A Novel Reactive Separation Method for Carbon Dioxide Capture From Flue Gas

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Talk Outline

- Introduction
- Experimental Approach
- Preliminary Results
- Conclusions and Future Work

Motivation and Project Goals

Fossil Fuel Extinction
Excessive CO_2 Emissions

CO_2 separation

RWGS

Syngas

Fuels (Methanol)

Methanol Synthesis

Overcome thermodynamic limitations

Membrane Contactor Reactor (MCR)

High conversion

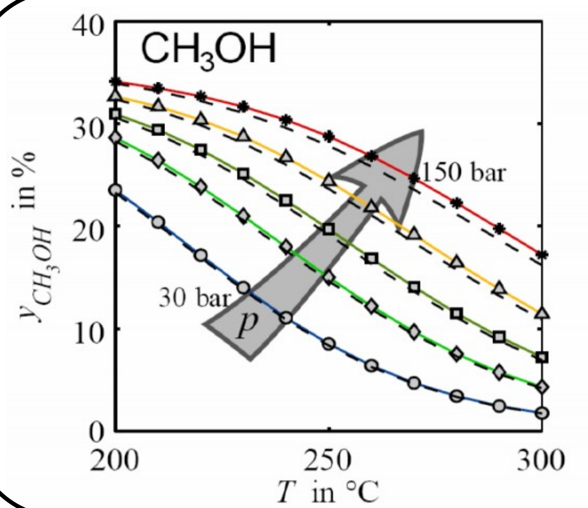
Overcoming MeS Equilibrium Limitations

P=30-100 bar

T=220 °Cz

Conversion per pass=<25%

Use a Membrane Contactor Reactor (MCR)

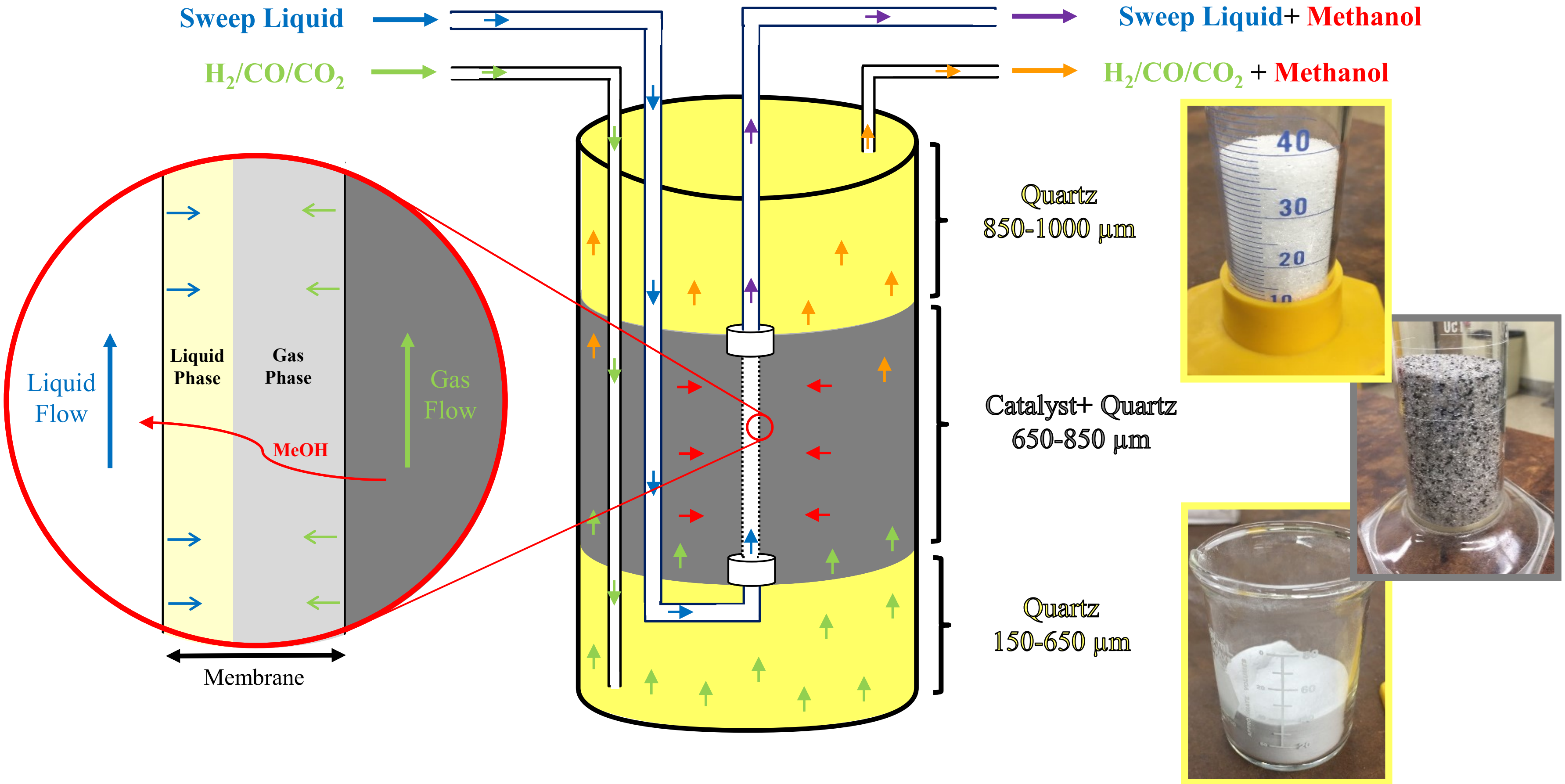


$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Lab-Scale MCR System



MeS-MCR Advantages

- **Higher Process Synergy** - From combining reaction and separation in the same unit
- **Overcoming Equilibrium Limitations** - Through in-situ product removal
- **Higher Energy Efficiency** - The liquid sweep also serves as an effective coolant
- **A More Compact and Flexible Design**

Project Objectives

- **Investigate the performance of novel integrated process combining a RWGS reactor (RWGSR) and a MCR for efficient methanol synthesis from waste CO_2. Study its performance for a broad range of pressure and temperature conditions.**

- **Use an experimentally-validated model to assess the full range of attainable conversions, aiming to obtain >90% carbon capture and utilization.**

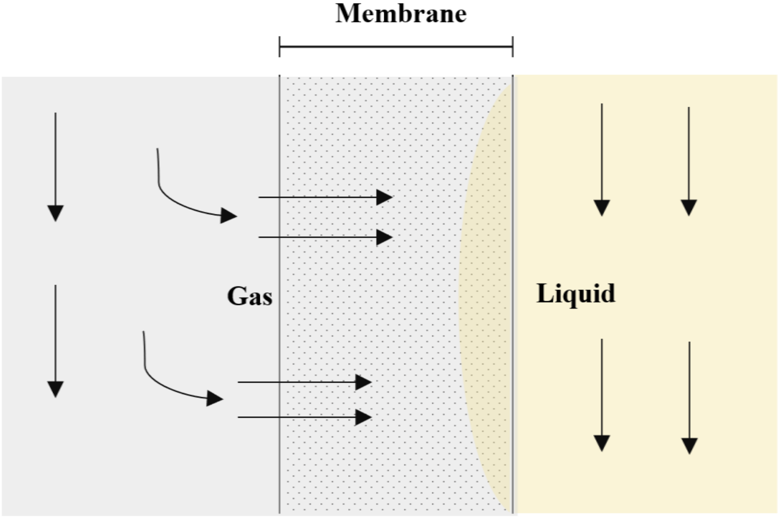
- **Carry out a techno-economic analysis (TEA) of the proposed RWGSR/MCR process to compare performance with that of the conventional, absorption-based carbon separation and capture (CSC) technologies.**

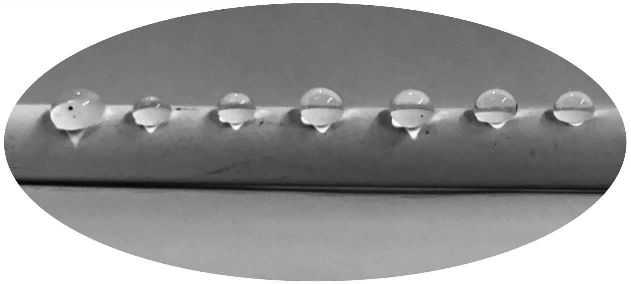
Project Tasks and Timeline

	Quarters							
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
Task 1.0 - Design and Construction of the RWGS-MCR MeS System	■							
Milestones								
a) RWGSR component constructed	◆							
b) WGSR and MCR-MeS components combined	◆							
Task 2.0 - Testing of the Individual RWGSR and MCR Sub-Systems	■	■	■					
Milestones								
c) Performance of the RWGSR determined		◆						
d) Performance of the MCR -MeS subsystem studied			◆					
Task 3.0 - Testing of the Proposed CO2 Separation/Capture Process in the RWGS-MCR MeS System				■	■	■	■	
Milestones								
e) Testing of the RWGSR-MCR system processing flue gas completed							◆	
f) Analysis of the experimental data completed							◆	
Task 4.0 - Mathematical Modeling and Process Optimization					■	■	■	
Milestones								
g) RWGSR-MCR model validated by experimental data					◆			
h) Design of scaled-up system completed						◆		
i)Optimization of scaled-up system completed							◆	
Task 5.0 - Preliminary Process TEA						■	■	■
Milestones								
j) Preliminary system TEA completed							◆	
k) Final report prepared and submitted								◆

Membrane Modification

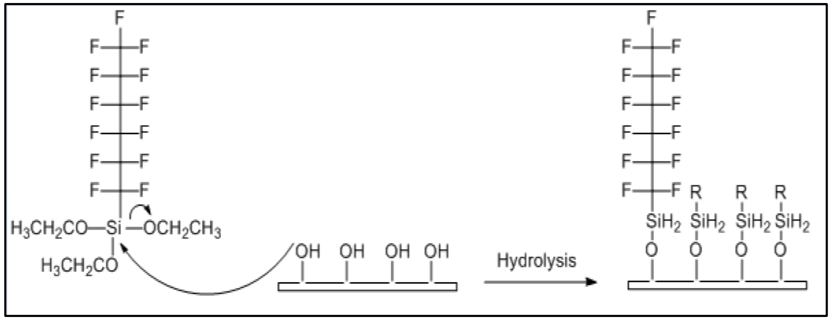
- **Modified Ceramic Membrane**
  - Hydrophobic Instead of Hydrophilic (OH-)
  - Avoid Complete Wetting of the Membrane
  - Fluoroalkylsilane (FAS) Agents





Properties of the ceramic membrane

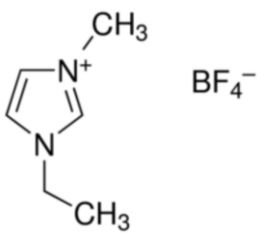
Layer	Material	Thickness (μm)	Average Pore Size (Å)
Support	α-Alumina	1100	2000-4000
First Layer	α-Alumina	10-20	500
Second Layer	γ-Alumina	2-3	100
Length (cm)			9
Outer Diameter (mm)			5.9
Inner Diameter (mm)			4.7



Sweep Liquid

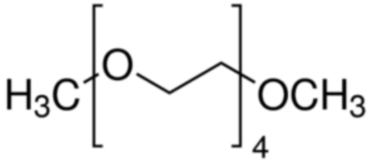
Ionic Liquid (IL)

Ethyl-3-methylimidazolium tetrafluoroborate



Organic Solvent

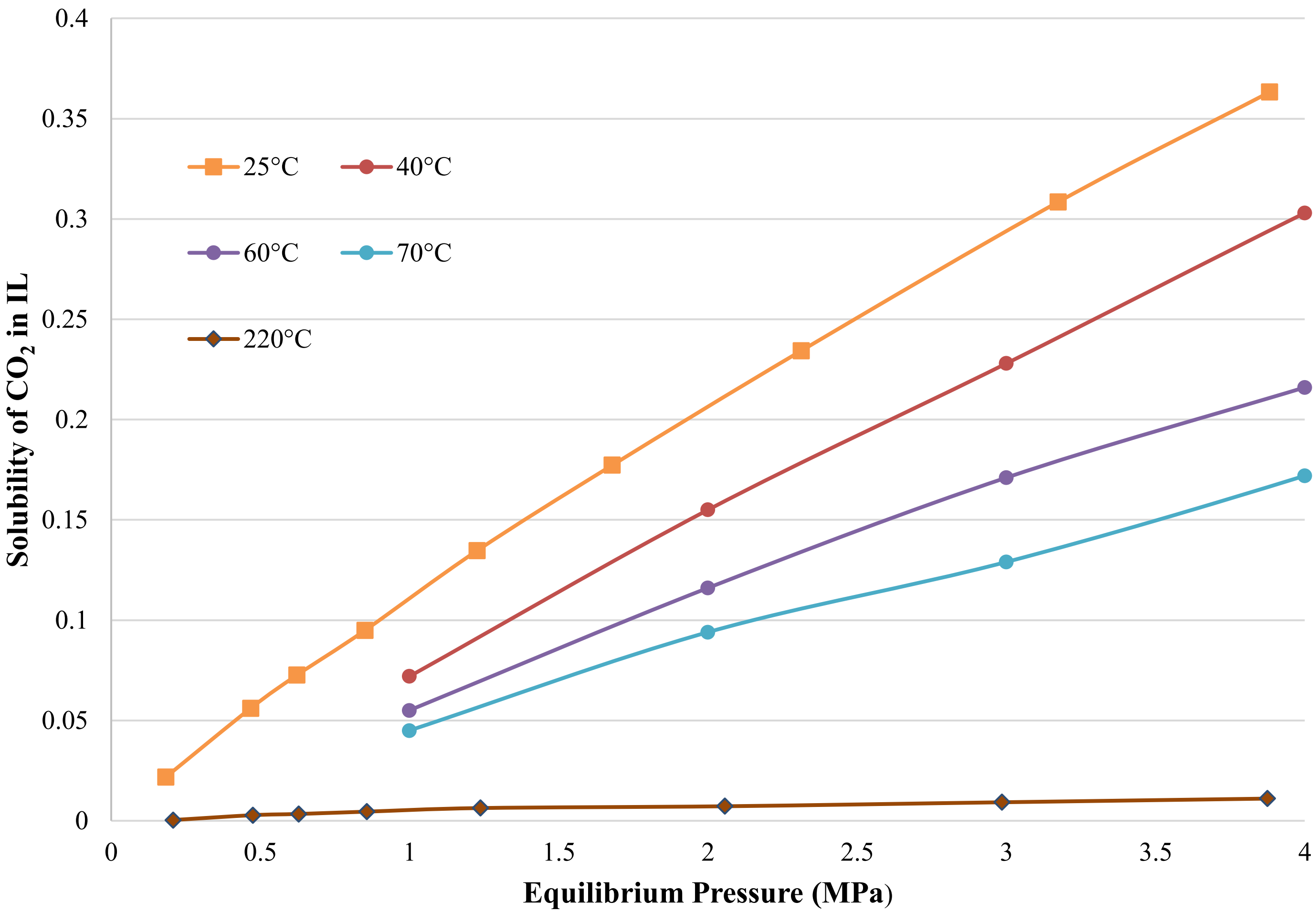
Tetraethylene glycol dimethyl ether (TGDE)



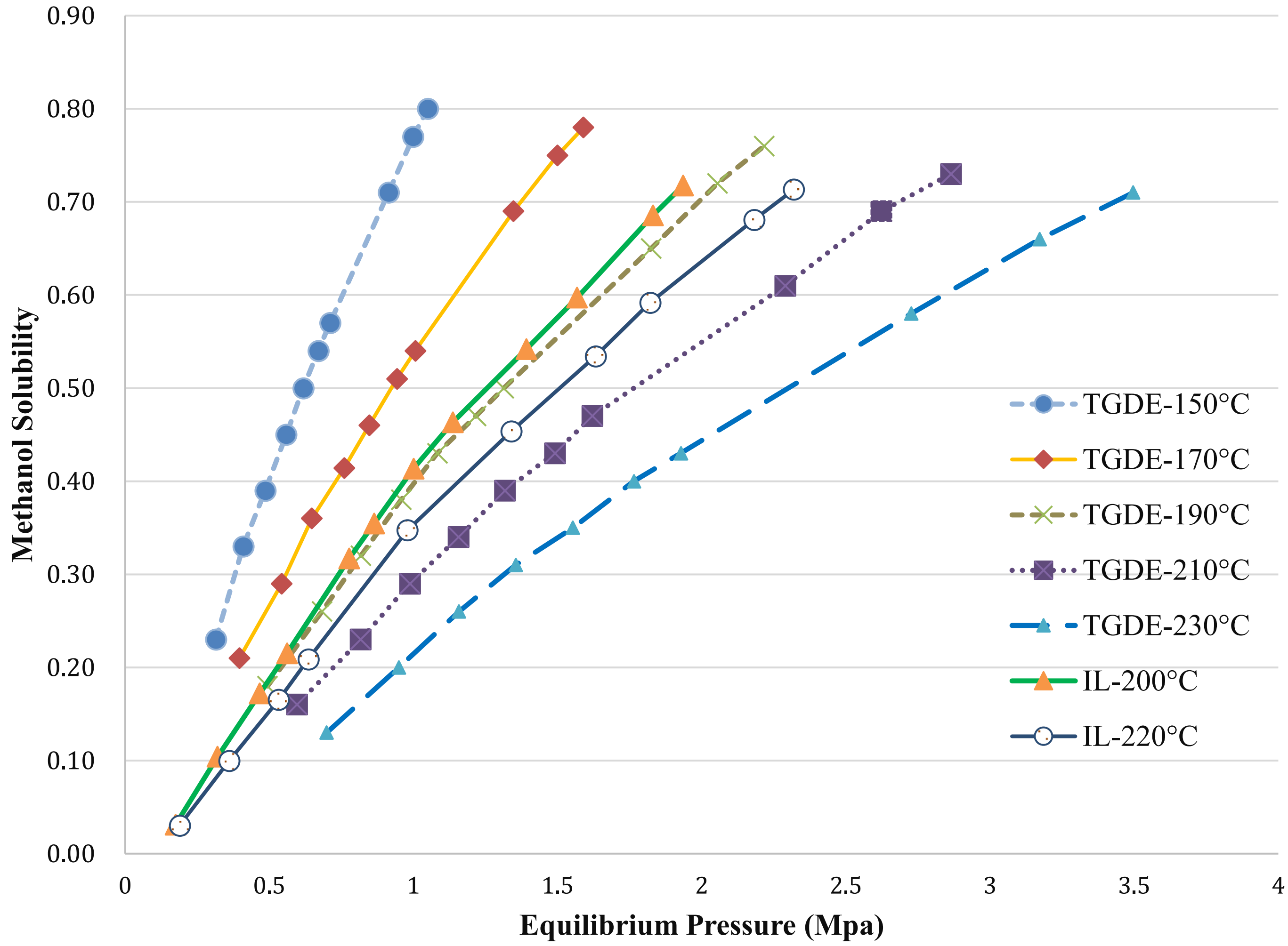
Ionic liquid advantages

- ❑ Highly polar compounds; MeOH has considerably higher solubility than CO and H_2 in them
- ❑ Typical IL's have extremely low vapor pressures ($<10^{-9}$ bar), which is advantageous when compared to other low boiling point (B.P.) organic solvents
- ❑ Significantly simplified downstream separation of the MeOH from the solvent
- ❑ Very high decomposition temperatures
- ❑ High thermal capacity (thermal energy storage)

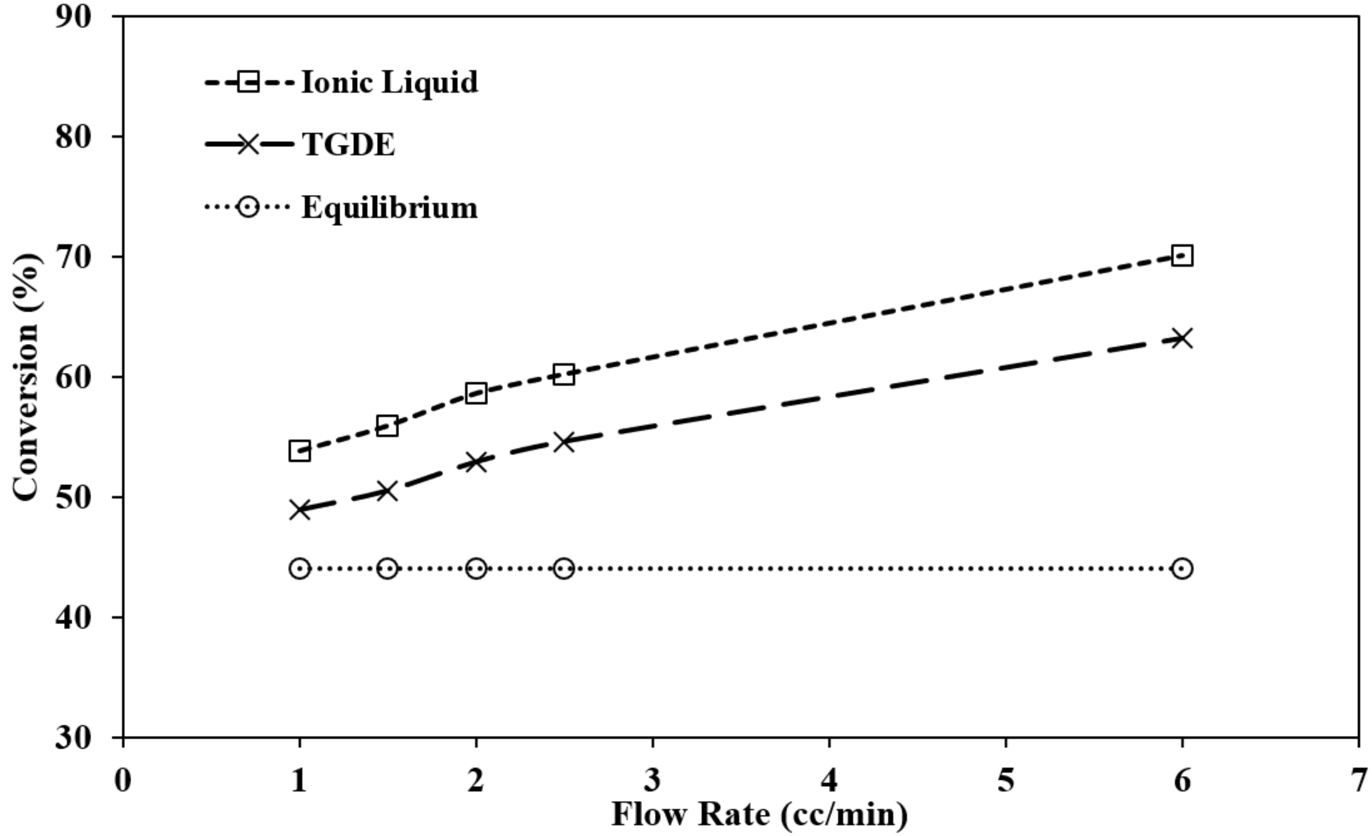
CO_2 Solubility in the IL



MeOH Solubility in the IL and TGDE



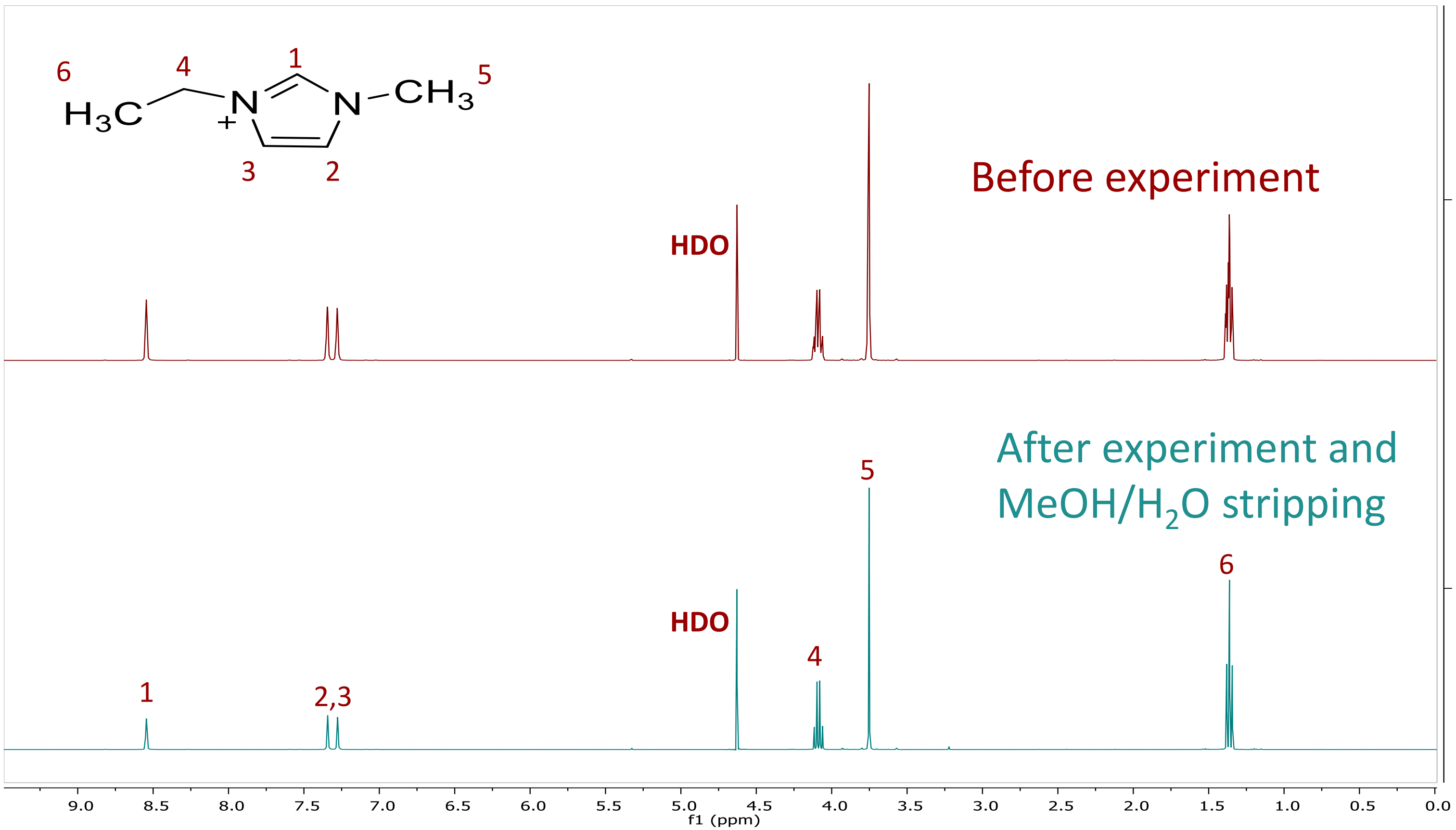
MeS-MCR Performance



Effect of liquid sweep flow rate on MR conversion. P = 32 bar, T = 220ºC, W/F = 47.2 g*h/mol

IL Stability Under Reaction Conditions

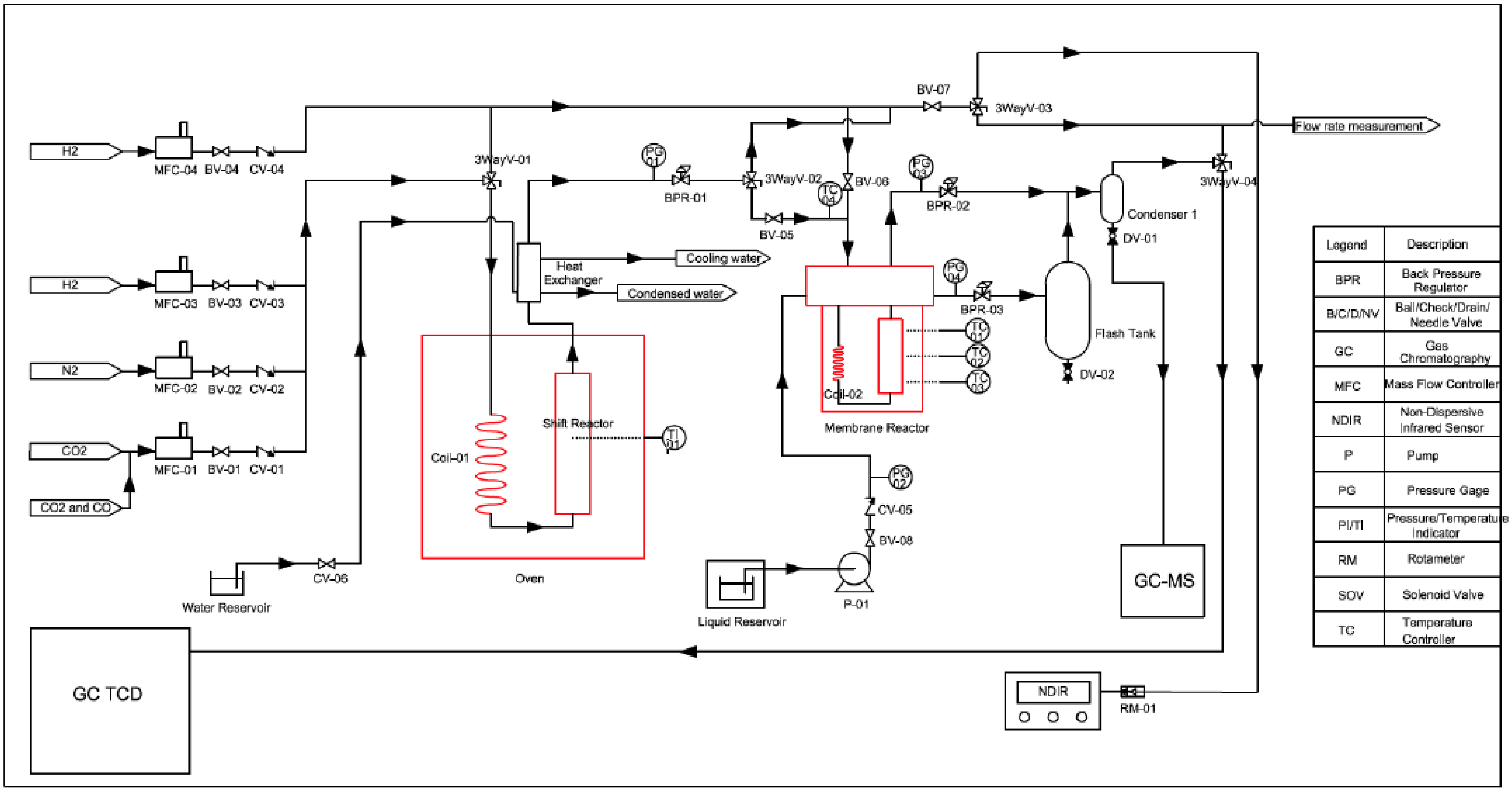
NMR studies show that the IL structure is stable and no irreversible bonds with methanol and water are created.



400 MHz ^{1}H Nuclear Magnetic Resonance (NMR) Results of the [EMIM][BF_4] IL

Task 1.0 – Design and Construction of the RWGSR/MCR MeS System

Schematic of Experimental Set-up



Lab-Scale Experimental Set-Up

The combined RWGSR and MCR-MeS system.

Task 2.0 – Testing of the Individual RWGSR and MCR MeS Subsystems

MeS Kinetic Studies

- **Packed-Bed Reactor Model**

$$\frac{dF_{CO}}{dW} = r_{RWGS}$$

$$\frac{dF_{CO2}}{dW} = -r_{MeOH} - r_{RWGS}$$

$$\frac{dF_{H2O}}{dW} = r_{MeOH} + r_{RWGS}$$

$$\frac{dF_{H2}}{dW} = -3r_{MeOH} - r_{RWGS}$$

$$\frac{dF_{CH3OH}}{dW} = r_{MeOH}$$

- **Rate Expressions**

Van den Bussche et al. (1996)

$$r_{MeOH} = \frac{k'_{5a}K'_2K_3K_4P_{CO_2}P_{H_2}[1-(1/K_1^*)(P_{CH_3OH}P_{H_2O}/P_{H_2}^3P_{CO_2})]}{(1+(K_{H_2O}/K_3K_4K_{H_2})(P_{H_2O}/P_{H_2})+\sqrt{K_{H_2}P_{H_2}}+K_{H_2O}P_{H_2O})^3}$$

$$r_{RWGS} = \frac{k'_1P_{CO_2}[1-(K_3)(P_{CO}P_{H_2O}/P_{H_2}P_{CO_2})]}{(1+(K_{H_2O}/K_3K_4K_{H_2})(P_{H_2O}/P_{H_2})+\sqrt{K_{H_2}P_{H_2}}+K_{H_2O}P_{H_2O})}$$

$$\log_{10}K_1^* = \frac{3066}{T} - 10.592$$

$$\log_{10}1/K_3^* = \frac{-2073}{T} + 2.029$$

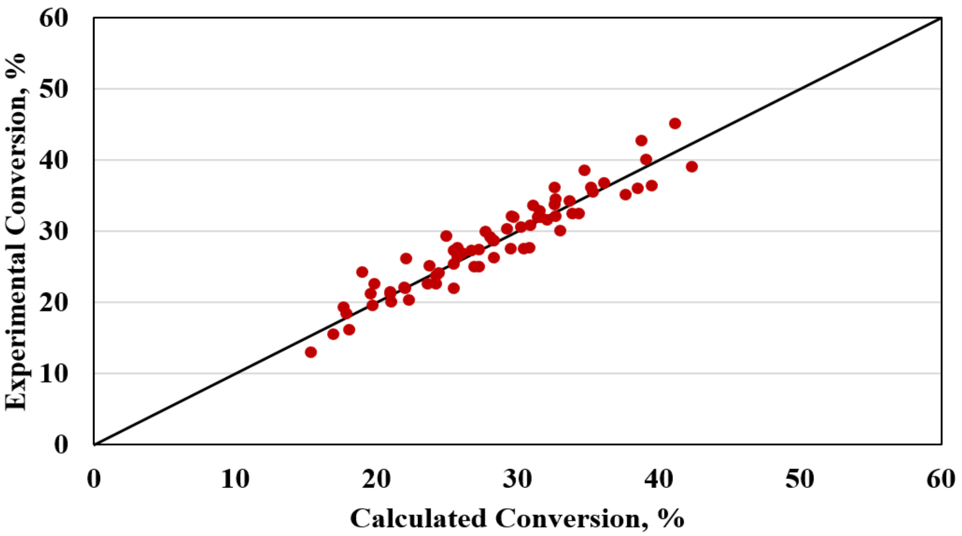
$$k_1 = k'_{5a}K'_2K_3K_4 \qquad k_2 = K_{H_2O}/K_3K_4K_{H_2} \qquad k_3 = \sqrt{K_{H_2}} \qquad k_4 = K_{H_2O} \qquad k_5 = k'_1$$

Rate Parameter Estimation

Temperature-Dependent Rate Constants

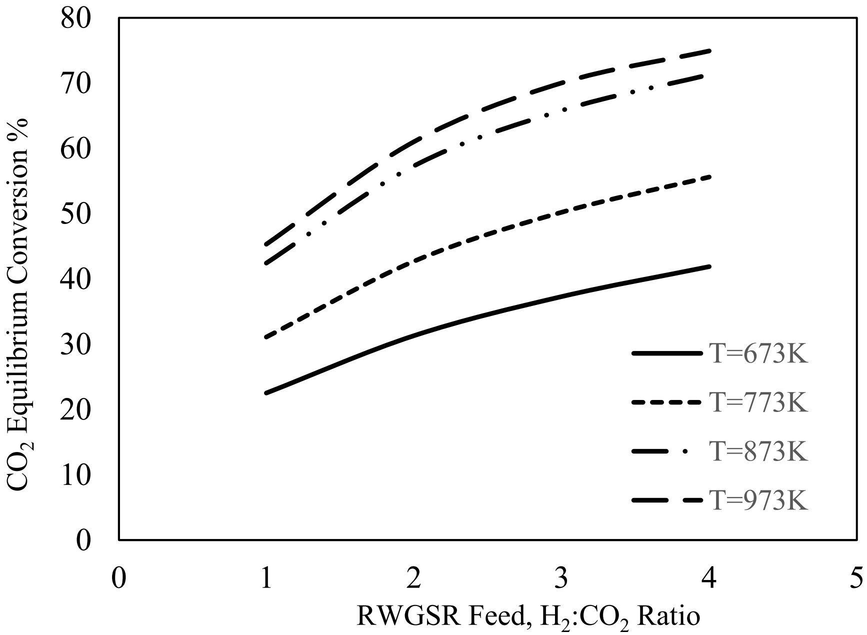
$$K = A(i)\exp(-B(i)/RT)$$

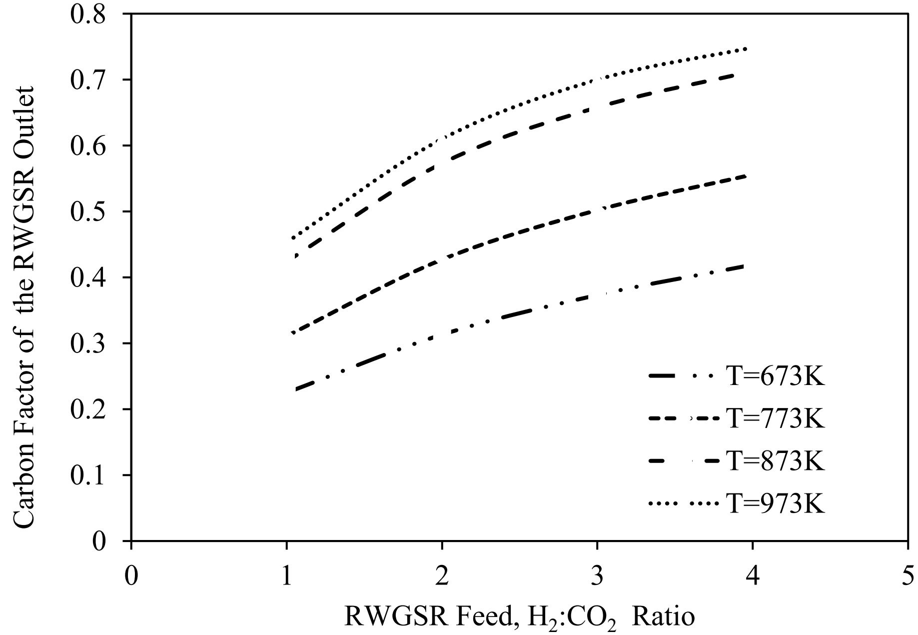
	A(i)	B(i)
k_5	1.459928	31575.31
k_4	18766.2	-0.00451
k_3	7.79461E-7	91306.78
k_2	4.64815E-11	126110.78
k_1	153463133.88	-73698.32



Comparison of experimental vs. calculated carbon conversions

RWGSR Performance at Equilibrium

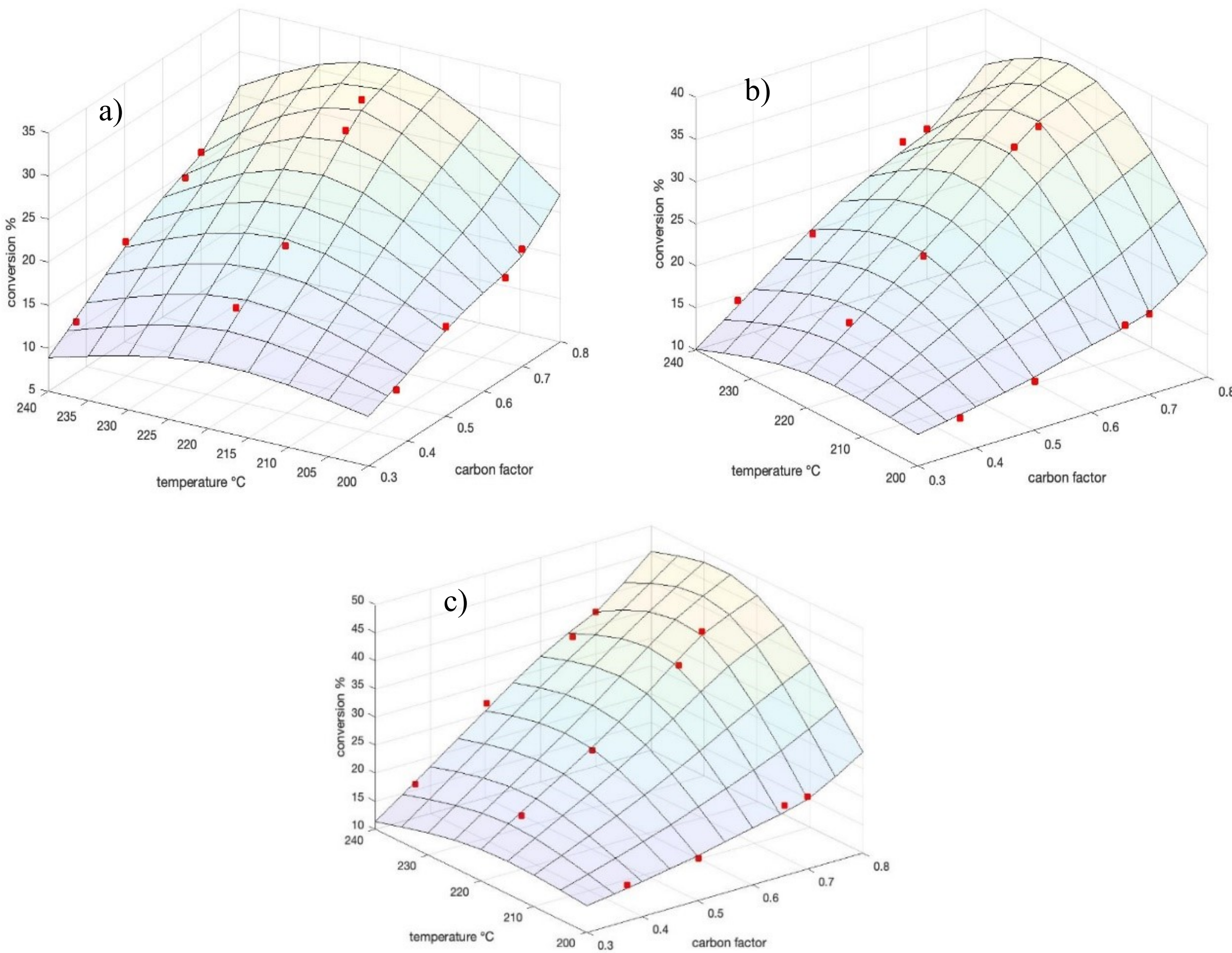




CO_2 equilibrium conversion in the RWGSR

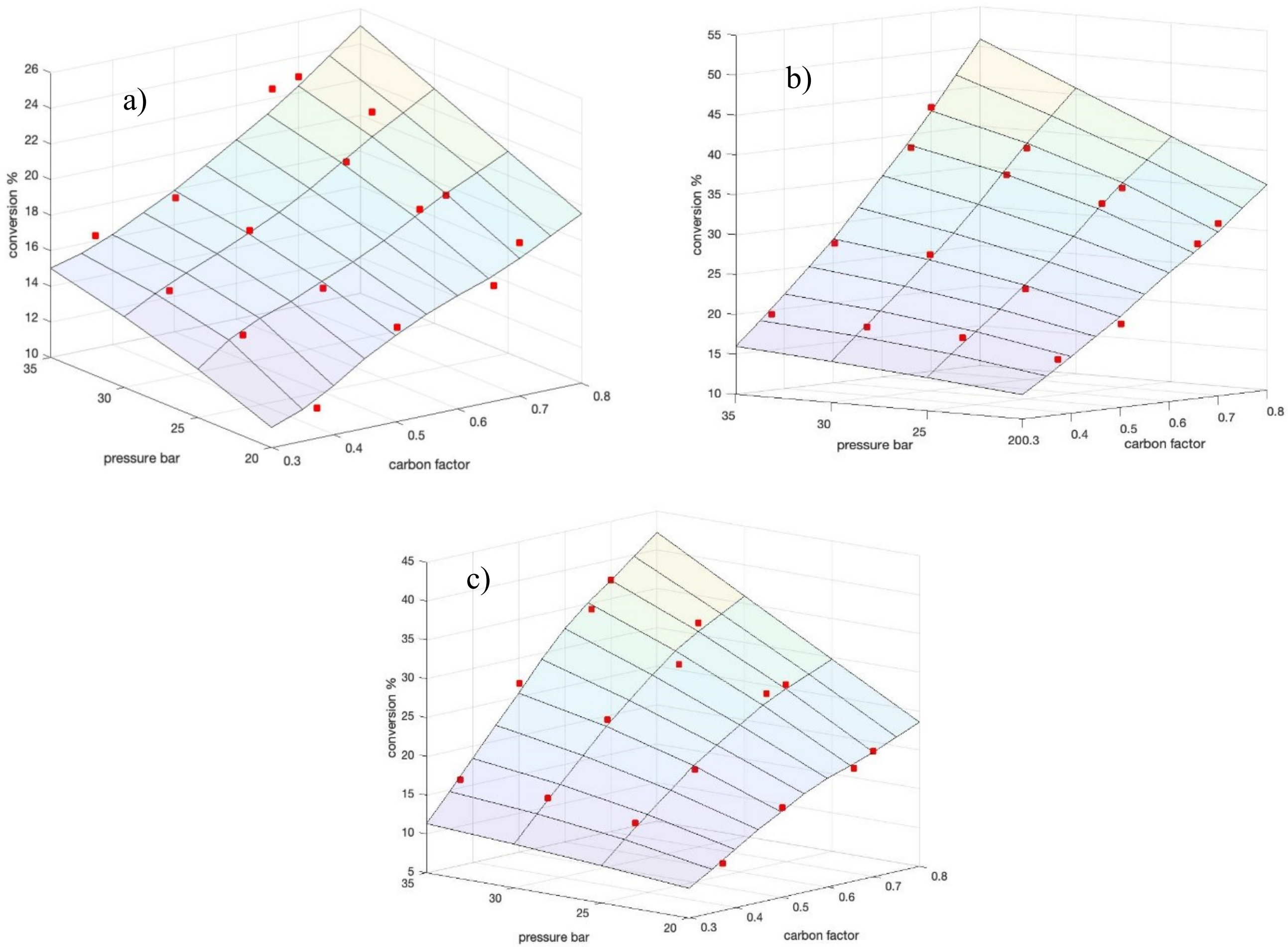
CF of gas mixture at the exit of the RWGSR at equilibrium.

MeS-PBR Conversion at Various T and CF



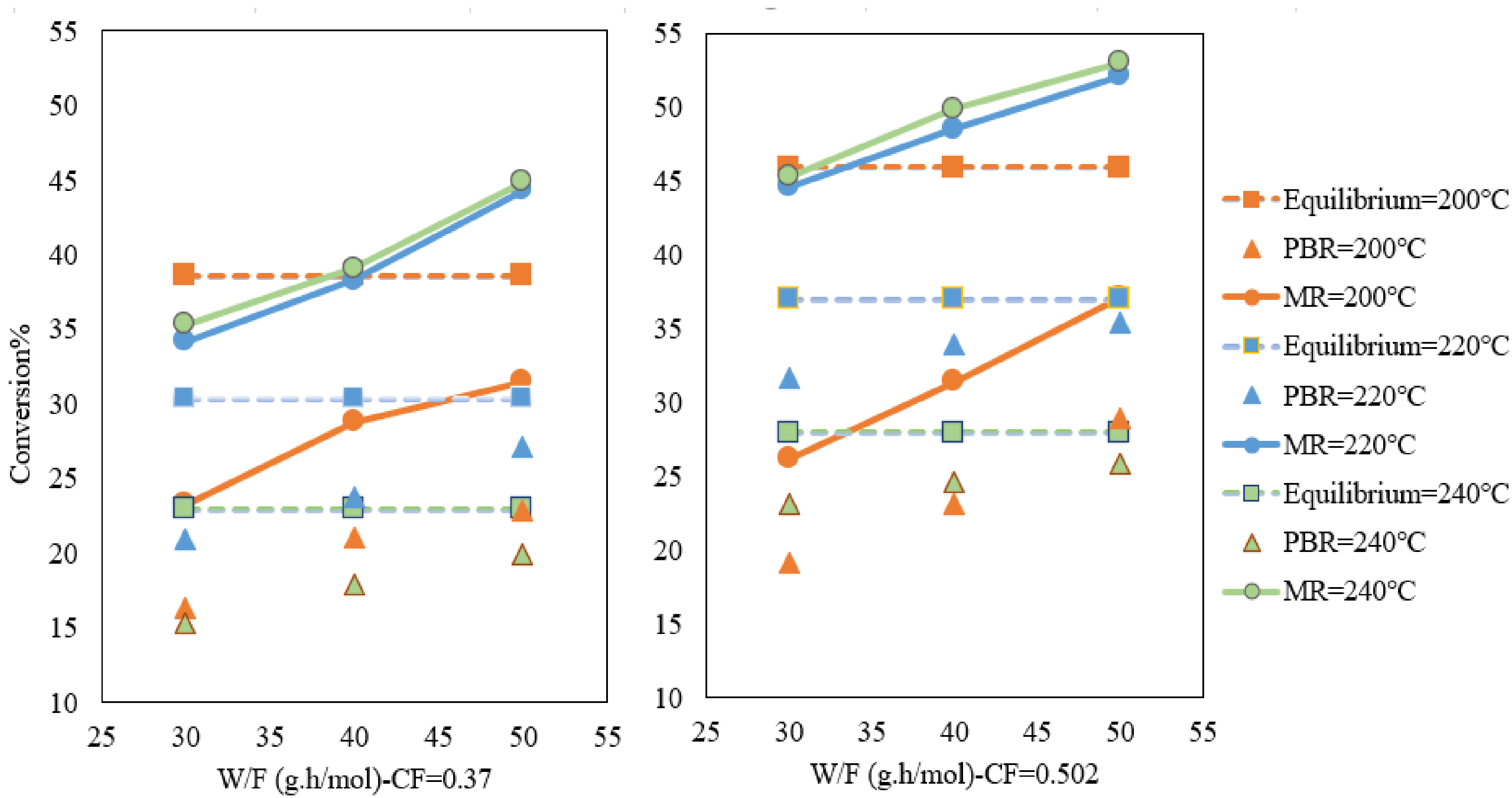
(a) P= 20 bar, (b) P=25 bar, (c) P=30 bar; dots are the experimental points and surfaces are model calculations

MeS-PBR Conversion at Various P and CF



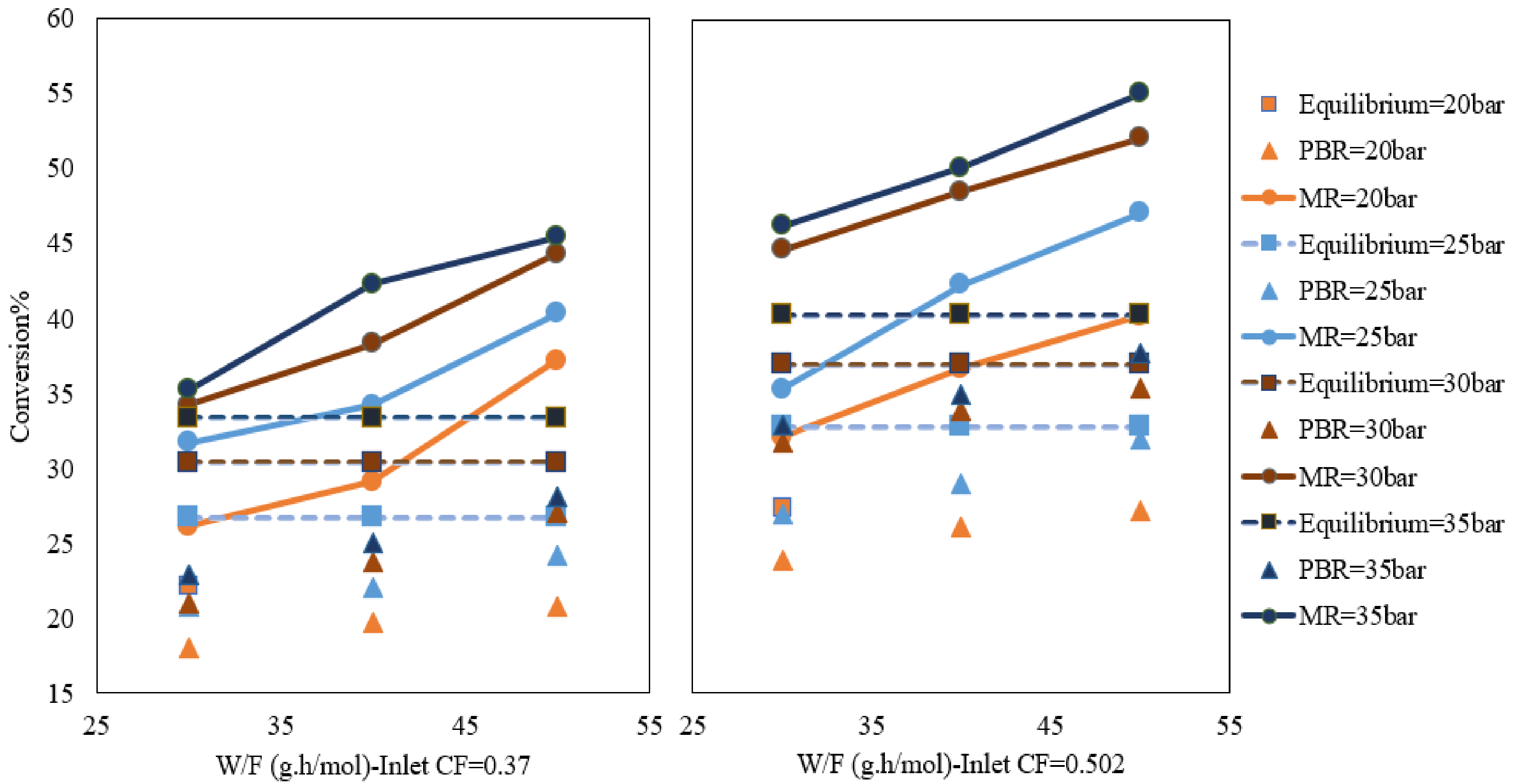
(a) T= 200 ^{o}C, (b) T=220 ^{o}C, (c) T=240 ^{o}C; dots are the experimental points and surfaces are model calculations

PBR and MCR Conversion vs. W/F, Varying T



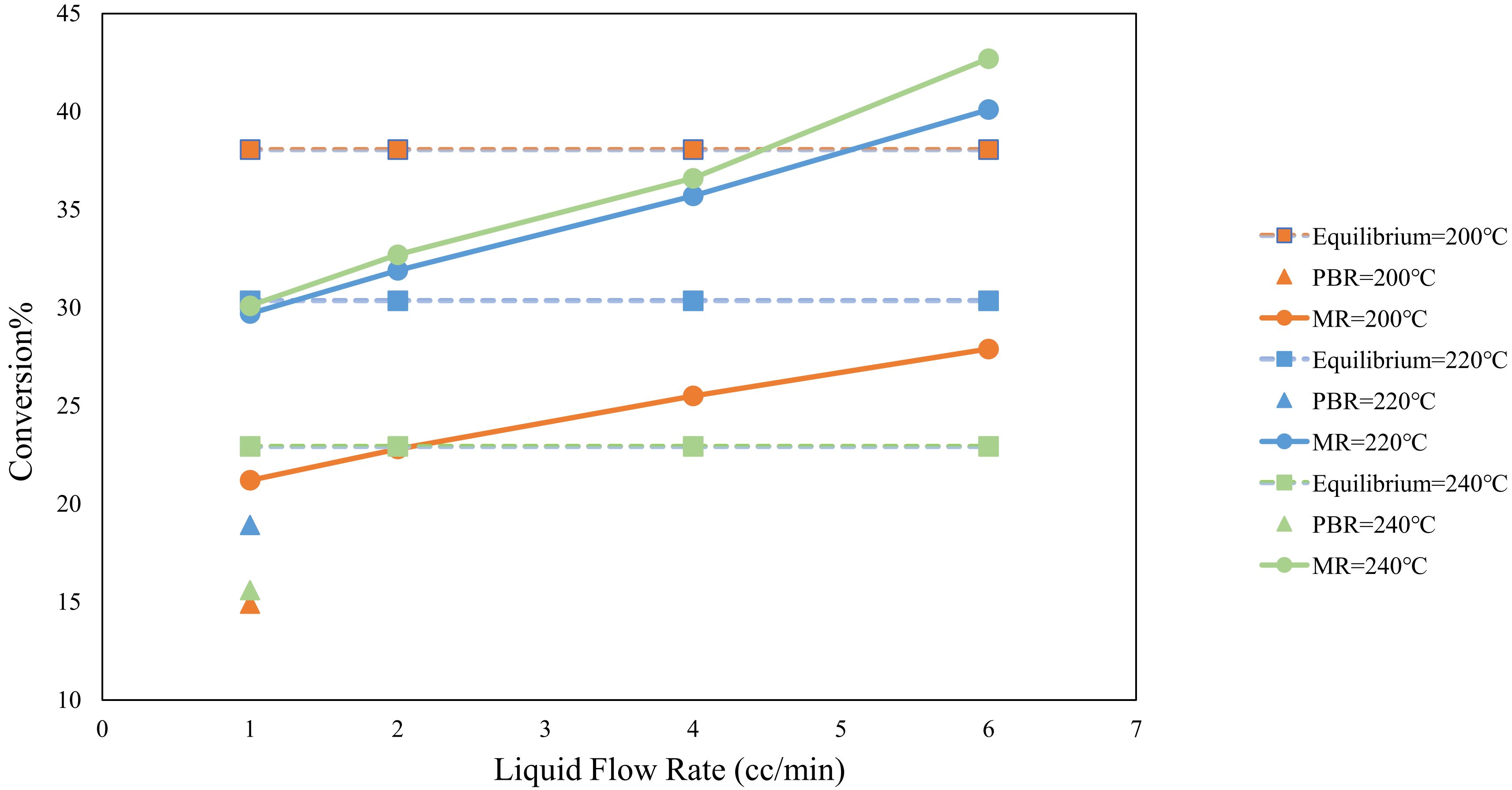
SN=2, P=30 bar, CF=0.37 (Left Side Plot), CF=0.502 (Right Side Plot)

PBR and MCR Conversion vs. W/F, Varying P



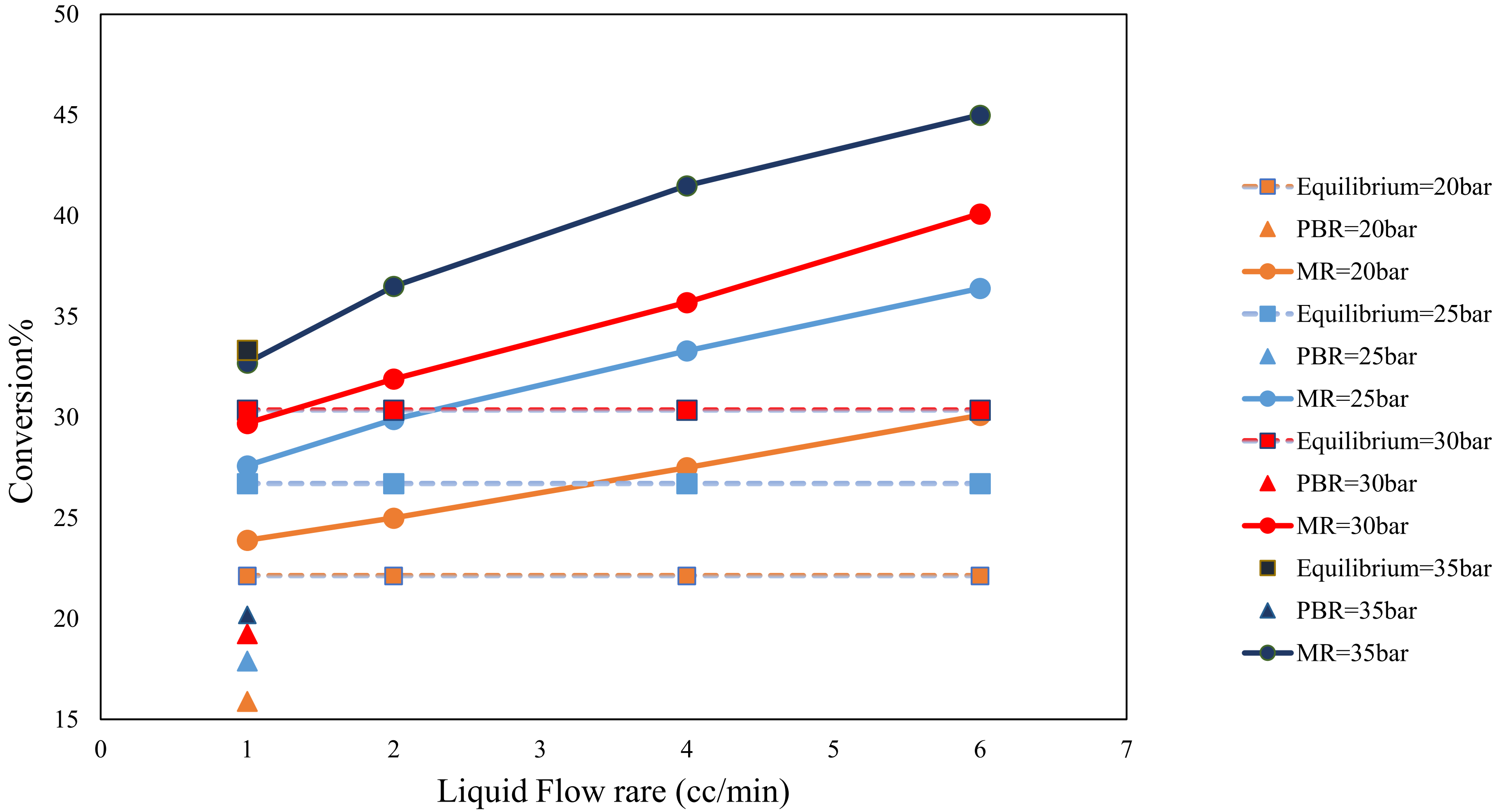
SN=2, T=220 °C, CF=0.37 (Left Side Plot), CF=0.502 (Right Side Plot)

PBR and MCR Conversion vs. LF, Varying T



SN=2, P=30 bar, CF=0.37, W/F=20 Kg*s/mol

PBR and MCR Conversion vs. LF, Varying P



SN=2, T=220 ^{o}C CF=0.37, W/F=20 Kg*s/mol

Progress To Date

- **RWGSR/MeS-MCR lab-scale system designed and constructed.**
- **Performance of the MeS-MCR subsystem studied and its ability to functions as a 2^{nd} stage following the RWGSR validated.**
- **In-house MeS kinetic model validated with the additional MeS-PBR data generated under conditions relevant to the proposed application.**
- **RWGS catalyst prepared and characterized. Testing to evaluate its catalytic performance under relevant experimental conditions currently ongoing.**

Future Work

- **Continue and complete the performance evaluation of the RWGSR subsystem. Initiate and complete the study of the integrated RWGSR/MeS-MCR system to evaluate its performance for a broad range of pressure and temperature conditions.**

- **Use the experimentally-validated model for process design and scale-up to assess the attainable region of conversions, aiming to obtain >90% carbon capture and utilization.**

- **Carry out a techno-economic analysis (TEA) of the proposed RWGSR/MeS-MCR process to compare performance with that of the conventional, absorption-based carbon separation and capture (CSC) technologies.**

Potential Areas of Collaborative Work with NETL

- Preparation and characterization of novel RWGS catalysts (ongoing).
- Optimizing engineering design and reaction conditions for the novel CSC process and evaluating their impact on the balance of plant.
- Evaluating the economics and environmental aspects of the CSC process, and comparing them with those of the absorption-based processes.

Acknowledgements

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