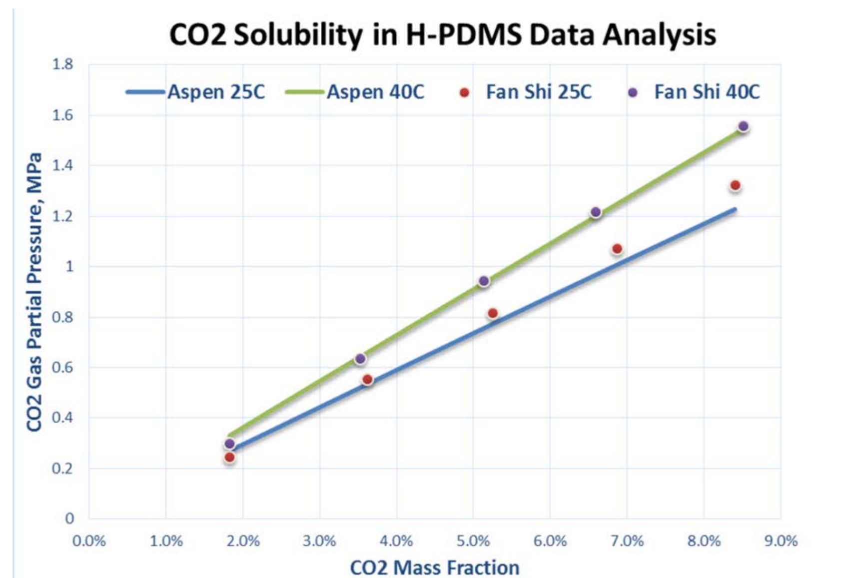


$$p(t) - p_f = (p_i - p_f) \cdot e^{-k_l \cdot t}$$

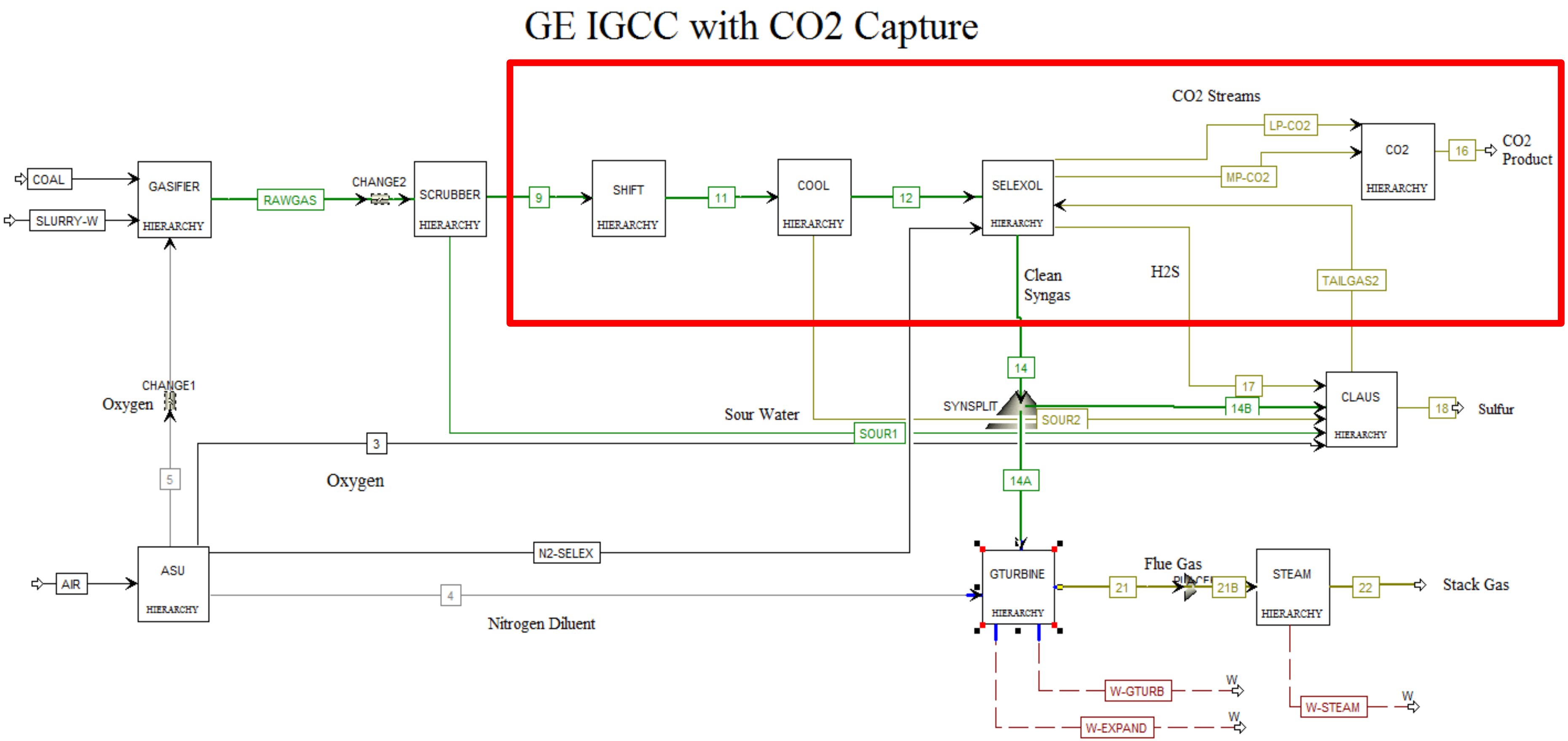
System & Exergy Modeling

System Modeling: Regression into Aspen Plus

- Regression of available experimental data on Hybrid PDMS solvent into Aspen to estimate required unary and binary parameters of PC-SAFT
- In order to regress CO_2/H_2 solubility, PC-SAFT method also required specific heat vs. T, density vs. T, and viscosity. vs. T
- ENRTL-RK method used for Ionic Liquid

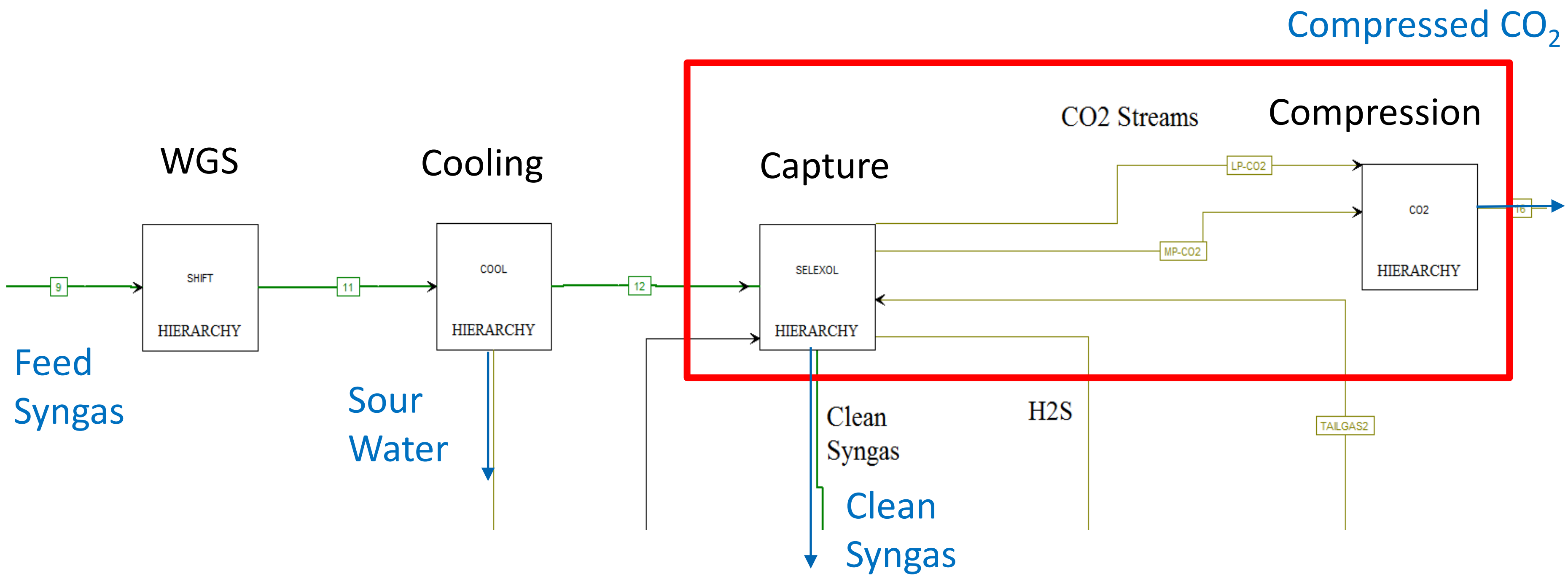


Overall IGGC-CCS Power Plant



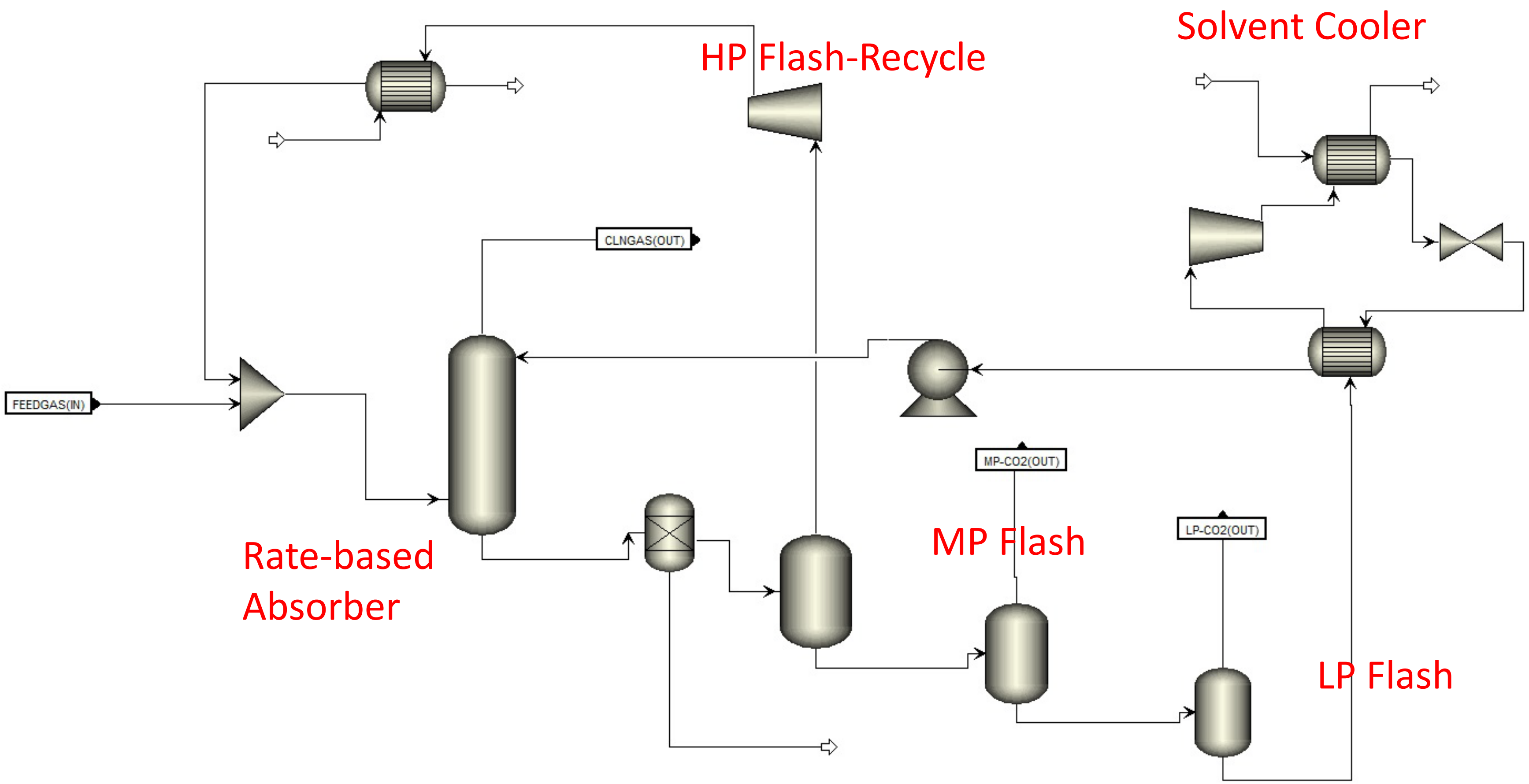
Field and Brasington, "Baseline Flowsheet Model for IGCC with Carbon Capture," Ind. Eng. Chem. Res., 2011, 50 (19), p 11306.

Portion Unique to CCS



System Modeling:
Aspen Plus Modeling

- **Base Model for CO_2 capture using flash regeneration adapted from MIT IGCC-Selexol capture Aspen Model**



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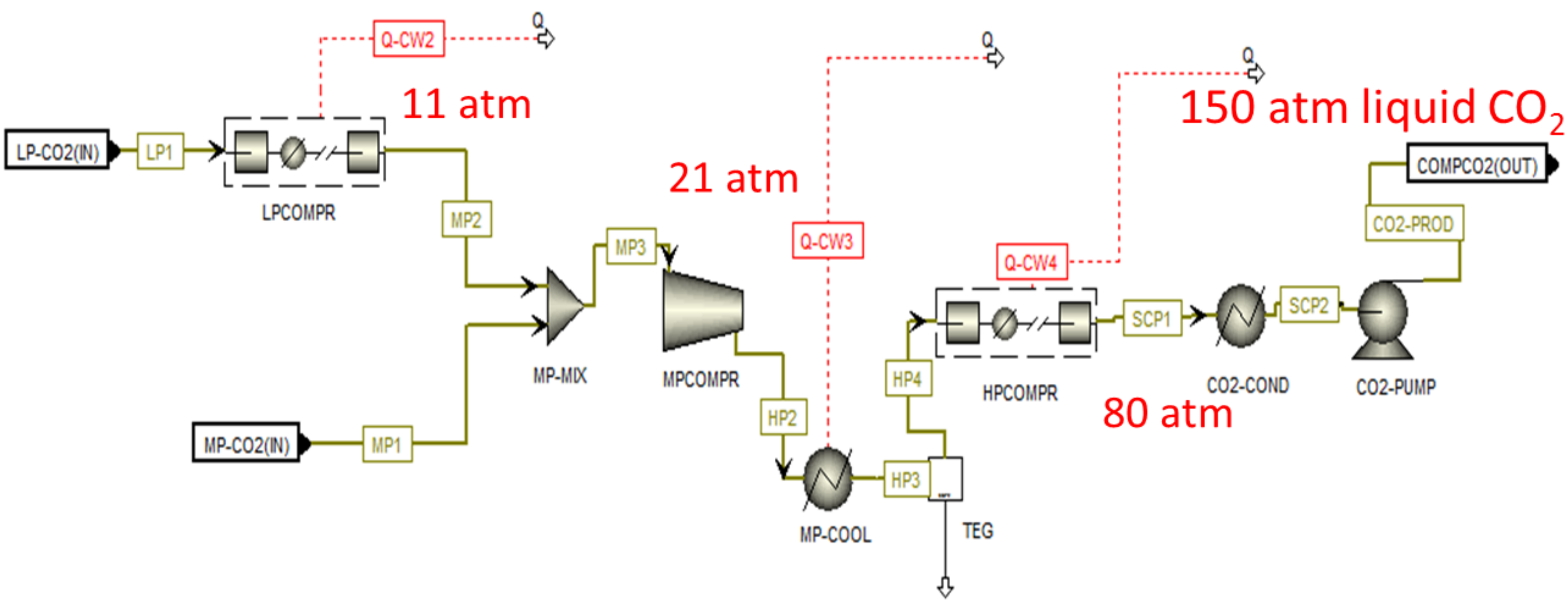

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Exergy Analysis

- **Exergy is the maximum possible useful work that can be generated by bringing a system into thermal, mechanical, and chemical equilibrium with its surrounding environment.**
  - Reference state is: 0.1 MPa, 300 K, 77% N_2, 21 % O_2, 2% H_2O, and 400 ppm CO_2

$$\hat{e} = \left[\hat{h}(T,p) - \hat{h}_{env}(T_{env},p_{env})\right] - T_{env} \cdot [\hat{s}(T,p) - \hat{s}_{env}(T_{env},p_{env})]$$

- Exergy destruction is the loss of work potential due to irreversible entropy generation.

$$\dot{\Phi}_{des} = T_o \cdot \dot{\sigma}_{irr}$$

Exergy Analysis: Standard IGCC-CCS

		Subsystem				Exiting Stream			
		WGS	Cooling	Capture	Compression	Clean Syngas	Compressed CO_2	Sour Water	Total
Power	[MW]	0.00	0.00	-14	-26	0.00	0.00	0.00	
Exergy Destruction	[MW]	21	0.04	20	6	0.00	0.00	0.00	
Exergy in Heat Leaving	[MW]	80	15	0.4	1	0.00	0.00	0.00	
Exergy Remaining	[MW]	0.00	0.00	0.00	0.00	2114	151	2	
		Inlet exergy to WGS = 2371 MW							
Power / Inlet Exergy	[%]	0.00%	0.00%	-0.58%	-1.09%	0.00%	0.00%	0.00%	-1.67%
Exergy Destruction / Inlet Exergy	[%]	0.89%	0.00%	0.84%	0.27%	0.00%	0.00%	0.00%	2.00%
Exergy in Heat Leaving / Inlet Exergy	[%]	3.39%	0.62%	0.02%	0.05%	0.00%	0.00%	0.00%	4.07%
Exergy Remaining / Inlet Exergy	[%]	0.00%	0.00%	0.00%	0.00%	89.17%	6.36%	0.07%	95.60%
Total	[%]								100.00%

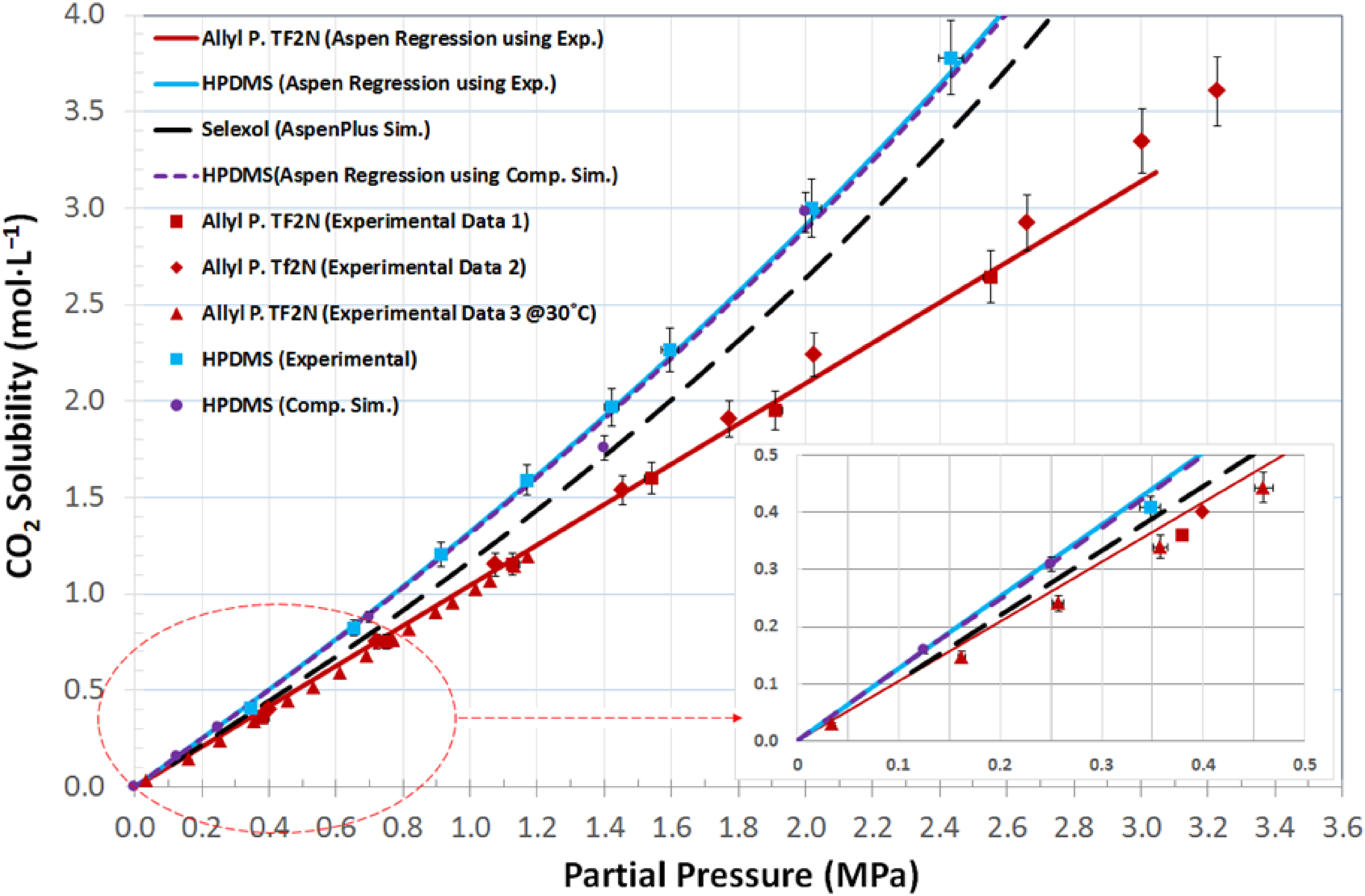
Thank You

- **Thanks to:** Sweta Agarwal, Hunaid Nulwala, Elliot Roth, Fan Shi, Wei Shi, Victor Kusuma, Megan Macala, Regina Woloshun, Brian Kail, Robert Thompson, Sarah Narburgh, David Miller, Dave Hopkinson, Bob Enick, John Kitchin, and Dave Luebke
- **Funding from the NETL Strategic Center for Coal**

- **Questions**:

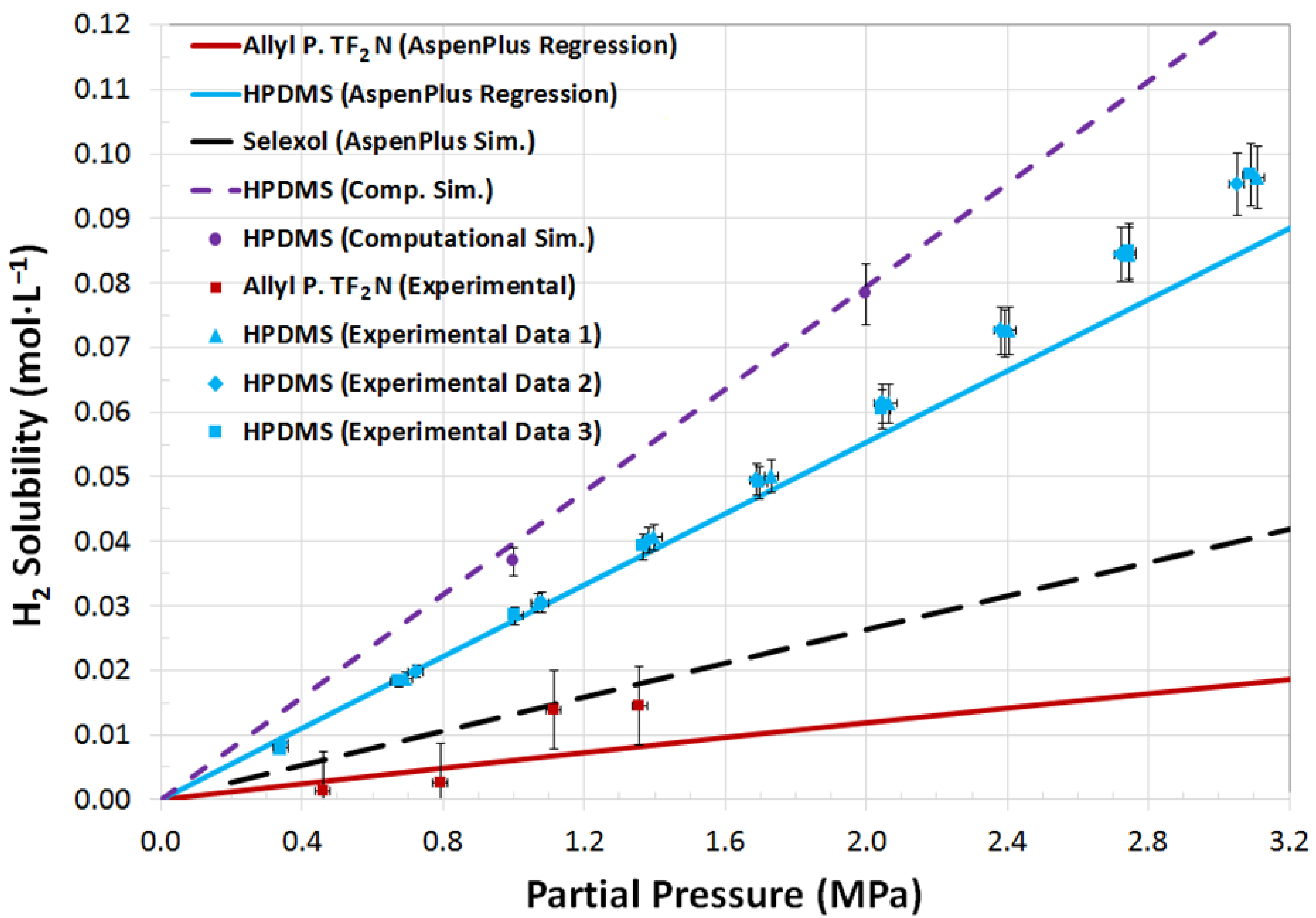
Back-up Slides

CO_2 solubility in physical solvents at 25˚C



CO_2 solubility = mol of CO_2 absorbed per liter of neat solvent

H_2 solubility in physical solvents at 25˚C



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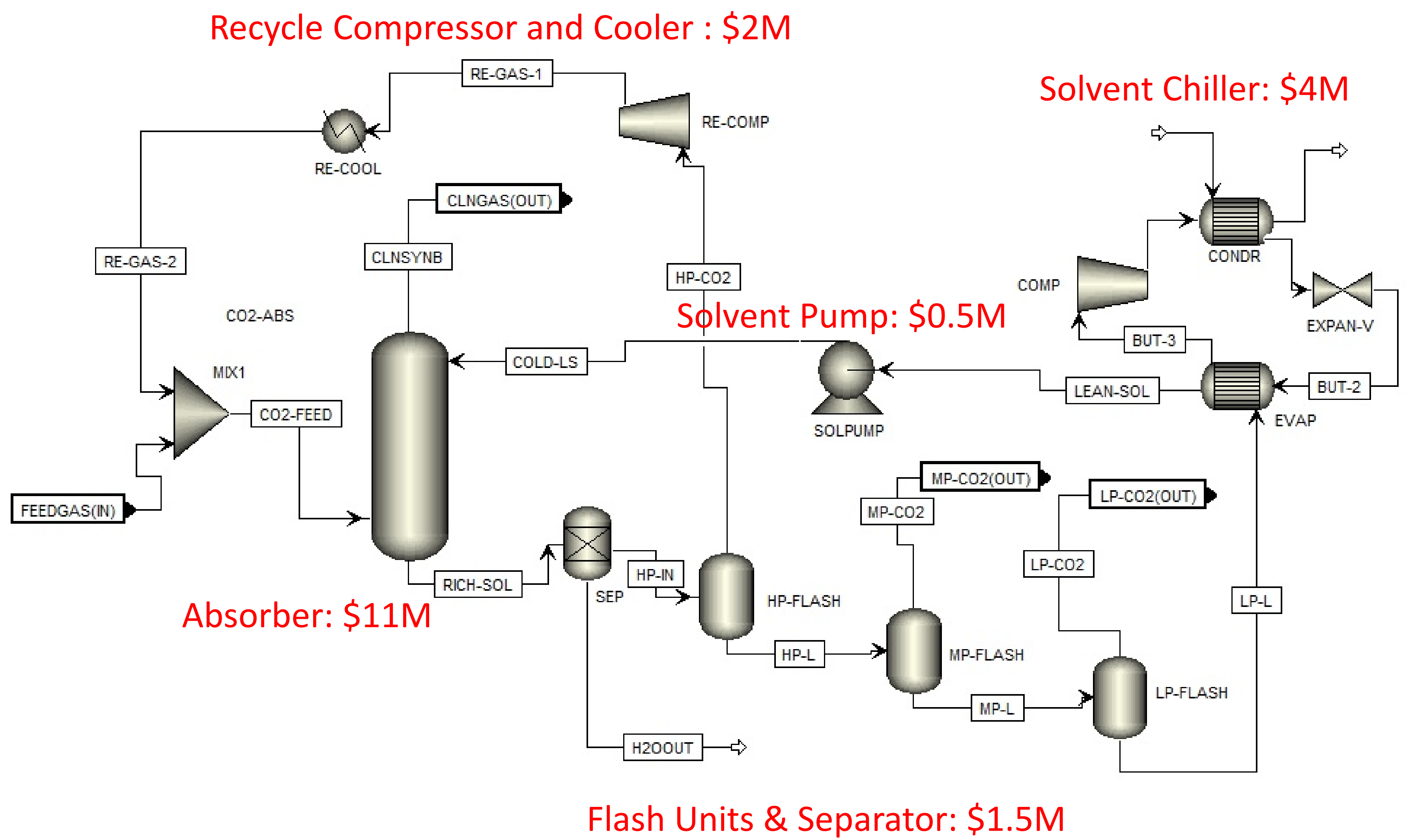
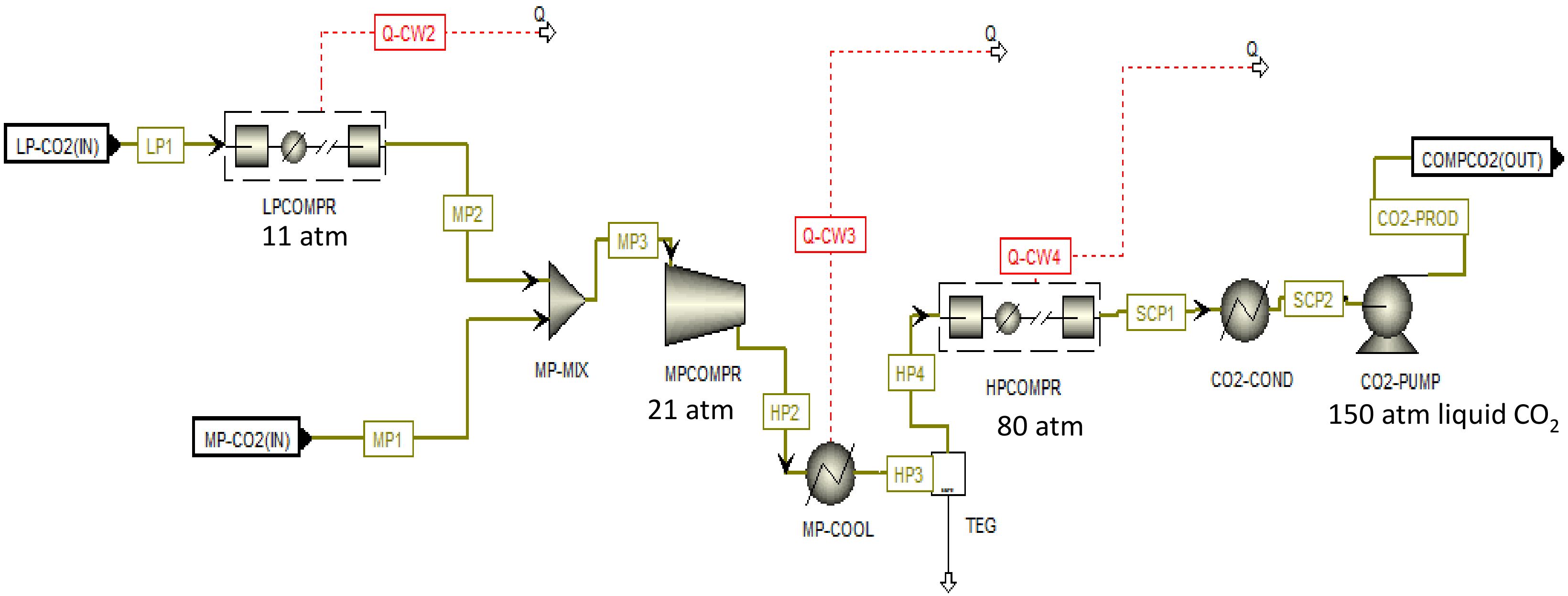
Bare Equipment Costs: H-PDMS



Bare Equipment Costs: CO_2 Compression Cycle

Cost of LP Compressor and Intercooler: $4.5M

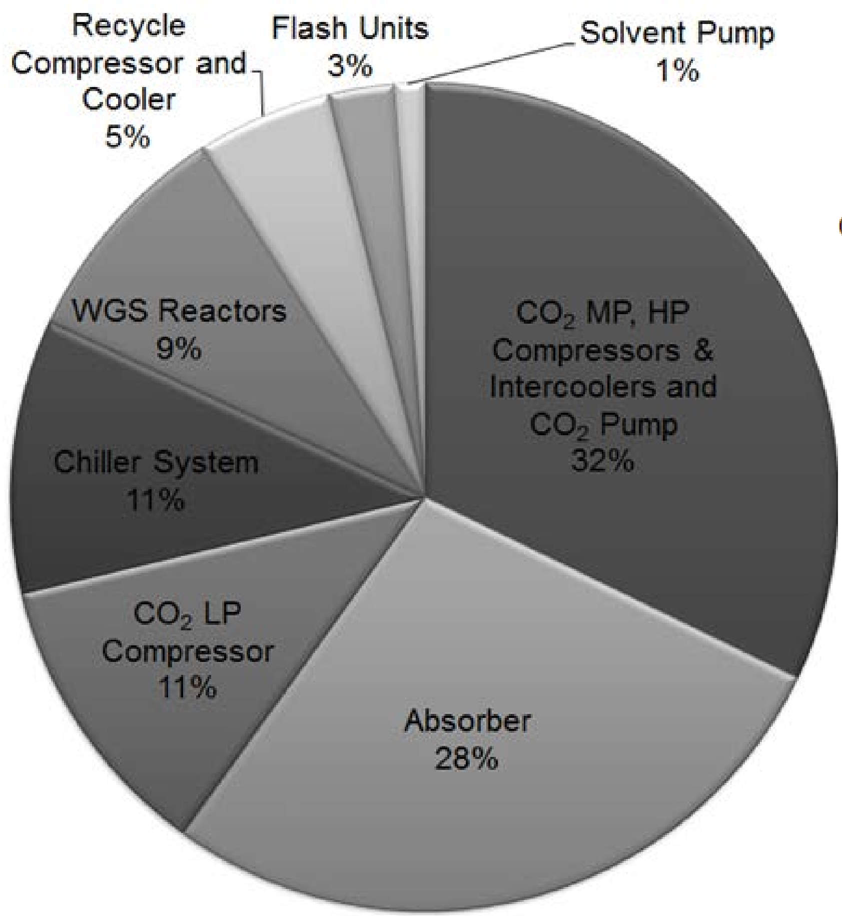


Cost of MP, HP Compressors, Intercoolers and Liquid CO2 Pump: $12.7M

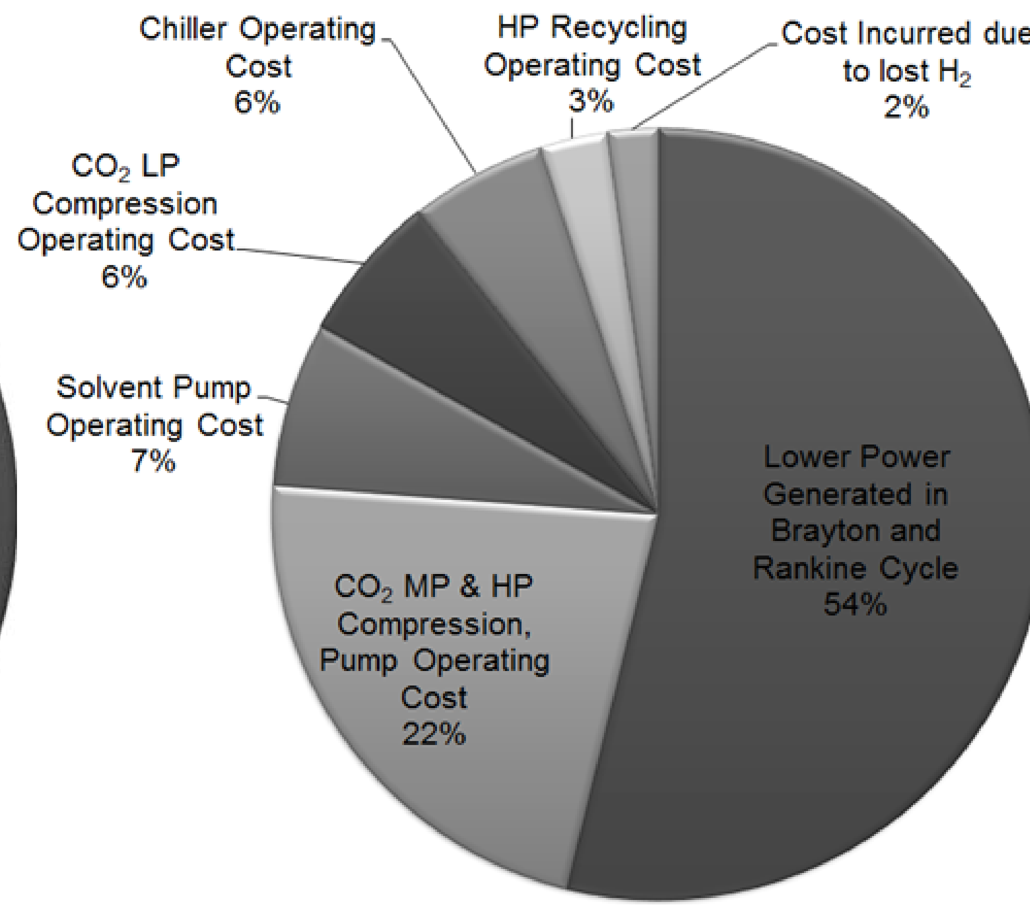
Our Economic Model

- **Economic Model Assumptions:**
  - There is an existing IGCC Power Plant with H_2S Removal
  - 1 Years for Construction (for CO_2 Capture Equipment)
  - 30 Years of Operations
  - 80% Capacity Factor
  - 7% Inflation-adjusted Discount Rate
  - Plant Cost Ratio = 5 = Total Capital Cost / Bare Equipment Costs
  - O&M = 4%/yr of upfront capital cost
  - Bare Capital Cost estimates calculated from equations taken from various sources (Sieder Textbook, AspenPlus, IECM)
- **Used to calculate the levelized cost of capturing CO_2**
  - Levelized cost = Operating costs plus capital costs levelized per ton of CO_2 captured

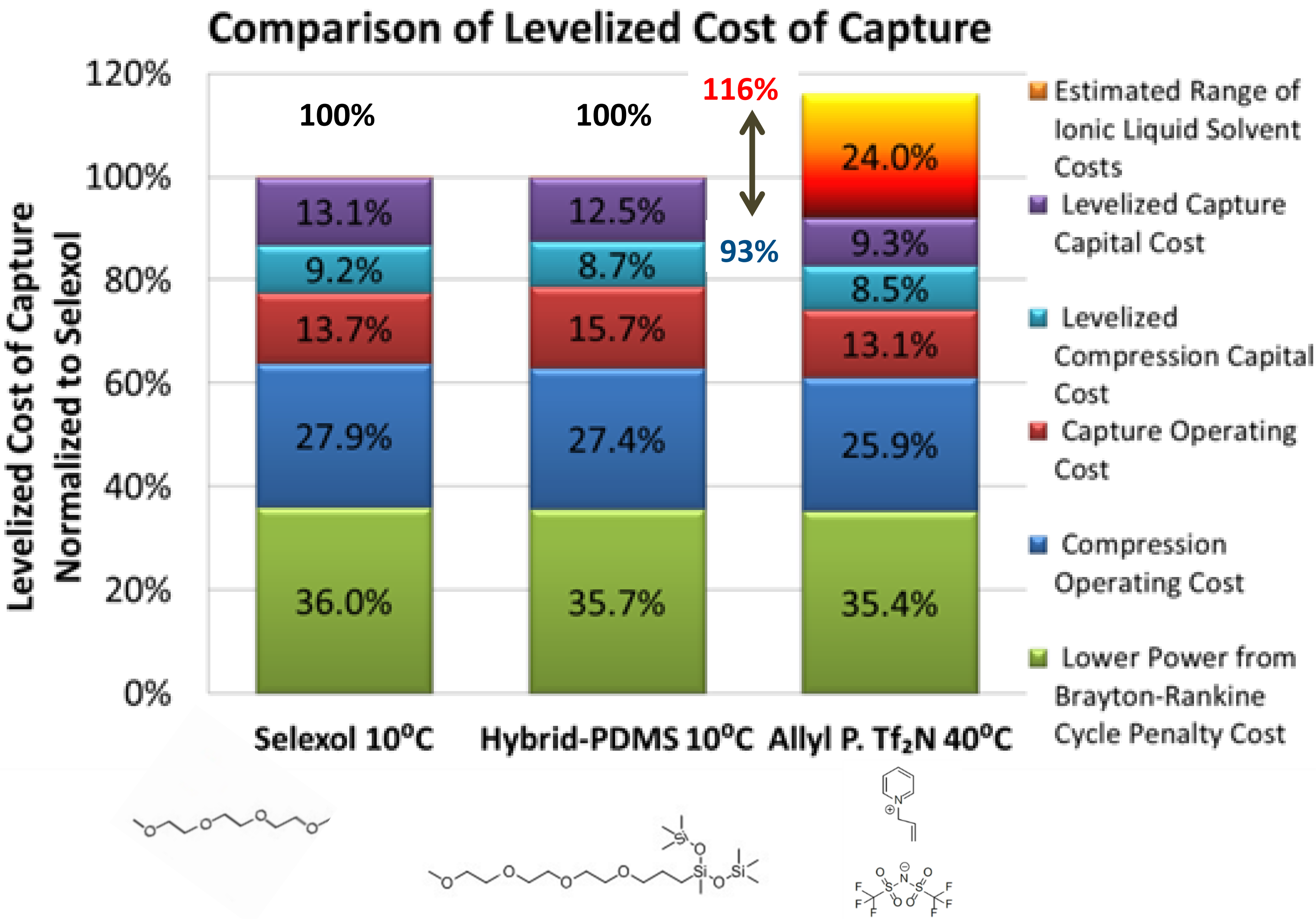
Capital & Operating Cost Distribution Chart for CO_2 Capture System using HPDMS



Capital Cost Breakdown



Operating Cost Breakdown


Comparison of Levelized Cost of Capture
Levelized Cost of Capture Normalized to Selexol
120%
100%
80%
60%
40%
20%
0%
100%
100%
116%
93%
13.1%
9.2%
13.7%
27.9%
36.0%
12.5%
8.7%
15.7%
27.4%
35.7%
24.0%
9.3%
8.5%
13.1%
25.9%
35.4%
Selexol 10°C
Hybrid-PDMS 10°C
Allyl P. Tf₂N 40°C
Estimated Range of Ionic Liquid Solvent Costs
Levelized Capture Capital Cost
Levelized Compression Capital Cost
Capture Operating Cost
Compression Operating Cost
Lower Power from Brayton-Rankine Cycle Penalty Cost