Solubility and Diffusivity of Syngas Components into Novel Pre-combustion CO2 Capture Solvents

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Background

Issues:

The current baseline for pre-combustion carbon capture technology is a solvent based process, such as Selexol® (mixtures of dimethylethers of polyethelenglycol) and Rectisol® (chilled methanol).

1. To obtain high CO_2 capture efficiency (>90%), sub-ambient conditions are required for those solvents. Cooling the syngas to below room temperature is costly and requires energy-intensive chillers.

2. High hydrophilicity of Selexol and Rectisol can introduce corrosion issues for equipment.

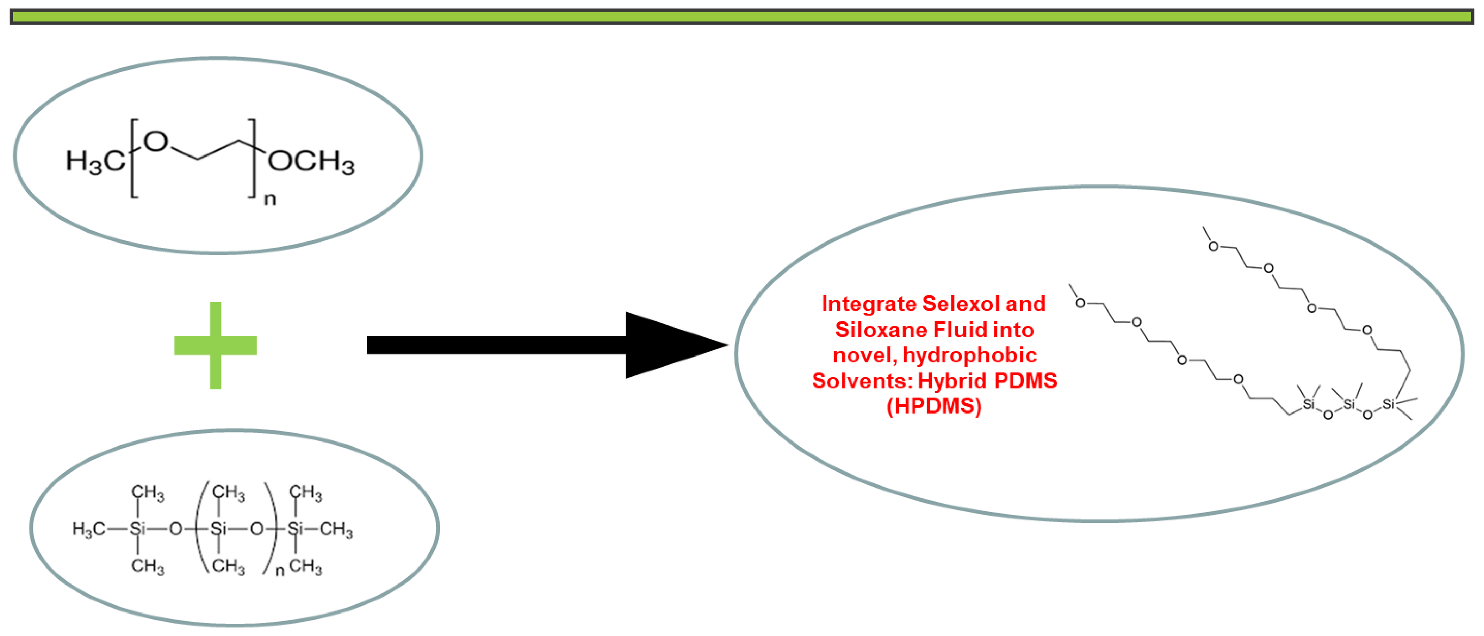
Our Solution:

A process based on a hydrophobic solvent which can achieve a warm CO_2 separation would improve power plant efficiency as much as 2-3% compared to those processes requiring sub-ambient temperatures. [1]

Project Goals:

The solubility and diffusivity of different gases including H_2, CO_2, N_2 and CH_4, which are the main components of syngas, will be presented, which are essential for a reliable process design.

Molecule Design



	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
CO_2 / H_2 Selectivity	High	Comparable to Selexol

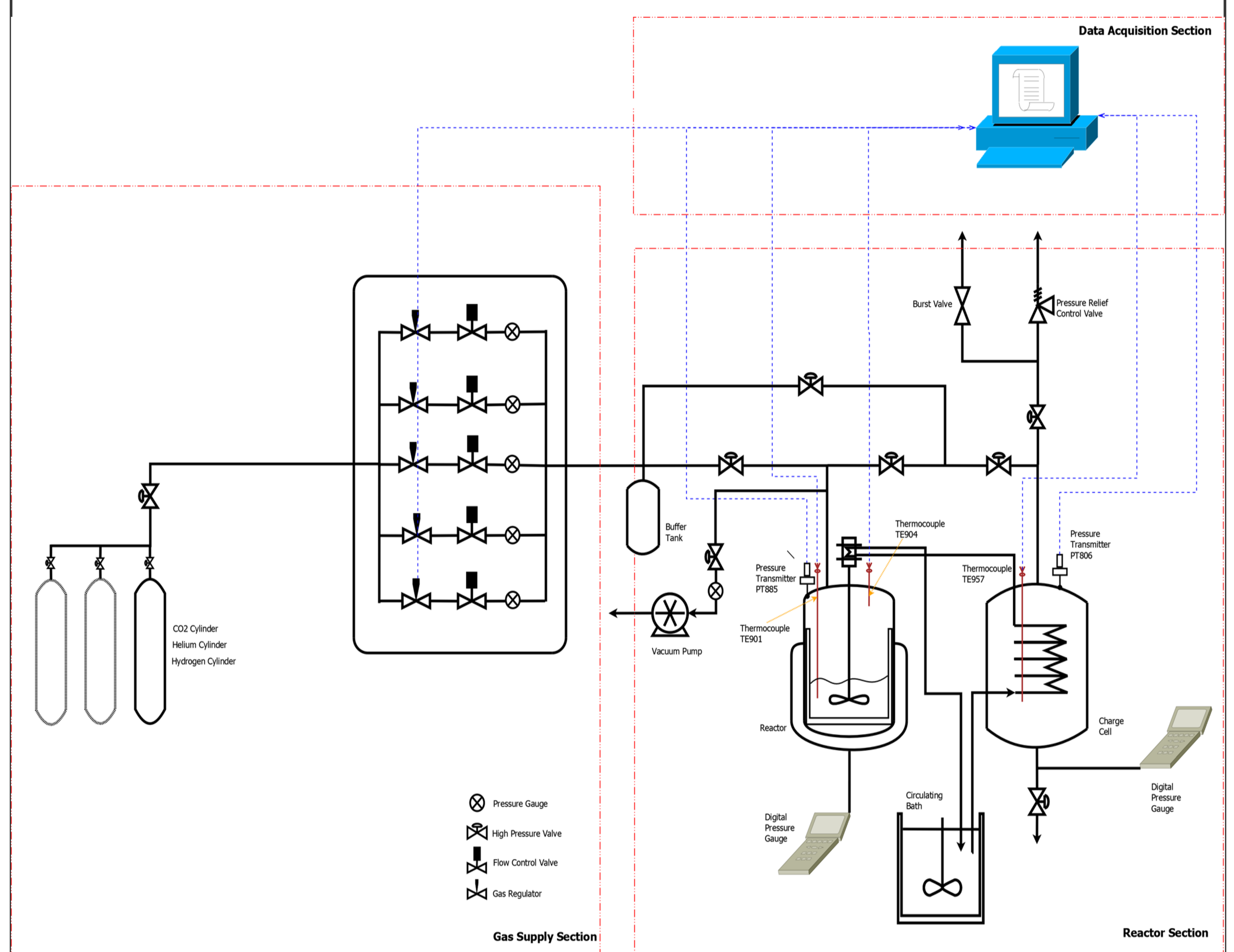
References

[1] Henry Pennline, David Luebke, Kenneth Johns, Christina Myers, "Progress in Carbon dioxide capture and separation research for gasification-based power generation point sources" Fuel Processing Technology, 2008, 89(9), 897-907.

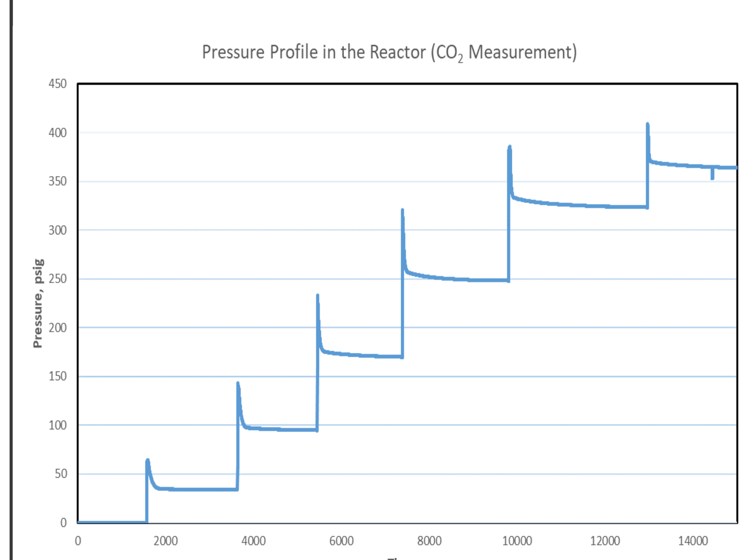
[2] Michael Friedrich, et al. Measuring Diffusion and Solubility of Slightly Soluble Gases in [C_nMIM][NTf_2] Ionic Liquids, Journal of Chemical and Engineering Data, 2016, 61, 1616-1624.

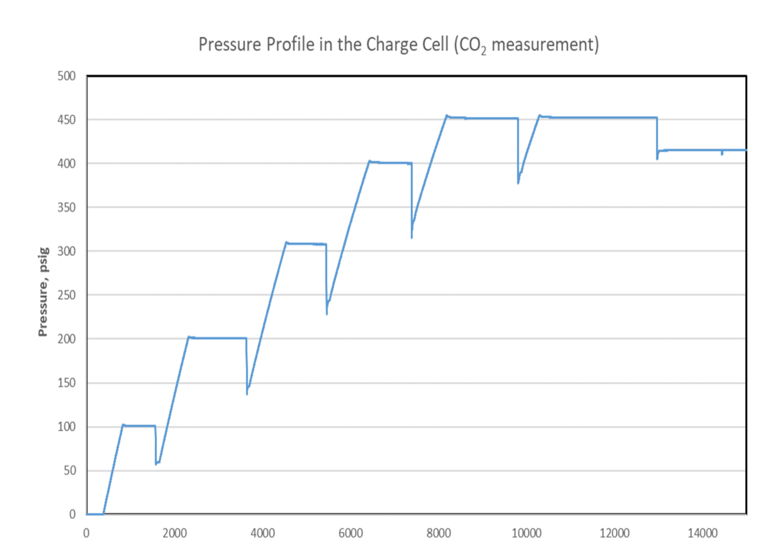
[3] Ying Hou and Ruth Baltus, "Experiment of the Solubility and Diffusivity of CO2 in Room-Temperature Ionic Liquids Using a Transient Thin-Liquid-Film Method", Ind. Eng. Chem. Res. 2007, 46, 8166-8175

Experimental Equipment and Measurements

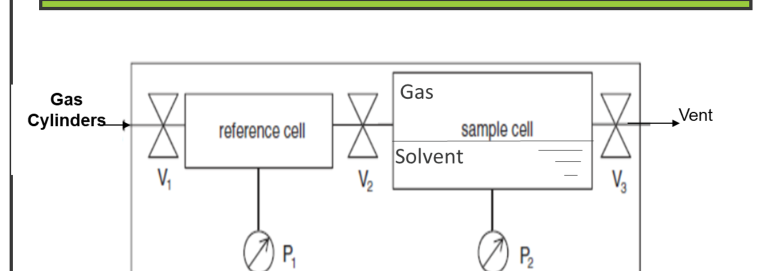


Pressure Profiles





Methods for gas solubility measurement



Method 1

$$\Delta n = \frac{P_{sam,i} \cdot V_{sam,i}}{z_f \cdot R \cdot T_{sam,i}} - \frac{P_{sam,f} \cdot V_{sam,f}}{z_f \cdot R \cdot T_{sam,f}}$$

Method 2

$$\Delta n = \left\{ \frac{P_{ref,i} \cdot V_{ref,i}}{z_i \cdot R \cdot T_{ref,i}} - \frac{P_{ref,f} \cdot V_{ref,f}}{z_f \cdot R \cdot T_{ref,f}} \right\} - \frac{P_{sam,f} \cdot V_{sam,f}}{z_f \cdot R \cdot T_{sam,f}}$$

Method for gas diffusivity in solvent [2,3]

$$\ln \frac{p}{p_0} = \left(\frac{k}{H_{gas}}\right) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \left\{ \exp\left[-\frac{(2n+1)^2 \pi^2 D_{gas} t}{4L^2} \right] - 1 \right\} \quad (1a)$$

with

$$k = \frac{8RTV_{IL}\rho_{IL}}{\pi^2 V_{gas} MW_{IL}} \quad (1b)$$

E_a = activation energy (kJ/mol)
D_{gas} = diffusion coefficient of a gas in an ionic liquid ($m^2 s^{-1}$)
H_{gas} = Henry's Law constant of a gas in an ionic liquid (Pa)
L = depth of the ionic liquid in the sample chamber (m)
MW_{IL} = molecular weight of ionic liquid (g/mol)
n = number of terms in eq 1a; usually 110
p = total pressure in the vapor phase (bar)
p_0 = initial pressure of gas in the vapor phase (bar)
R = gas constant (8.31434 m^3 Pa mol^{-1} K^{-1})
T = temperature (K)
t = time (s)
$u_{c,r}(y)$ = relative combined standard uncertainty of y
V_{gas} = volume of the gas (cm^3)
V_{IL} = volume of ionic liquid (cm^3)
α = association factor in Wilke−Chang equation
η_{IL} = viscosity of ionic liquid (cP, mPa·s)
ρ_{IL} = density of ionic liquid at measuring temperature (g/cm^3)

Disclaimer

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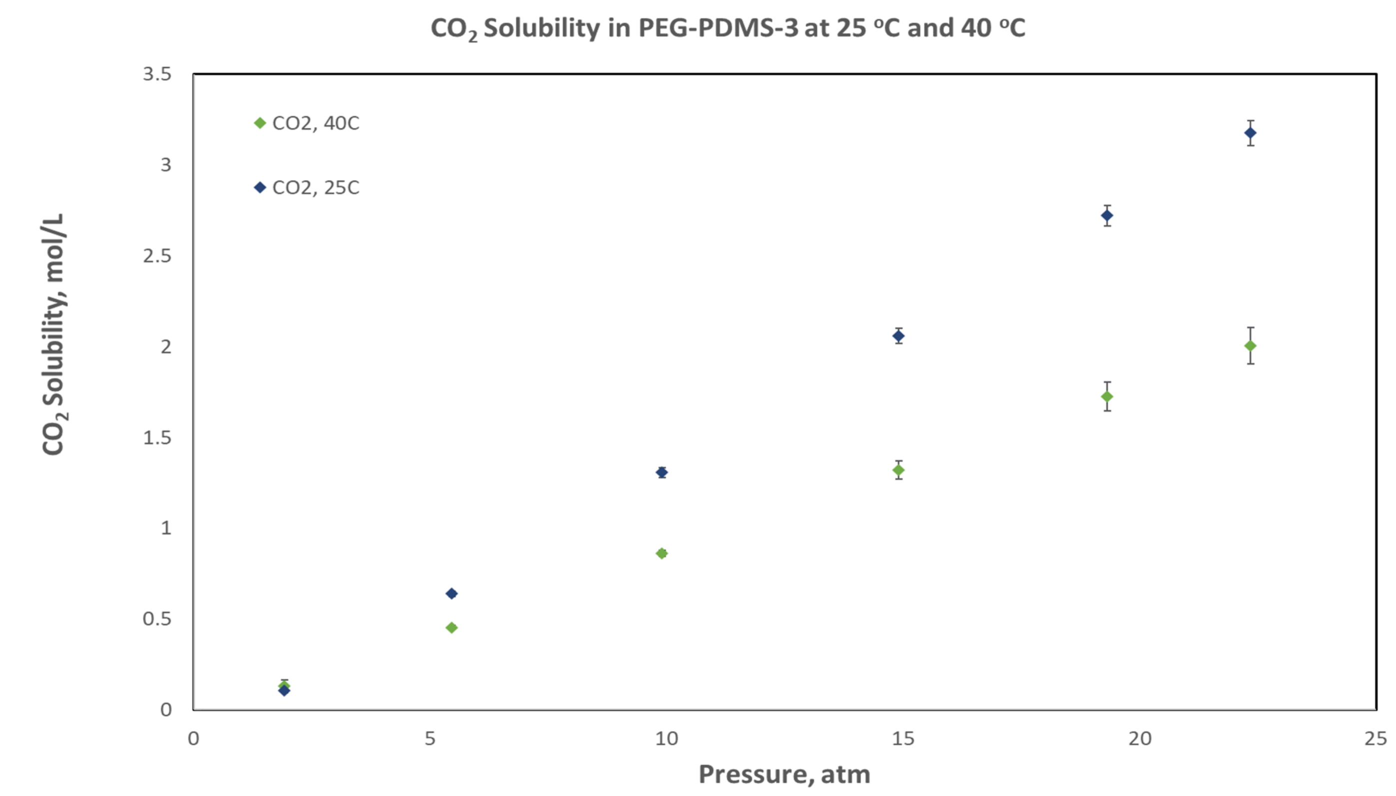
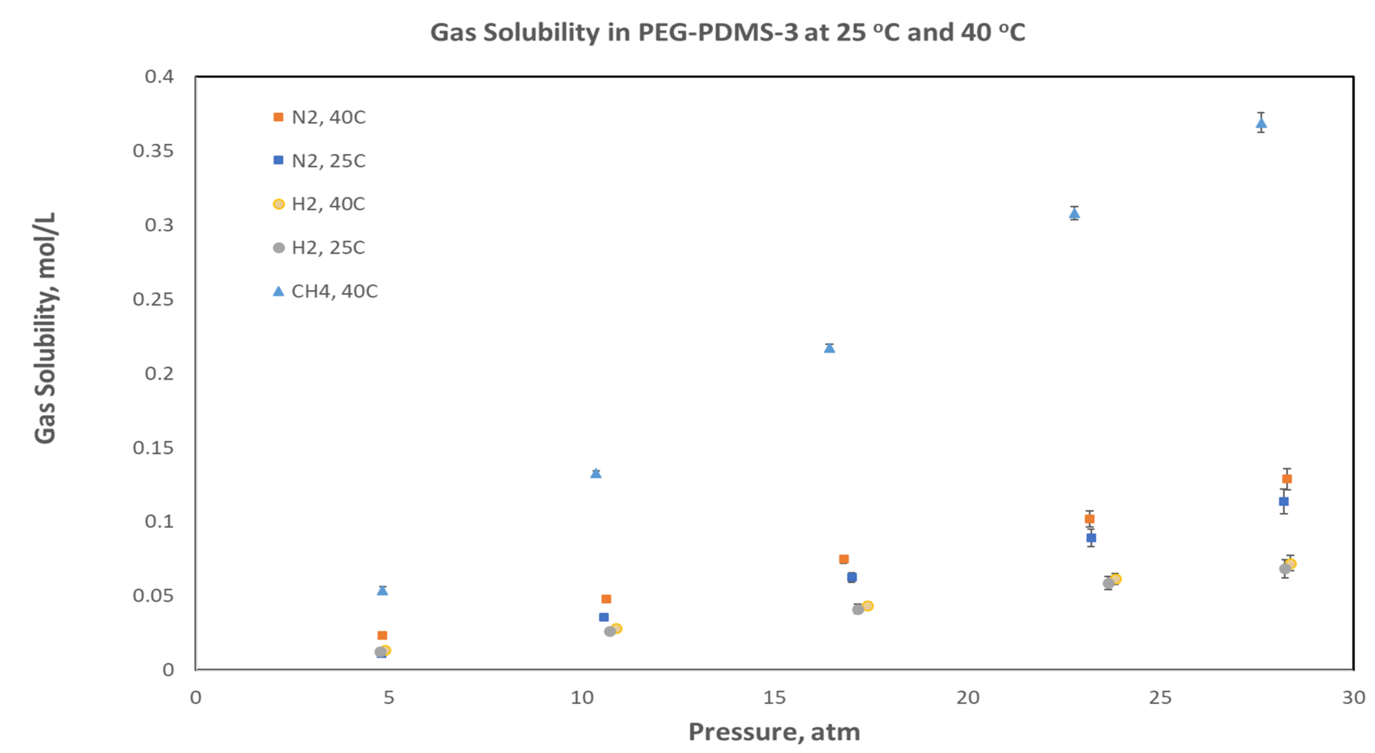
Data and Results





• 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	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

• Henry's law constant and diffusivity

	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 and Future Work

- Weak absorbates, such as, hydrogen and nitrogen, have higher solubilities at higher temperature, however, CO_2 as a strong absorbate shows higher solubilities at lower temperature, e.g. 25 °C. This observation indicates stronger CO_2 interaction with solvent during absorption;
- Henry's law constants and diffusion coefficients for hydrogen, nitrogen, methane, and carbon dioxide will be double-checked;
- The solubility and diffusivity of other novel, hydrophobic solvents will be studied in the CSTR units using the developed methods;
- Other than pure gas, the gas absorption will be evaluated and studied using gas mixtures mimic the actual syngas composition.