Solubility and Diffusivity of Syngas Components in a Next Generation Pre-Combustion Solvent

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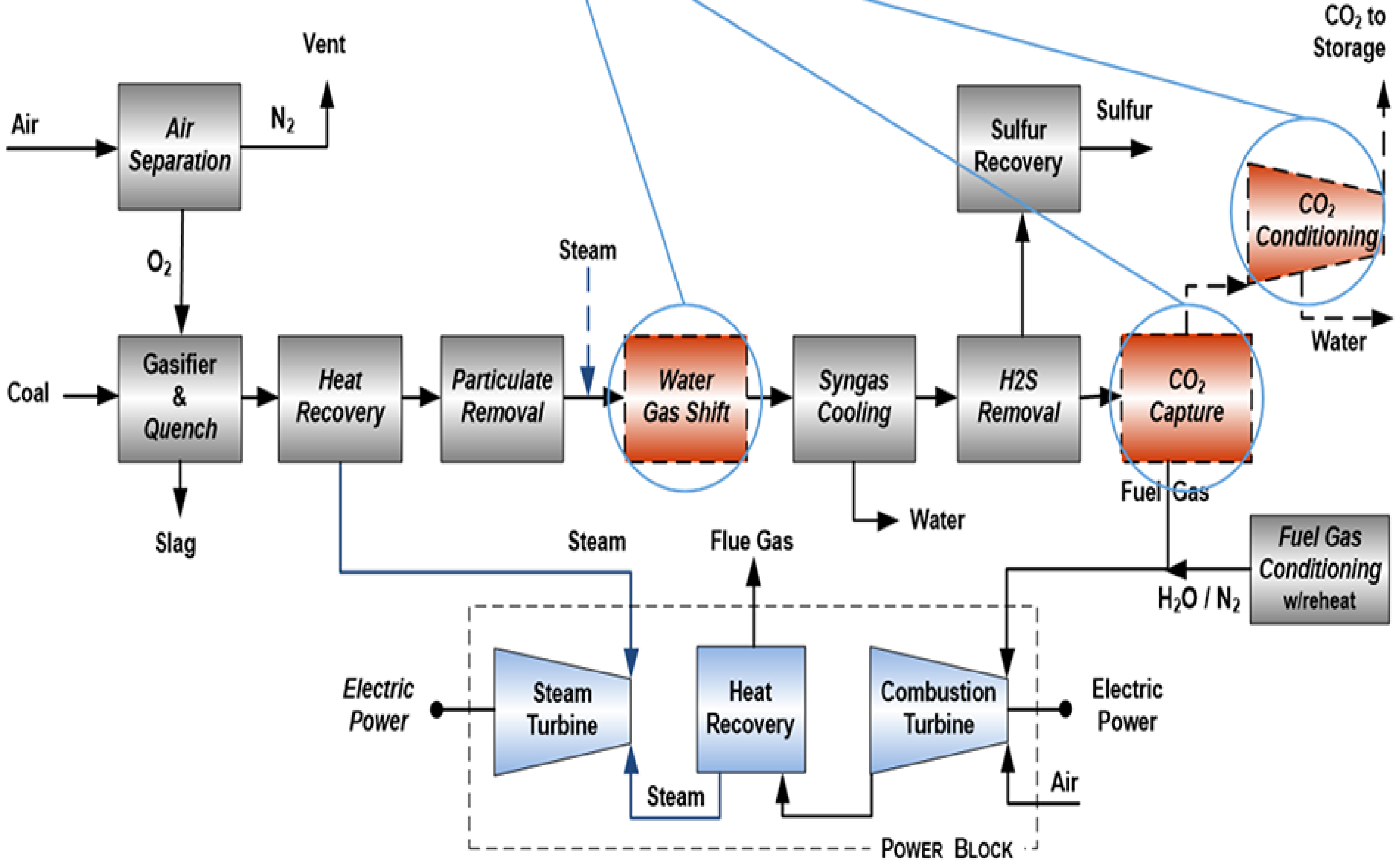
Applications for Pre-Combustion CO_2 Capture Solvents

- **Pre-combustion CO_2 Capture at IGCC-CCS**
- Adjust CO/H_2 ratio for coal & biomass to liquids
- Generation of H_2 from reformed natural gas
- Remove CO_2 from syngas to produce ammonia

Pre-combustion CO_2 capture from shifted syngas which is ~40% CO_2



Commercial Solvents and Challenges

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	Current Solvents	Our Proposed Solvents
Hydrophilicity/Hydrophobicity	Hydrophilic	Hydrophobic
Corrosion	Mid (need to be determined)	Expected to be low
Operation temperature	Subambient • Selexol® (UOP) operates at 10°C Kemper County IGCC-CCS, MS • Rectisol® (Air Liquide) operates at -10°C Great Plains Synfuels Plant, ND	25°C and above
Vapor Pressure	Relatively high, sub-ambient absorption temperature is required	Low, no sub-ambient temperature is required for absorption
Electricity Consumption	Required to chill solvent	No
Use of Waste Heat	No	Yes

Schematic of Advanced CO_2 Capture

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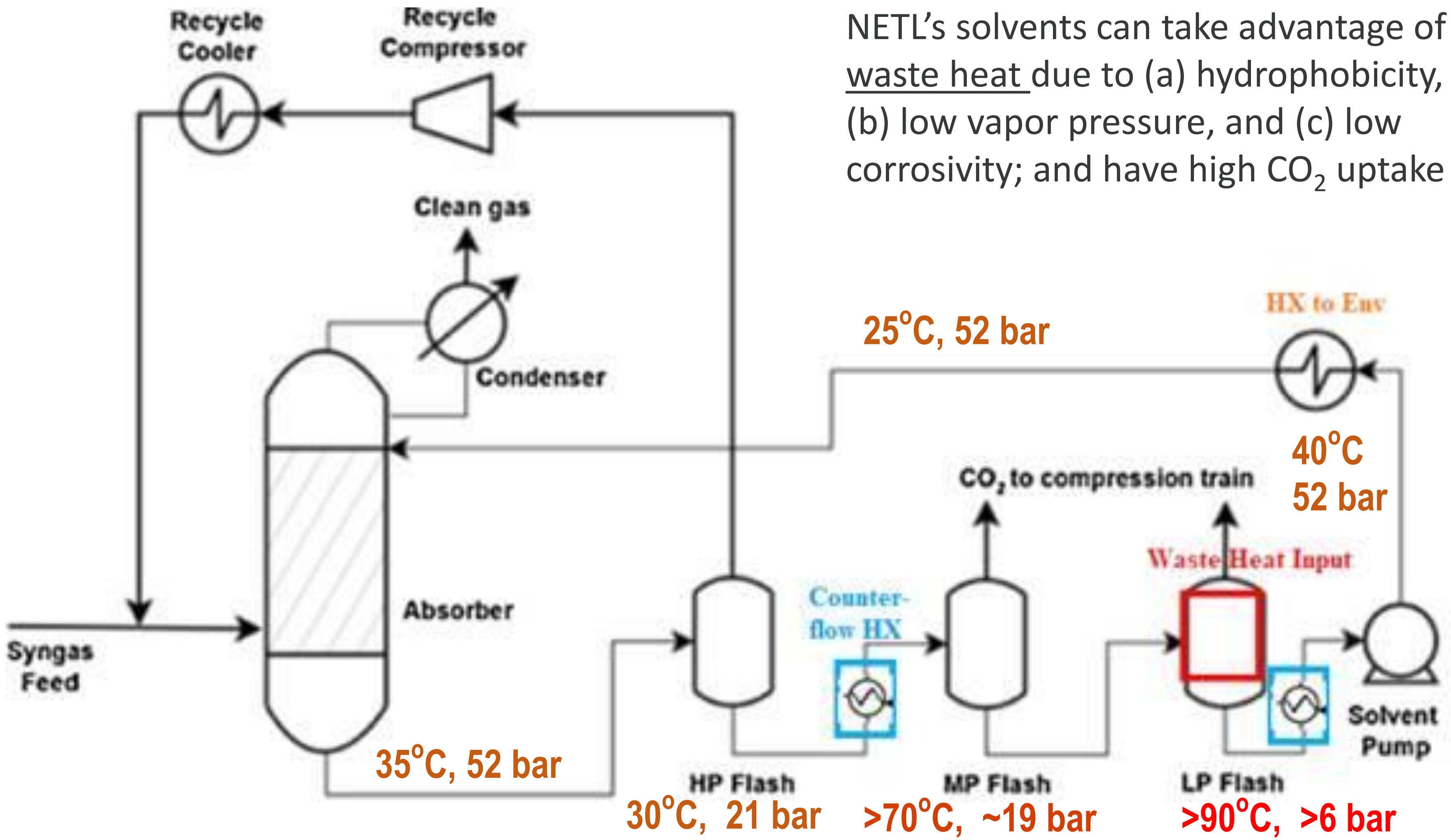


NETL's solvents can take advantage of waste heat due to (a) hydrophobicity, (b) low vapor pressure, and (c) low corrosivity; and have high CO_2 uptake

Advantages of New Approach

- Regeneration of the solvent at higher MP and LP Flash pressures reduces the electricity consumption and the capital cost of the CO_2 compressors

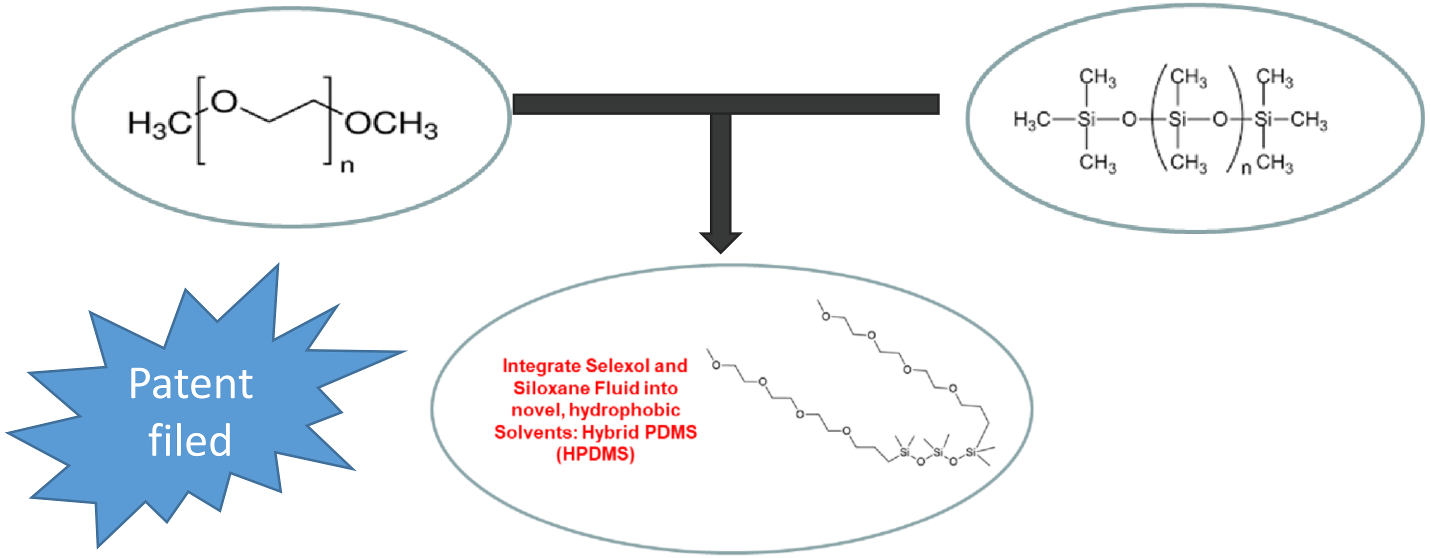
Waste Heat Locations

- Combined Cycle exhaust leaves stack at 140°C in Field and Brasington IGCC-CCS model
  - **55 MW_{th}** is available if exhaust heat exchanges down to 85 °C
- If gypsum rather than elemental sulfur is the output of the Claus unit
  - **30 MW_{th}** is available

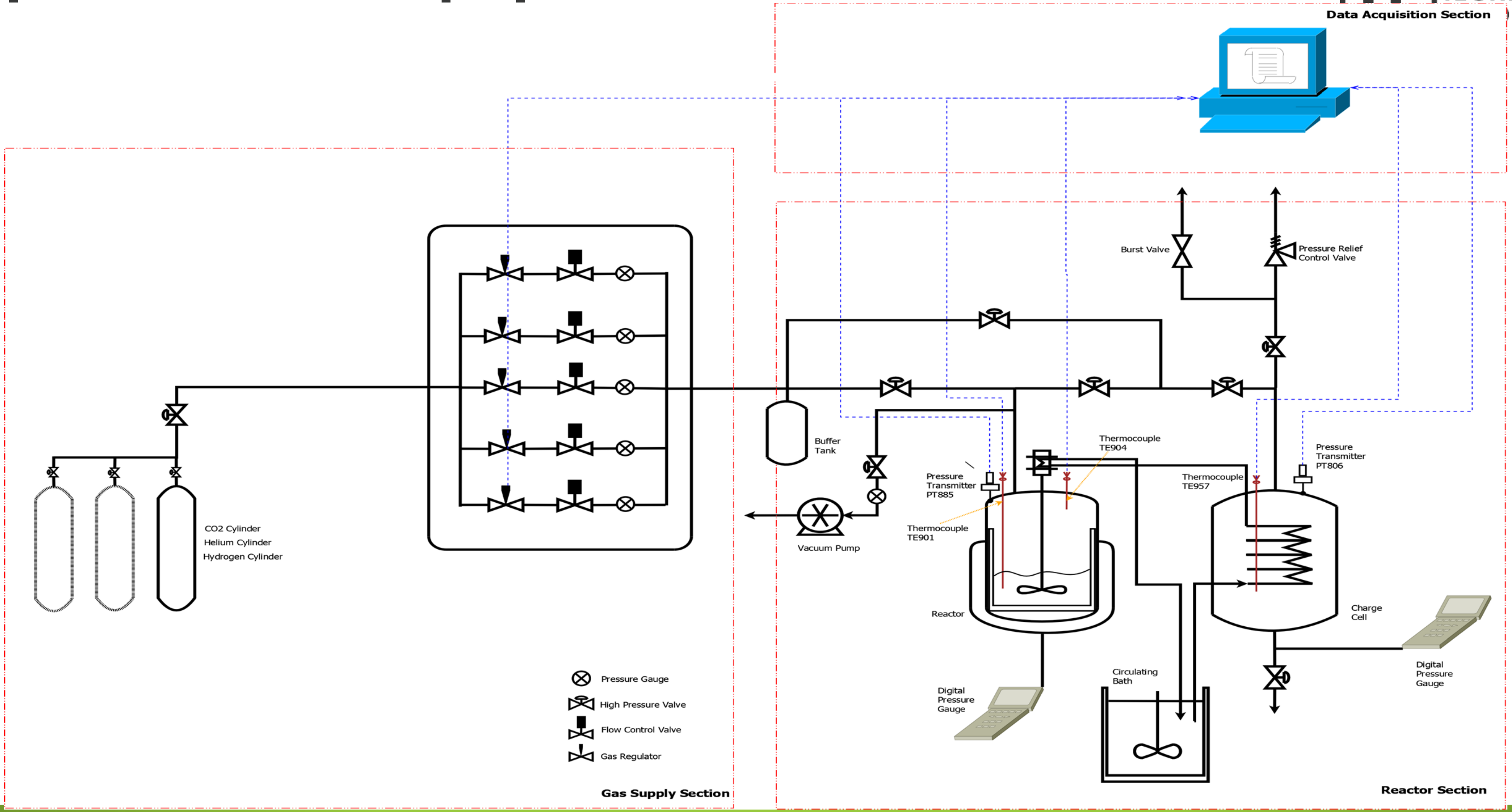
*Field and Brasington, Baseline Flowsheet Model for IGCC with Carbon Capture, Industrial & Engineering Chemistry Research 50(19) · August 2011

Molecular Design for the Physical Solvent

	Processes based on Selexol or similar hydrophilic solvents	Processes based on similar hydrophobic solvents
Operating Temperature	Below room temperature	Above room temperature
Chemical Stability	Mid	High
Corrosion	Mid	Low
Cost of the Solvent	Low	Mid
Viscosity	Low	High



Experimental Equipment for Measurement



Project Objectives: Solubility and Diffusivity

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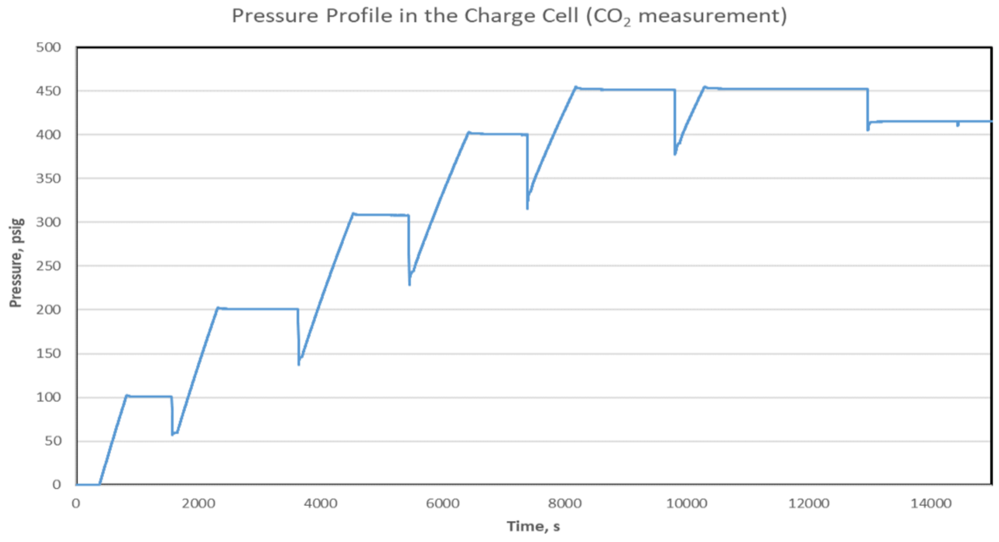
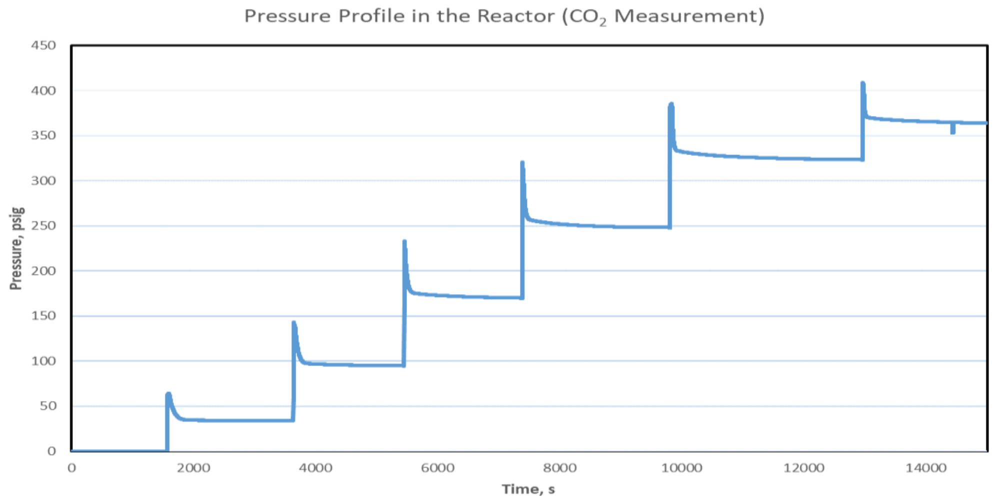
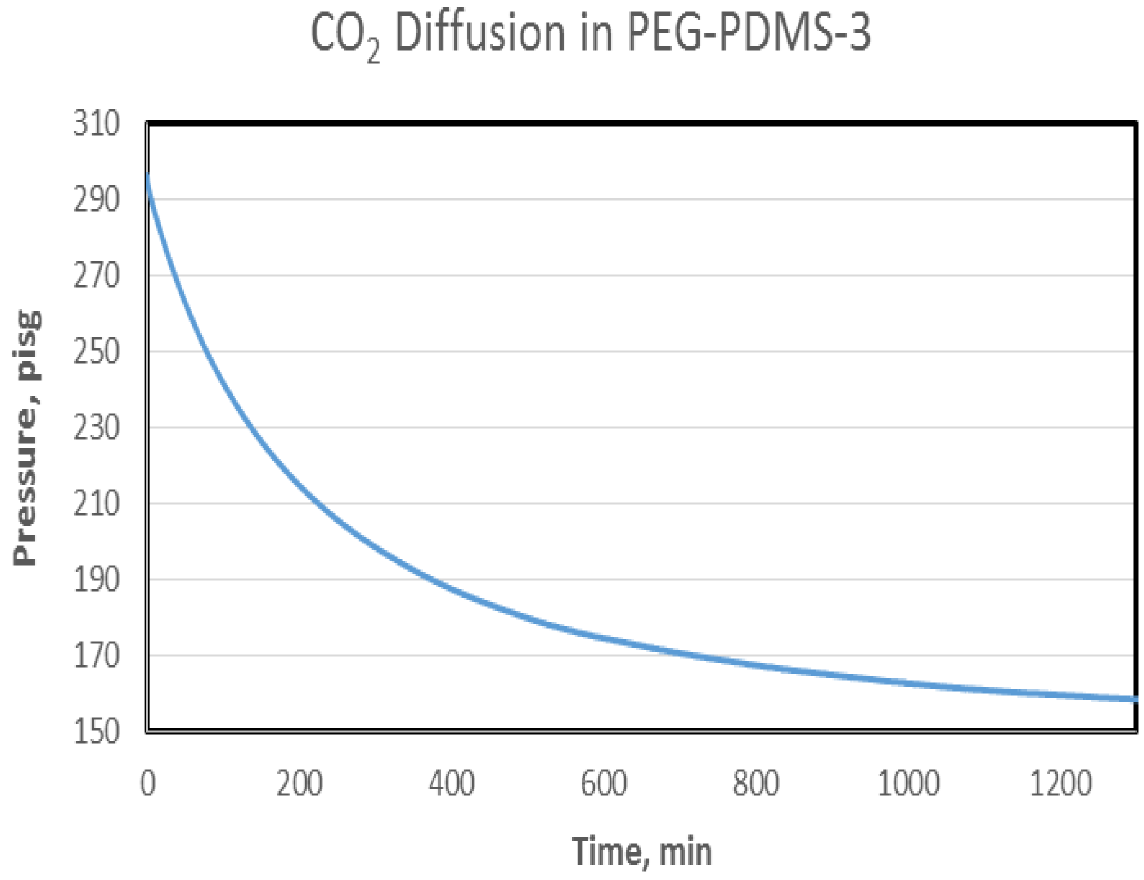
Solubility





Diffusivity



One-Dimensional Mass Diffusion Model

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}$$

Initial Condition: $C = C_0$ when $t = 0$ and $0 < z < L$

Boundary Conditions: $C = C_S$ when $t > 0$ and $z = 0$

$$\frac{\partial C}{\partial z} = 0 \quad \text{at } z = L$$

$$< C > = C_s\left[1 - 2\left(1 - \frac{C_0}{C_s}\right)\sum_{n=0}^{\infty}\frac{\exp(-\lambda_n{}^2 Dt)}{L^2\lambda_n{}^2}\right]$$

Where:

$\lambda_n = (n + 1/2)\pi/L.$

C_0 = initial concentration ($mol{\cdot}m^{-3}$)

C_s = saturation concentration ($mol{\cdot}m^{-3}$)

$< C >$ = space-averaged concentration ($mol{\cdot}m^{-3}$)

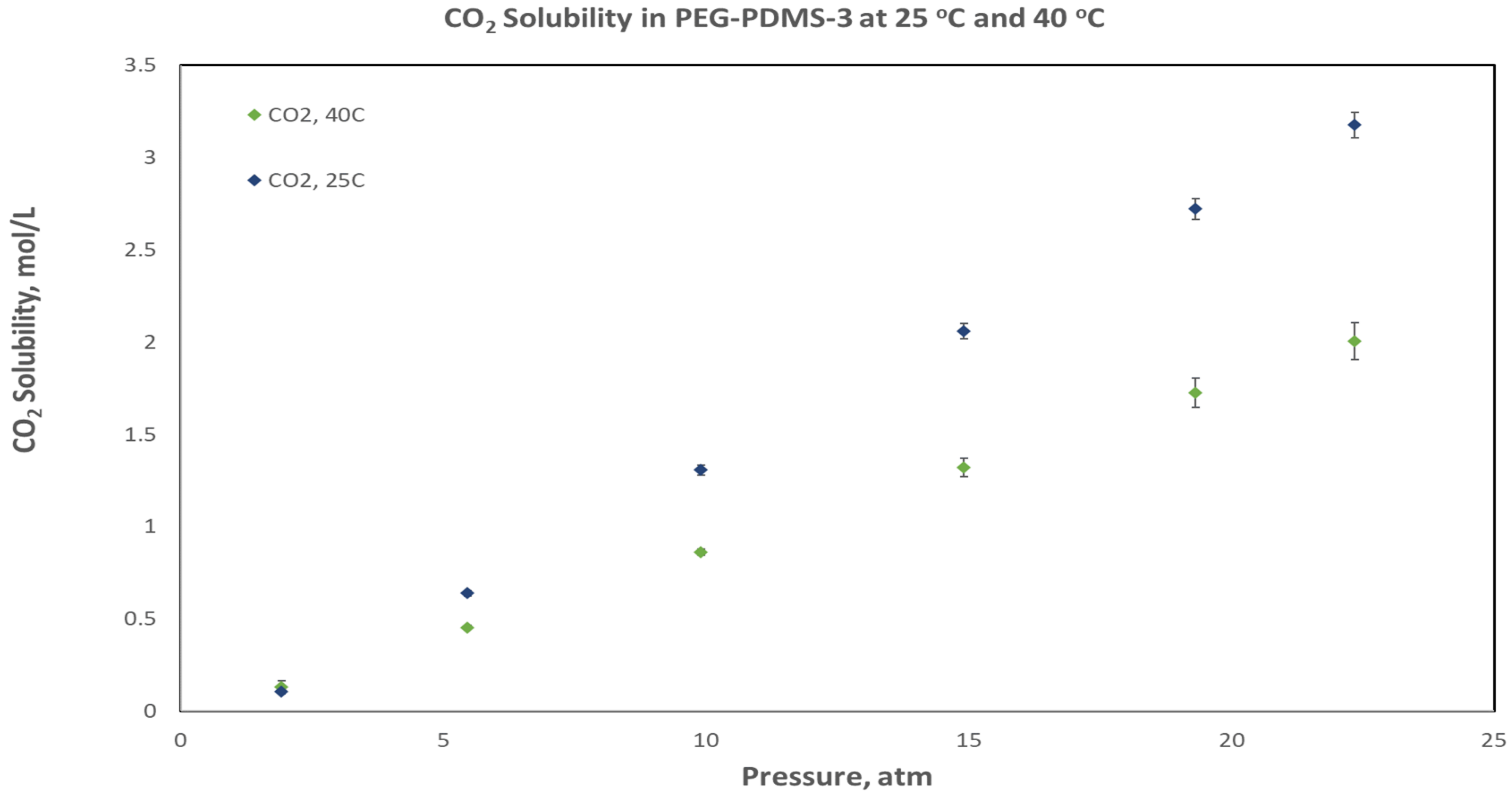
L= depth of the solvent in the reactor,

Assumptions:

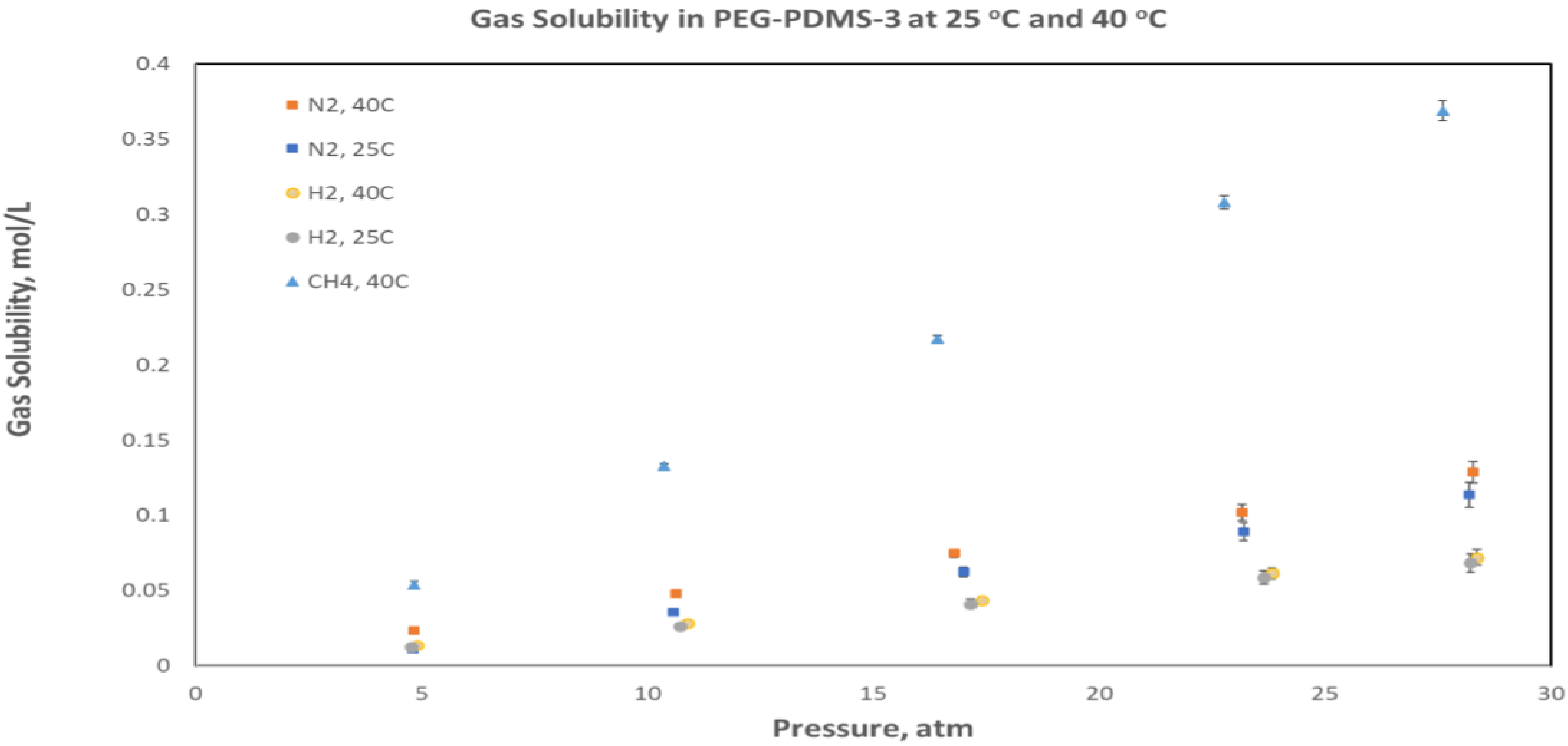
- Gas dissolves through a one-dimensional vertical diffusion, where there is no convection flow in the liquid;
- A thin boundary layer between the gas and liquid phases exists, where the thermodynamic equilibrium is instantly established with the saturation concentration and where the concentration is constant all the time at a given temperature and pressure;
- Temperature and pressure are constant during the diffusion;
- The gas-dissolved liquid is a highly dilute solution and so the relevant thermophysical properties of the solution do not change.

Mark Shiflett, A Yokozeki, Solubility and Diffusivity of Carbon Dioxide in Ionic Liquids: [bmim] [PF6] and [bmim][BF4], Ind. Eng. Chem. Res., 2005, 44, 4453-4464

Solubility of CO_2 in PEG-PDMS-3



Solubility of Weak Gas Absorbates



Selexol vs. PEG-PDMS-3

	MW, g/mol	Density, g/mL @25°C	Viscosity cP @25°C	Surface tension N/m	Selectivity CO_2/H_2 at 25°C	Selectivity CO_2/H_2 at 40°C	Selectivity CO_2/N_2 at 25°C	Selectivity CO_2/N_2 at 40°C	Selectivity CO_2/CH_4 at 25°C	Selectivity CO_2/CH_4 at 40°C
Selexol Surrogate	280	1.03	5.8	32	45	31	N/A	N/A	N/A	N/A
PEG-PDMS-3	617	0.987	12.2	22	62	37	35	21	N/A	7

Diffusion Coefficients in PEG-PDMS-3

	H_2		N_2		CH_4		CO_2	
	25°C	40°C	25°C	40°C	25°C	40°C	25°C	40°C
Henry's Law Constant (10^{-7} Pa)	5.3	5	3.4	2.8	N/A	0.9	N/A	N/A
Diffusion Coefficient ($10^{-9}m^2/s$)	2.25	3.25	0.48	0.60	N/A	0.65	N/A	N/A

Conclusions & Future Work

- PEG-PDMS-3 has shown higher CO_2/H_2 selectivity at both 25 and 40^{o}C over Selexol at same temperature;
- H_2 and N_2 solubility is higher at higher temperature; in contrast, CO_2 and CH_4 solubility is lower at higher temperature;
- Gas absorption is being studied using gas mixtures;
- PEG-PDMS-3 at 40^{o}C out-performed Selexol at 10^{o}C in the pilot scale testing at UND EERC;
- More performance data are expected to be collected from both the fluidized bed gasifier at UND EERC and the entrained flow gasifier at University of Kentucky, CAER;
- Develop processes & solvents compatible with modular-scale gasification.

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Thanks!

Any Questions?