Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid–Liquid Phase Separation for Post-Combustion Carbon Capture

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Project Overview

- Project objectives
  - Developing new biphasic solvents
  - Demonstrate phase separation-coupled CO_2 absorption process
  - Generate and assess engineering and scale-up data

- Project duration
  - 10/1/15 – 9/30/18 (36 months for two BPs)

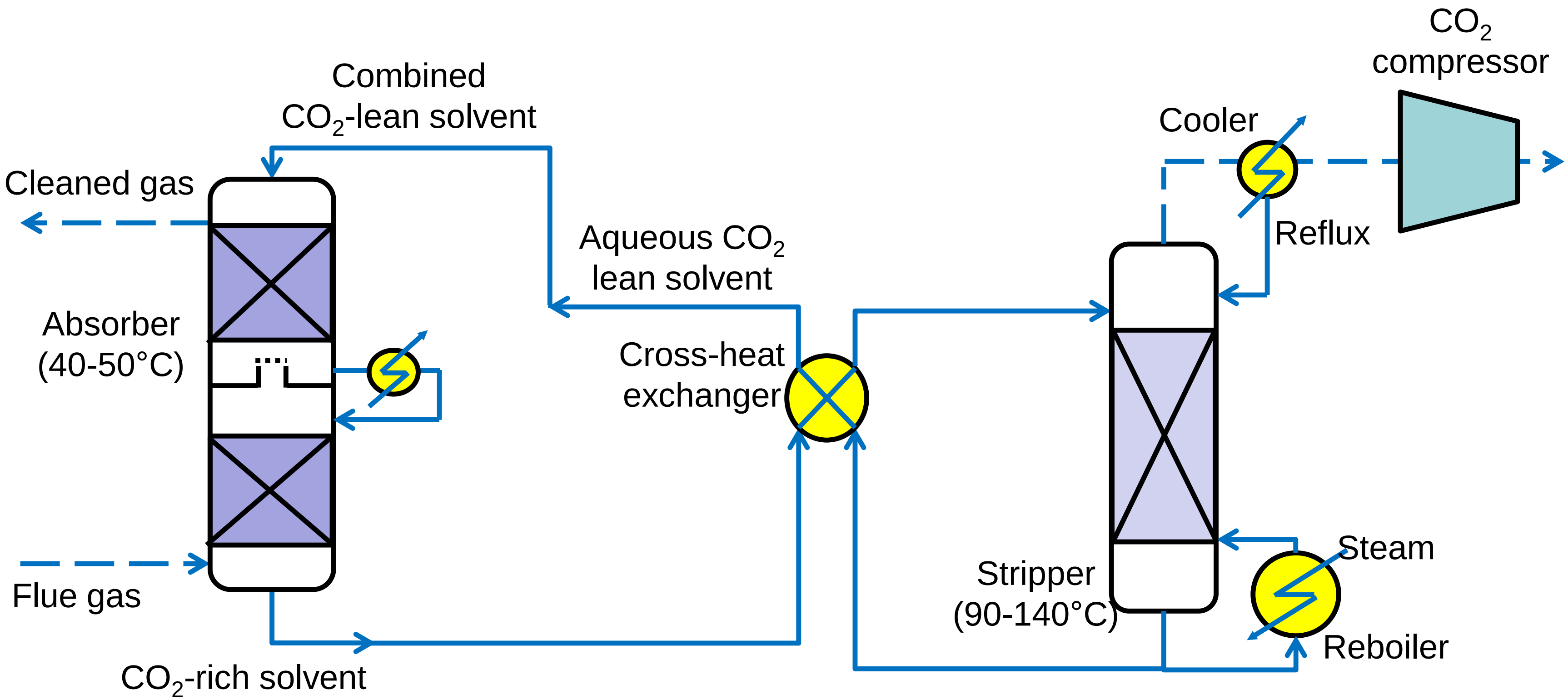
- Funding profile

DOE funding	**1,999,996**
BP1	1,079,663
BP2	920,333
Cost share (Cash & In-kind)	**501,052**
BP1	269,920
BP2	231,132
Total	**2,501,048**

Project Participants

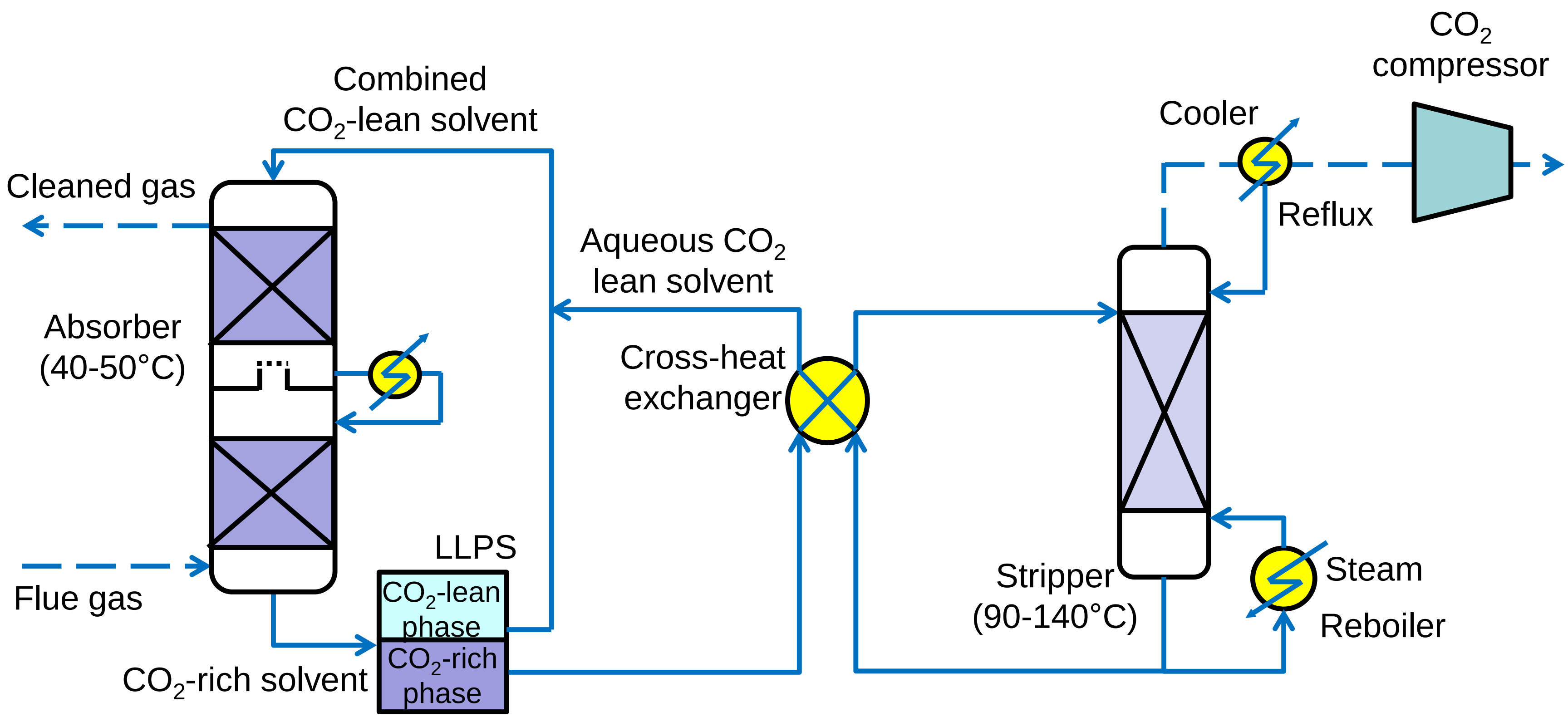
- **University of Illinois**
  - **Illinois State Geological Survey**
    - Solvent screening & development
    - Solvent equilibria, kinetics & properties measurements
    - Absorption and desorption column testing
  - **Illinois Sustainable technology Center**
    - Evaluation of solvent stabilities and corrosion impact
  - **Applied Research Institute**
    - Molecular dynamics simulation study for solvent screening
- **Trimeric Corporation**
    - Process feasibility and TEA analysis

Conventional Monophasic Absorption Approach



Conventional CO_2 Absorption Process (e.g., MEA)

Advantages of Biphasic CO_2 Absorption Processes

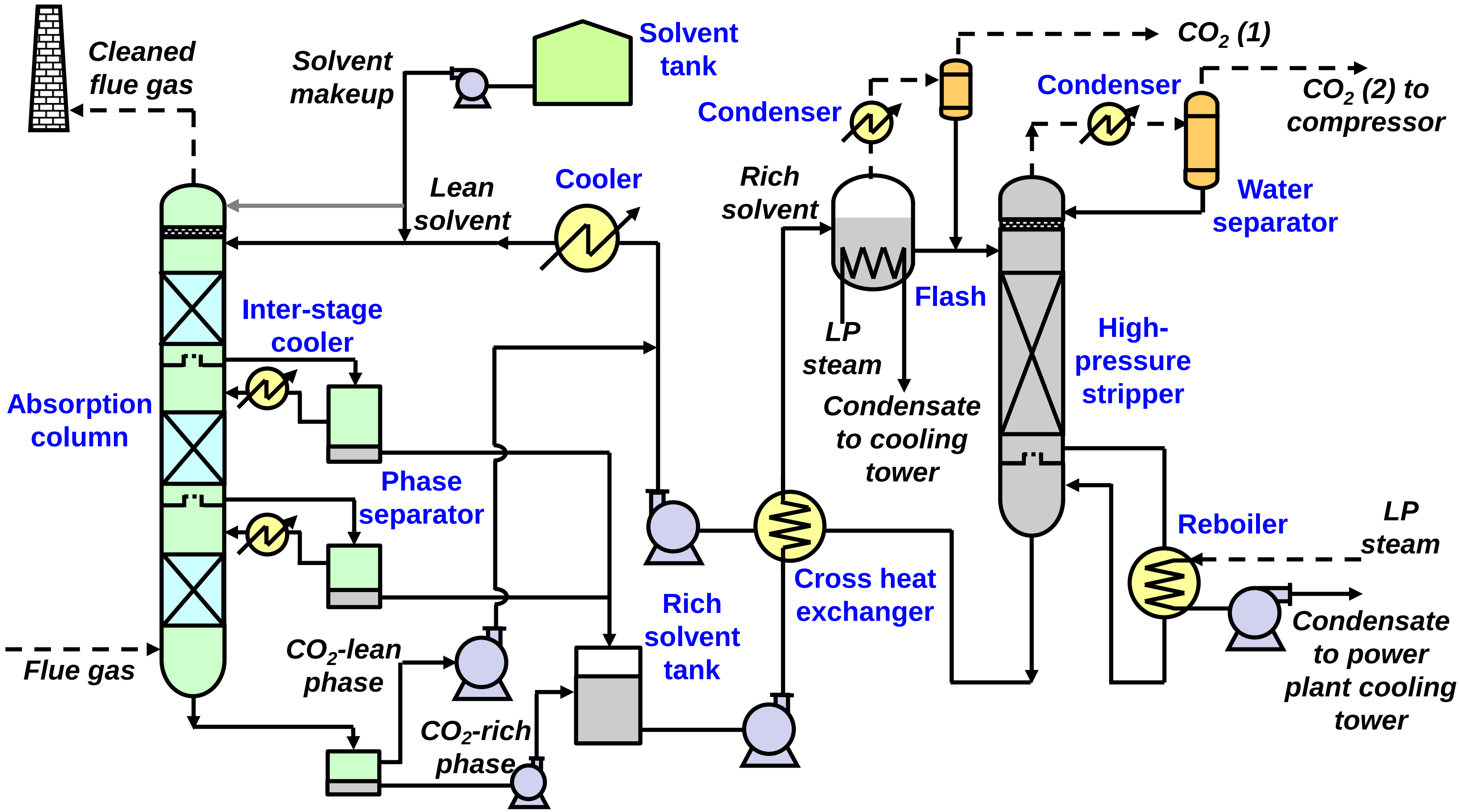


Conceptual of Biphasic Absorption Processes by Other Developers

Impacts on stripper:

- **Reduced equipment size due to reduced mass of solvent to be regenerated in stripper**
- **Reduced energy use and compression cost due to increased CO_2 loading capacity (concentrated feed), reduced mass, and increased stripping pressure**

Biphasic CO_2 Absorption Process with Multi-Stages of Liquid-Liquid Phase Separation (BiCAP)



Adds impacts on absorber to the impacts on stripper:

- **Reduced viscosity with separation of rich, viscous phase improves mass transfer rate**
- **Lean phase to next packed bed improves kinetics**
- **Reduced mass of solvent to next packed bed**

Advantages of Multi-Stage Phase Separation (LLPS) during CO_2 Absorption

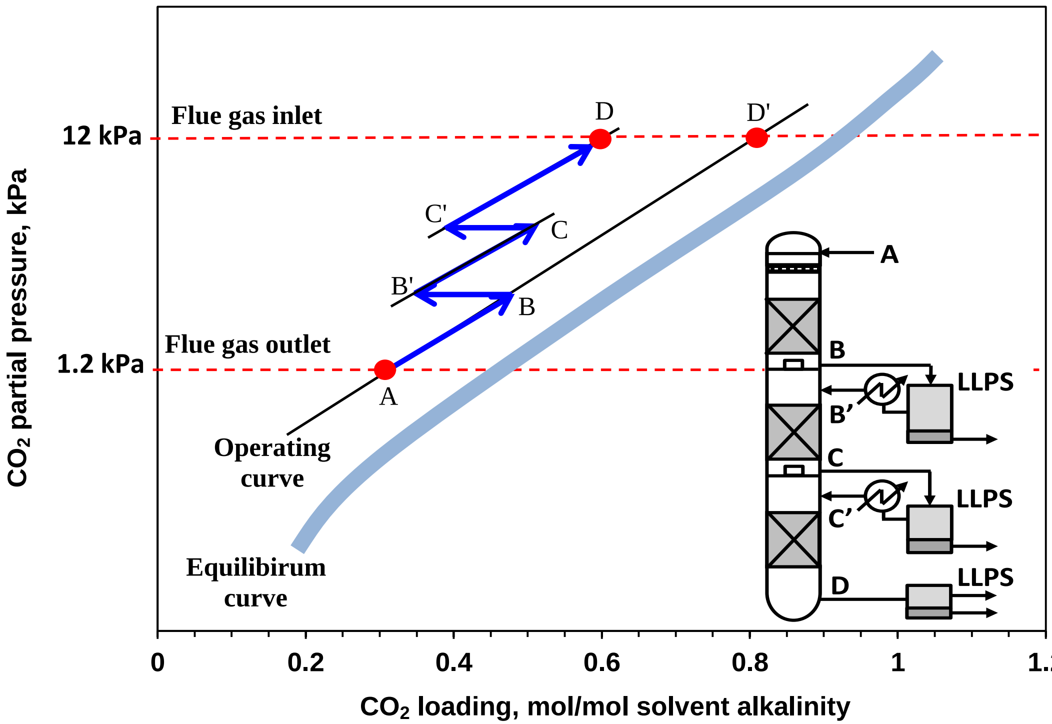


Illustration of operating & equilibrium curves with 3 stages of CO_2 absorption-LLPS
(the equilibrium curve that may change after each LLPS is not displayed in this illustration)

- **Modified operating curve allows for a higher mass transfer driving force and thus a faster absorption rate**

BiCAP vs MEA and Other Biphasic Processes

Biphasic processes vs MEA

- Biphasic solvents have larger loading capacity for CO_2 stripping due to absorbed CO_2 concentrated in one phase as feed solution to the stripper
- Reduced mass and elevated P for CO_2 stripping
  - Reduced heat duty (low sensible heat and stripping heat)
  - Reduced compression work requirement

BiCAP vs other biphasic processes

- ***Absorption process:***
  Multi-LLPS in BiCAP allows for low CO_2 loading and low viscosity throughout the absorber, resulting in a faster absorption rate and reduced absorber size
- ***Solvent*:**
  Phase transition behavior of BiCAP solvents are tunable, facilitated with the use of a unique solubilizer(s), allowing for a wide range of solvent component selection
- ***Desorption process:***
  Desorption with a flash step to obtain high-pressure CO_2 and reduce compression requirements

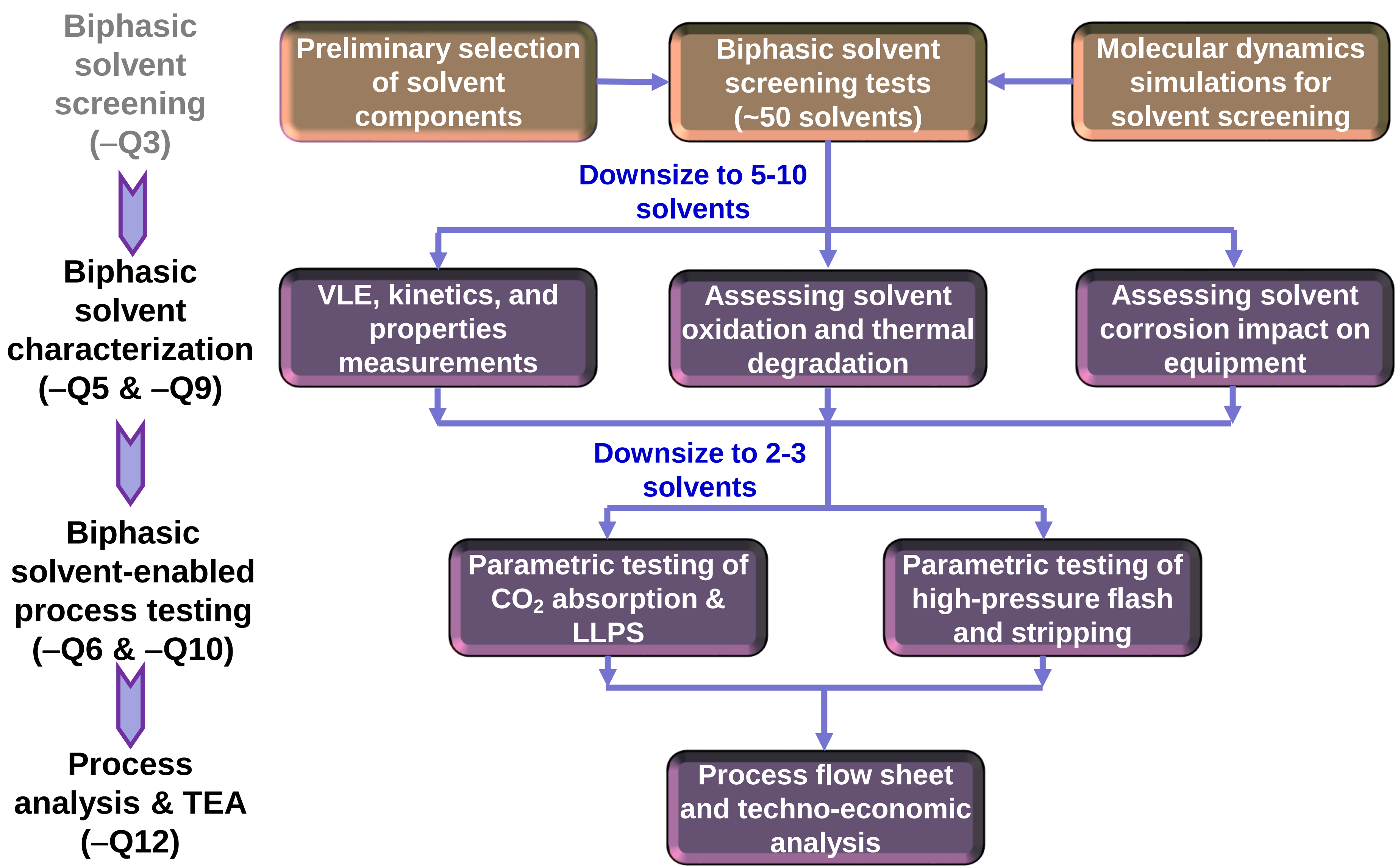
Project On-Track and Initial Milestones Achieved

SOPO BREAKOUT SCHEDULE			START/END		BUDGET PERIOD 1						BUDGET PERIOD 2					
WBS	**Lead**	**Description**	**Start**	**End**	**Q1**	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**	**Q8**	**Q9**	**Q10**	**Q11**	**Q12**
1.0		**Project management and planning**	**10/01/15**	**09/30/18**												
1.1	ISGS/All	Project management and planning	10/01/15	09/30/18												
1.2	ISGS/All	Briefings and reports	10/01/15	09/30/18												
2.0		**Screening and characterization of biphasic solvents**	**10/01/15**	**06/30/16**												
2.1	ISGS	Solvent screening tests on CO2 absorption and phase transition behavior	10/01/15	06/30/16												
2.2	ISGS	Solvent screening tests on CO2 desorption performance	10/01/15	06/30/16			a									
2.3	ARI	Molecular simulation study for solvent screening	10/01/15	06/30/16			b									
3.0		**Measuring phase equilibria, absorption kinetics, & solvent properties**	**01/01/16**	**09/30/16**				**A**								
3.1	ISGS	Measurement of VLE data under absorption & desorption conditions	01/01/16	09/30/16												
3.2	ISGS	Measurement of CO_2 absorption kinetics	04/01/16	09/30/16				c								
3.3	ISGS	Measurement of solvent properties	07/01/16	09/30/16												
4.0		**Determining thermal and oxidation stabilities of the selected solvents**	**04/01/16**	**12/31/16**												
4.1	ISTC	Oxidation stability of solvents under simulated absorption conditions	04/01/16	12/31/16												
4.2	ISTC	Thermal stability of solvents under simulated desorption conditions	04/01/16	12/31/16					e							
5.0		**Testing CO_2 absorption and phase separation in a packed-bed column**	**04/01/16**	**03/31/17**						**B**						
5.1	ISGS	Modification of absorption column to incorporate multi-LLPS operation	04/01/16	09/30/16				d								
5.2	ISGS	Parametric testing of CO_2 absorptionand LLPS in the packed-bed column	07/01/16	03/31/17						f						
5.3	ISGS	Rate-based modeling of CO_2 absorption in the packed-bed column	10/01/17	03/31/17												
6.0		**Development of a process sheet and preliminary process analysis**	**04/01/16**	**03/31/17**												
6.1	Trimeric	Development of a conceptual process flow sheet	04/01/16	12/31/16												
6.2	Trimeric	Preliminary process analysis	07/01/16	03/31/17						g						
7.0		**Testing CO_2 desorption in a high-pressure flash and stripping column**	**04/01/17**	**03/31/18**										**C**		
7.1	ISGS	Modification of an existing packed-bed column by incorporating a flash ur	04/01/17	09/30/17								h				
7.2	ISGS	Parametric testing of high-pressure flash and stripping	07/01/17	03/31/18										j		
7.3	ISGS	Design modeling of CO_2 desorption in the flash and stripping column	10/01/17	03/31/18												
8.0		**Assessing the impact of solvent corrosion on the equipment**	**04/01/17**	**12/31/17**												
8.1	ISTC	Assessing the impact of solvent corrosion on the equipment	04/01/17	12/31/17									i			
9.0		**Technical and economic feasibility study**	**10/01/17**	**09/30/18**												**D**
9.1	Trimeric	Process simulation and mass & energy balance calculations	10/01/17	06/30/18												
9.2	Trimeric	Technical and economic feasibility study	01/01/18	09/30/18												k

COMPLETE

Aug 11, 2016

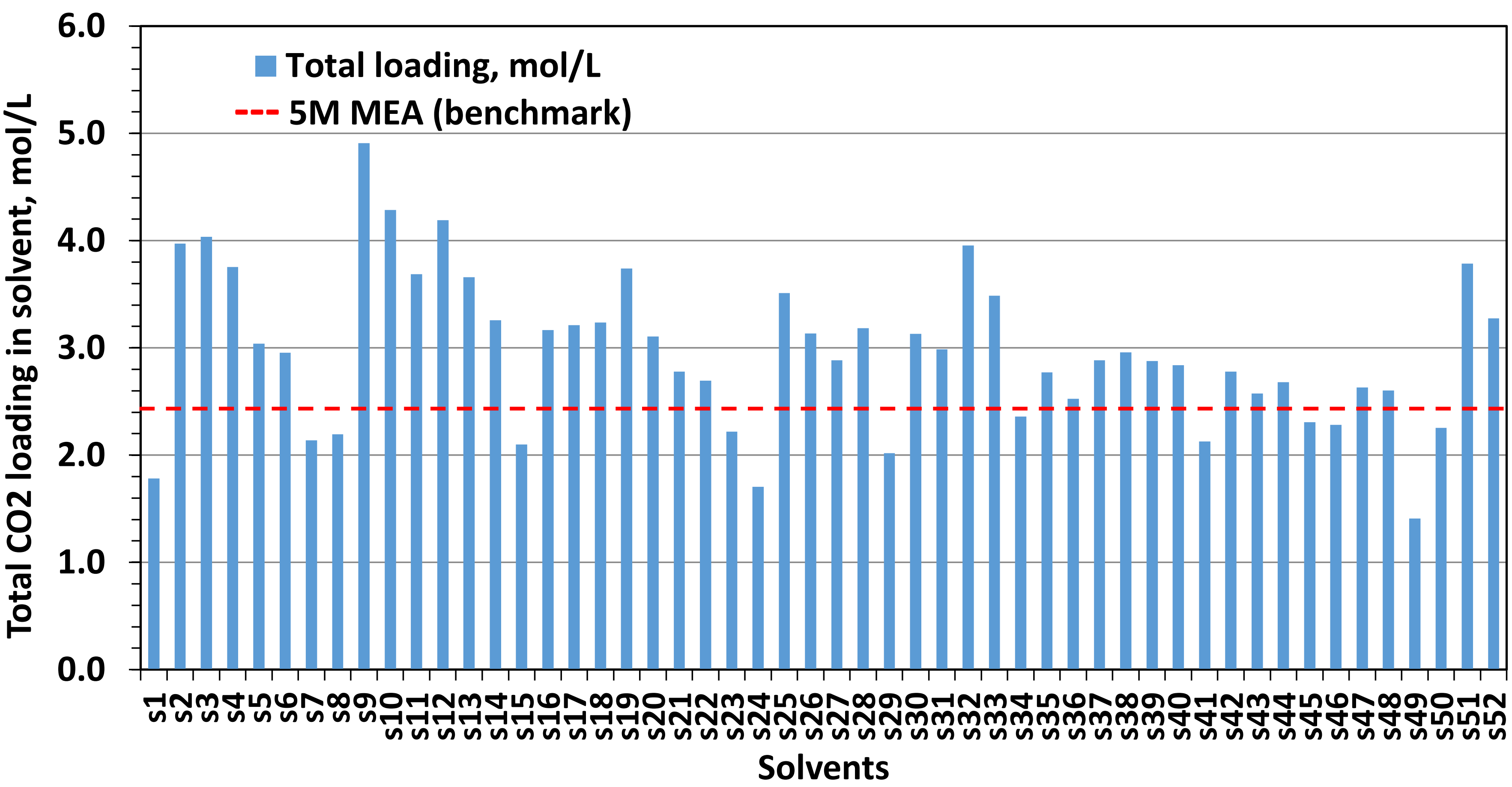
Project Scope and Technical Approach



Key Milestones and Success Criteria

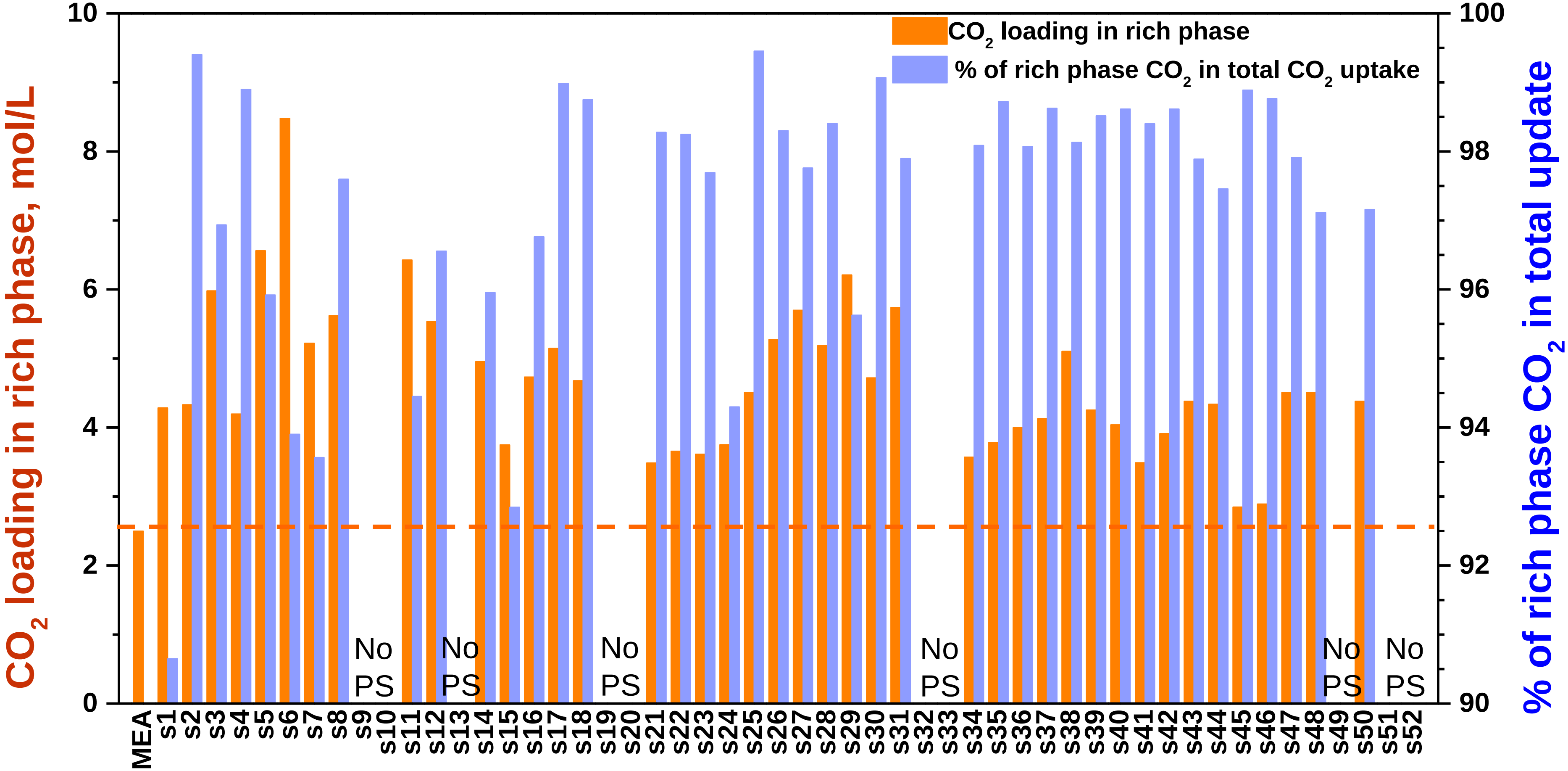
BP1 (by Q6):
Identify 2-3 top-performing solvents (based on phase transition & CO_2 enrichment behavior, CO_2 loading capacity, absorption kinetics, and viscosity)
Complete lab testing of 2-3 solvents in an absorption column with multi-LLPS (CO_2 capacity and kinetics ≥5 M MEA; each LLPS stage ≤ 5 min; ≥ 80% CO_2 enrichment in the rich liquid phase)
Demonstrates reliable operability of the multi-stage absorption & LLPS configuration during lab-scale testing
BP2: (by Q12)
Complete lab testing of 2-3 solvents in a flash / stripping system (≥5 bar stripping pressure; working capacity ≥2 times that of 5M MEA)
Initial techno-economic feasibility study shows significant progress toward achievement of DOE performance goals

Task 2. Solvent Screening Experiments: Absorption Capacity



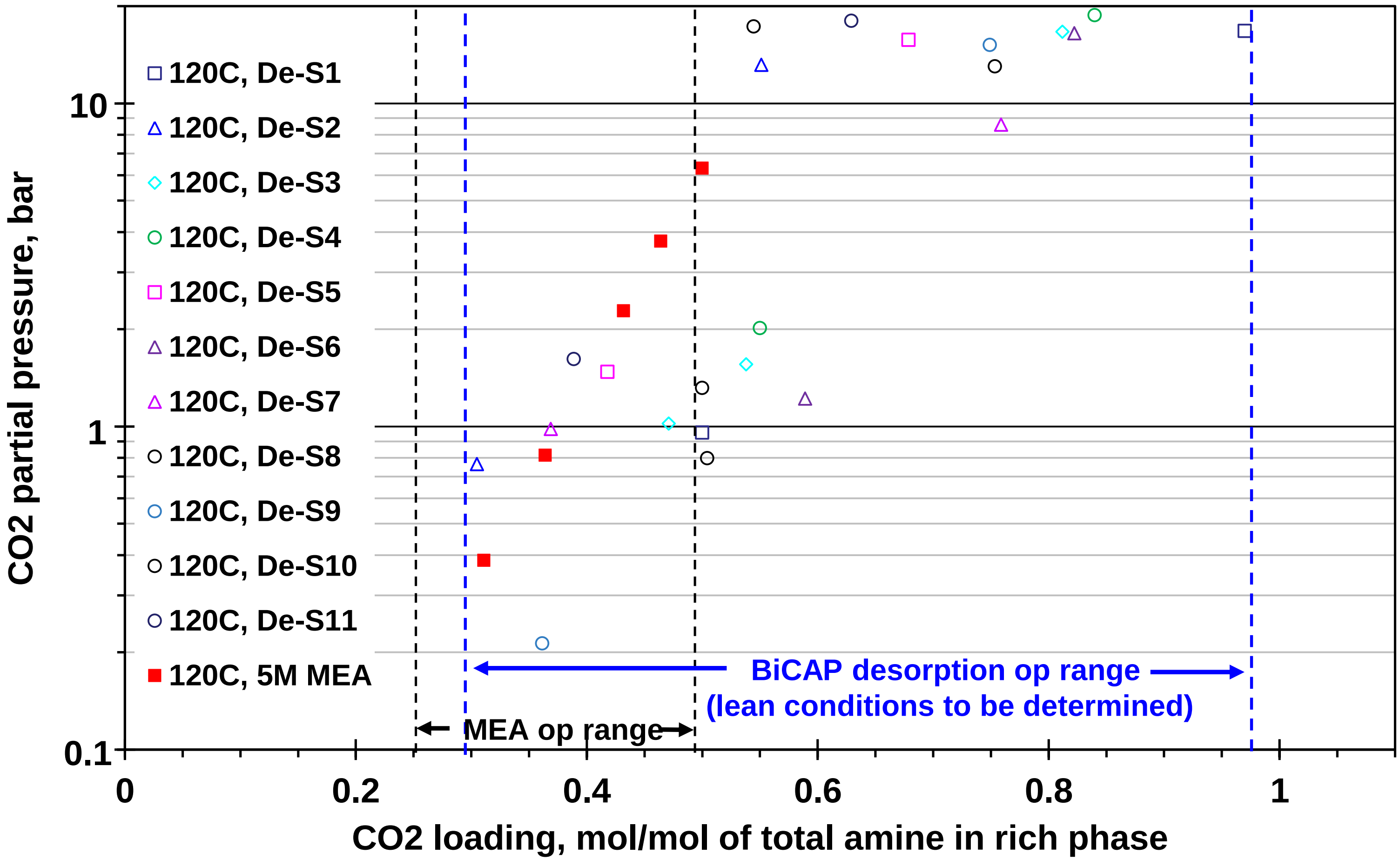
- Overall CO_2 capacity tested in gas impingers for 60 min of absorption under atmospheric CO_2 at 40°C:
- Most solvents achieved a comparable or slightly higher CO_2 loading than 5M MEA for absorption

Phase Transition Behavior



- Formation of dual phases and their volumes are tunable
- CO_2 loading is highly concentrated in rich phase (91-99% of total loading)
- Loading capacity of CO_2 desorption for most solvents is improved by 37-234% over 5M MEA (as only rich phase solution is used for regeneration)

Desorption Pressure



- P_{CO2} = 0.7–10 bar at 120 °C at lean CO_2 loadings of ~0.3–0.5 mol/mol (determined to achieve 90% CO_2 removal), which is much higher than that of lean MEA (pressure at ~0.25 mol/mol)

Task 2. Molecular Dynamics Modeling for Solvent Screening: Methodology Flowchart

Characterization of reaction pathways and barriers
- Identified multiple reaction schemes as a function of solvent composition
- Characterized efficiency of bicarbonate protonation
- Computed energy barriers between transition states and carbonic acid via DFT
- Validated reactive molecular dynamics force field for proton transfer

Experimental Input
- NMR, MS-GS, water content in each phase, pH

Speciation completed

Efficiency of carbon capture
- Calculated enthalpy of formation for carbamate, zwitterions, and protonated amines
- Performed stability analysis for selected ion pairs via association energy in order to construct initial configurations for phase separation simulations
- Computed Gibbs free energy change of selected reactions

Efficiency of phase separation
- Implemented steered molecular dynamics simulation to characterize phase separation process
- Computed free energy change for phase separate system for selected solvent compositions including MEA
- Developed a method to characterize chemical potential differences for species in rich an lean phases

Predicted efficiency based on Gibbs free energy of carbamate formation

Predicted efficiency based on free energy change for phase separation

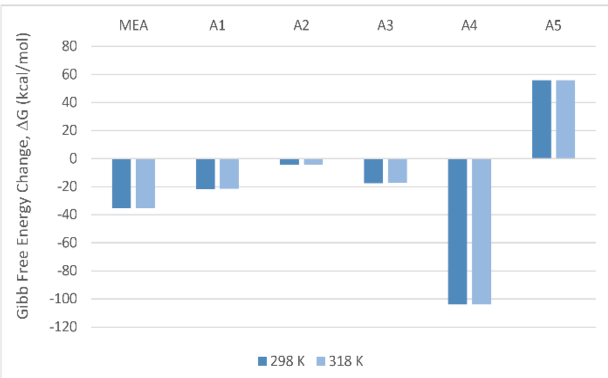
Transport and mixing properties
- Computed self-diffusion coefficient of reactants and products
- Computed viscosity for selected amines

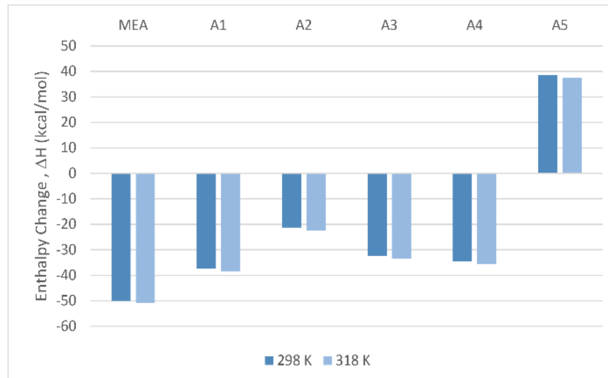
Characterized transport including diffusivity of species

Molecular Dynamics Modeling for Efficiencies of Carbon Capture and Phase Separation

- Carbon capture efficiency screening is performed via thermodynamic calculations using semi-empirical molecular orbital theory (18 reactions considered). Below is one example for the carbamate formation:

$$Am + CO_2 + Am \rightarrow AmCO_2^- + AmH^+$$

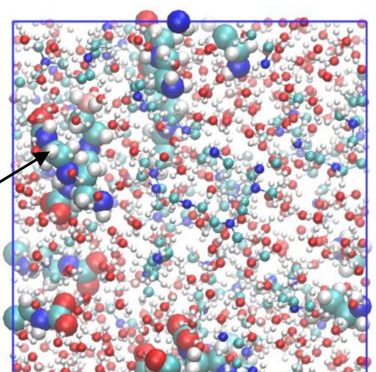




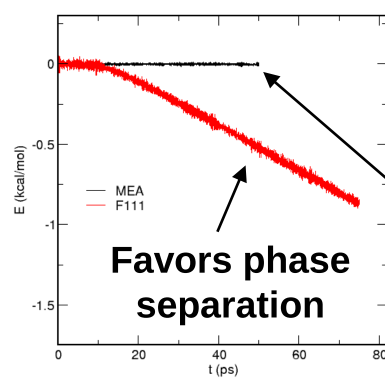
- ΔG < 0: spontaneous reactions; ΔH < 0: exothermic reactions
- Approach is general to screen any stoichiometry & reactions of interest.

- Phase separation efficiency screening is performed via steered molecular dynamics simulation

Zwitterions and carbamates “steered” to separate inside the simulation domain



System F111 after SMD run

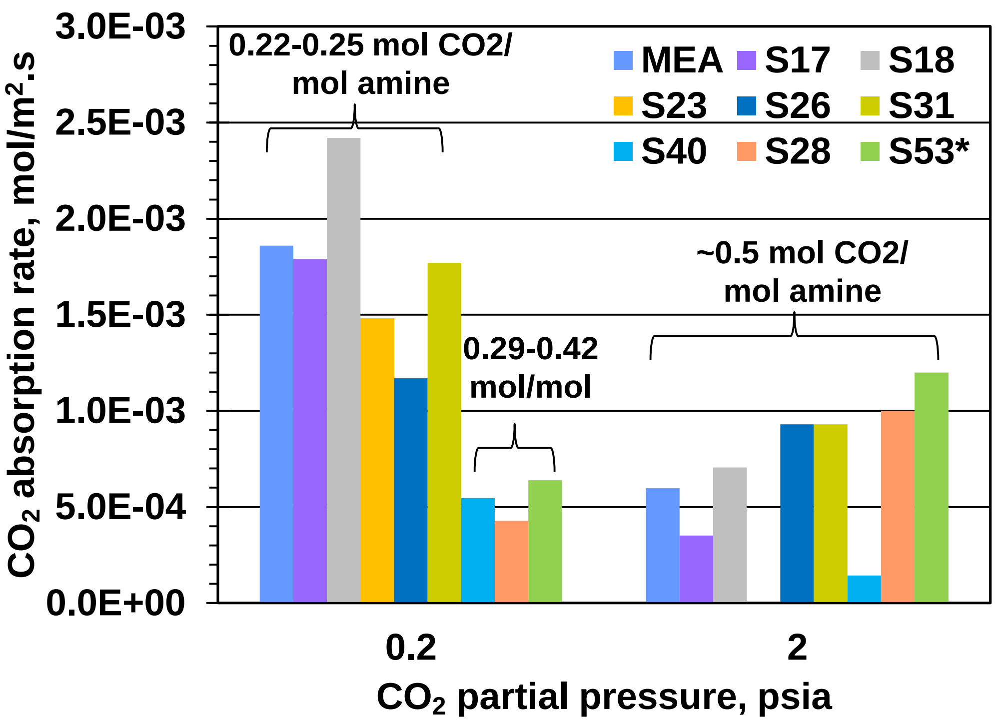


System’s energy change during SMD

Phase separation not favored

- Work done by the system or constraint is a measure of the driving force behind the phase separation process

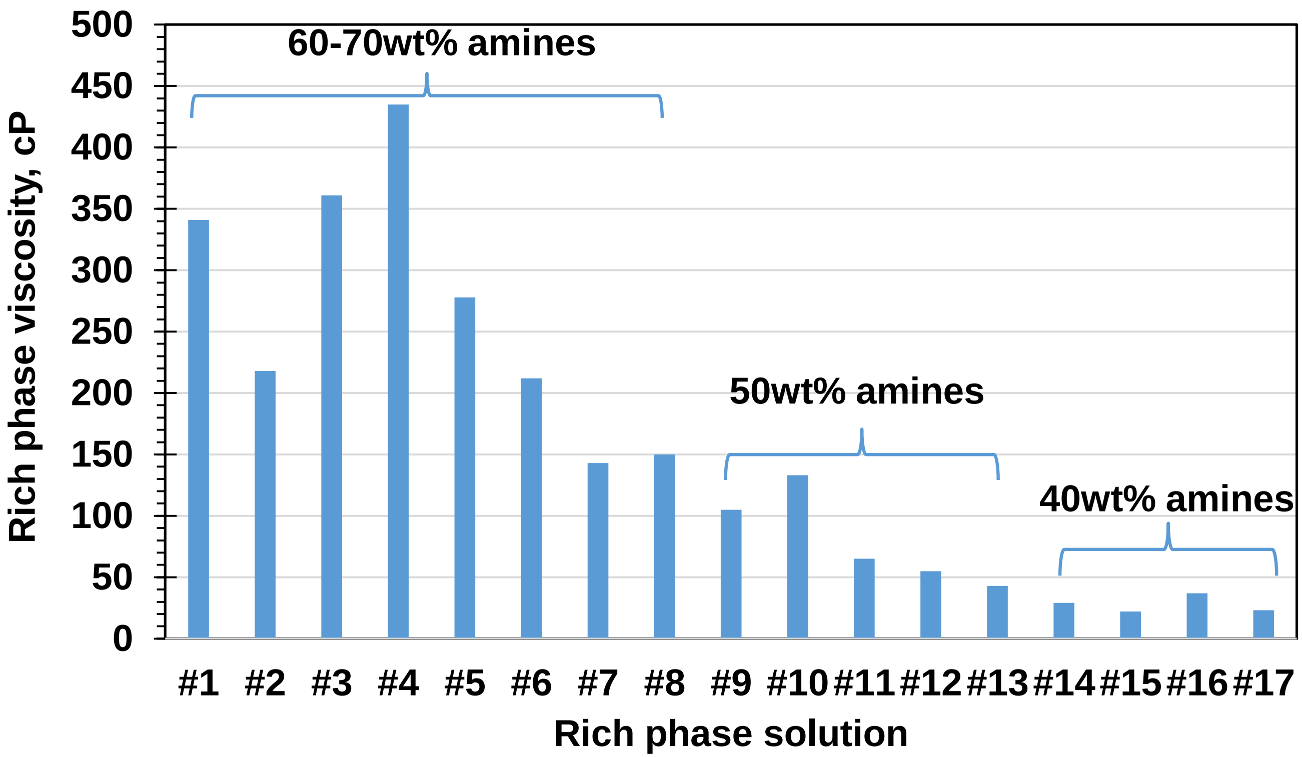
Task 3. Absorption Rate



- Rate tests using both a stirred tank reactor (exemplary results displayed in plot above) and a wetted wall column reactor (work is ongoing)
- Rates tunable by addition of a promoter or selection of a different solubilizer

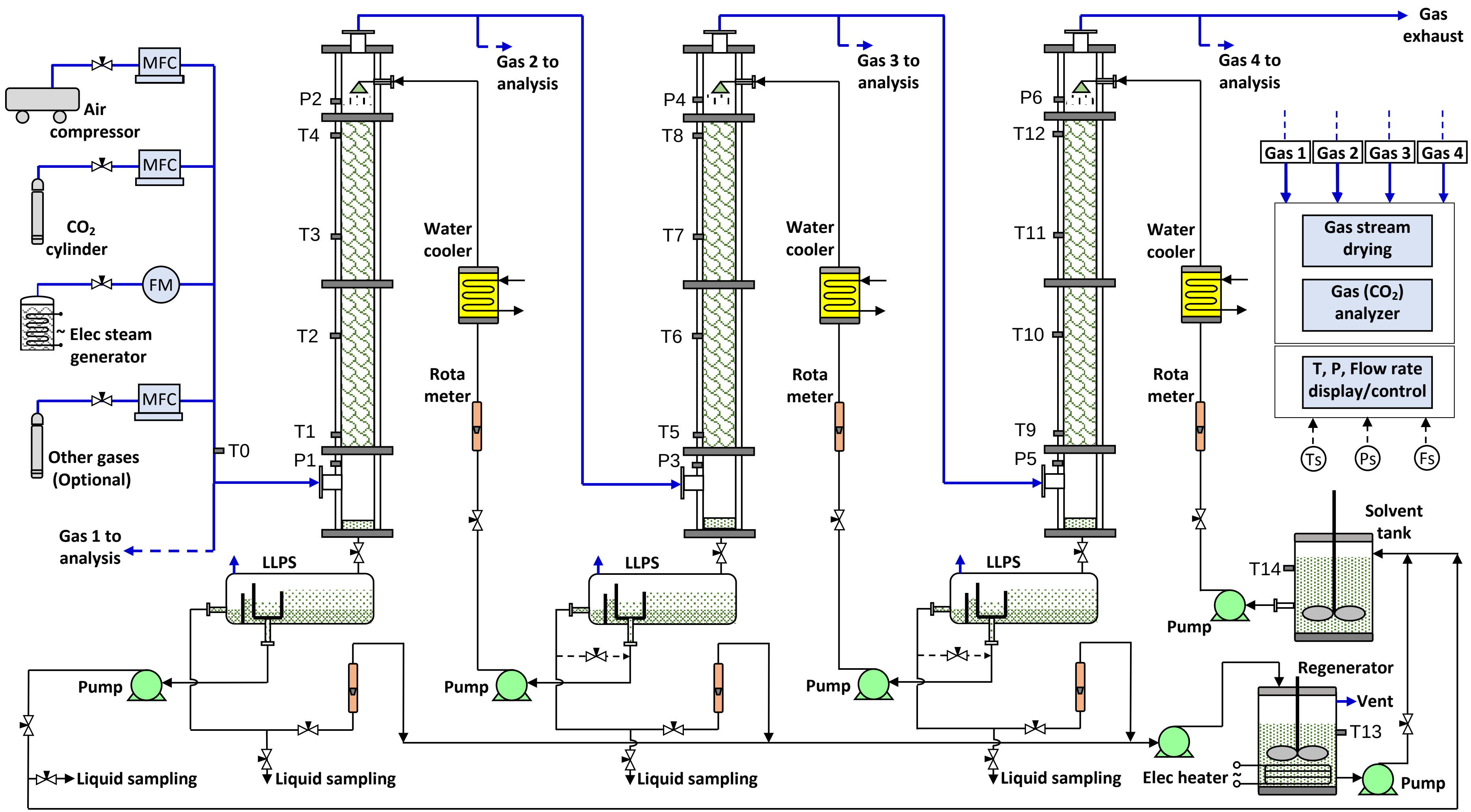
* S18 (S17+promoter) and S31 (solubilizer different from S17)

Task 3. Viscosity Measurement and Optimization



- Lean phase viscosity < 9 cP (data not displayed)
- Rich phase viscosity was successfully decreased from ~400 cP to ~30 cP by optimizing total solvent concentration and selecting suitable amine structures

Task 5. A Lab Absorption System with 3-Stages of Packed Beds and LLPS Vessels Designed and Under Fabrication



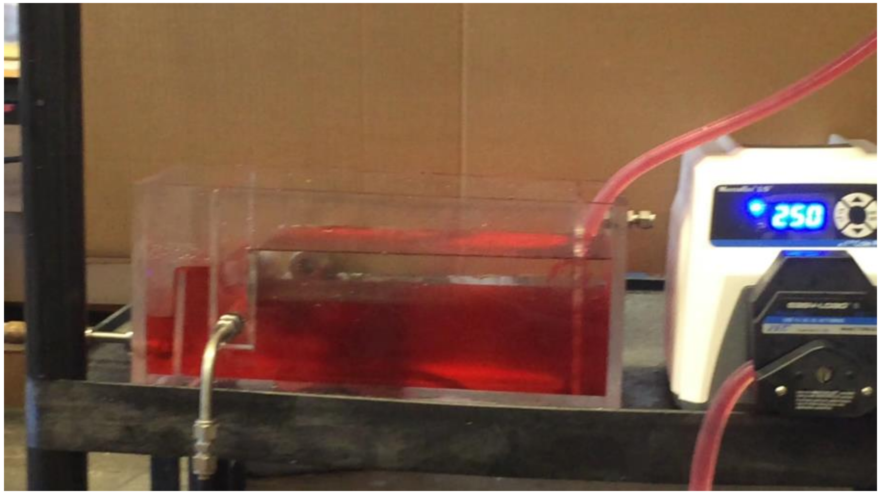
- 3 stages (4-in ID, 7-ft packed-bed for each stage) arranged horizontally to accommodate lab ceiling limit
- 3 stages in one vertical column envisioned for practical use

Lab Prototype Phase Separation Vessel Achieved Efficient and Stable Separation

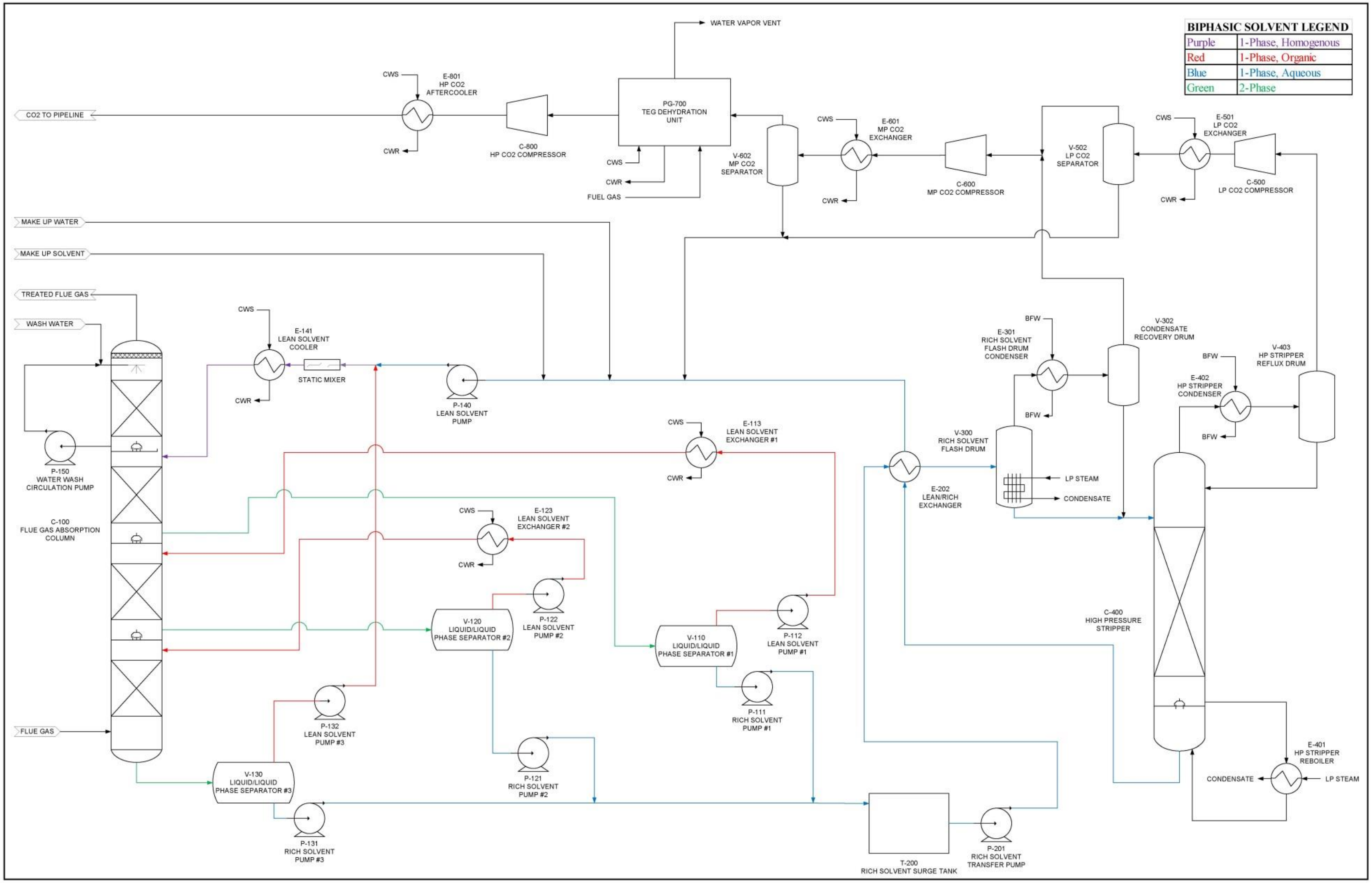
- Phase separation vessel design
  - Based on density difference (lean phase ~0.85 vs. rich phase ~1.1 g/cm^3)
  - Residence time ≤ 5 min (preferred at <1-2 min)

(Liquid volume of 10 L, total volume of 15 L, liquid flow rate of 2 L/min)

- Actual separation performance
  - Separation efficiency better than the design
  - Able to maintain constant levels of both G-L and L-L interfaces
  - Both interface levels adjustable by adjusting their weir heights
  - Very stable operation



Task 6. Preliminary Process Flow Diagram Developed for BiCAP



Work underway to improve process/unit configuration, identify opportunities to minimize equipment items to reduce cost, and assess integration options into a power plant

Future Work Plan in this Project

Biphasic solvent screening (–Q3)

Biphasic solvent characterization (–Q5 & –Q9)

- ❑ VLE data under absorption & desorption conditions
- ❑ Absorption kinetics
- ❑ Solvent properties (ΔHr; viscosity, diffusivity, Cp, density)
- ❑ Thermal & oxidation stabilities
- ❑ Solvent corrosion tendency

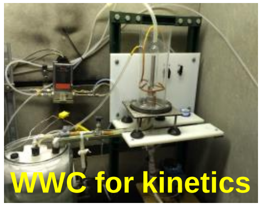
Biphasic solvent-enabled process testing (–Q6 & –Q10)

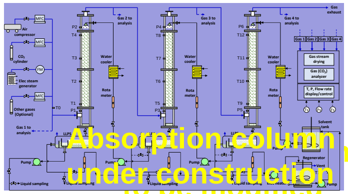
For 2-3 selected solvents:

- ❑ Testing CO_2 absorption and LLPS in a 3-stage packed-bed column
- ❑ Testing CO_2 desorption in a flash + stripping column

Process analysis & TEA study (–Q12)

- ❑ Preliminary process analysis and TEA feasibility study





Next-Stage Technology Development

- Current project is a laboratory development
- If process and TEA feasibility proven in the current project, next stage would be a close-loop bench or small pilot demo with simulated or actual flue gas
  - Rigorous process design and optimization modeling to enhance performance
  - Analysis of technical risks and mitigation for scale-up
  - Identify industrial partners (design, construction, and testing)

Acknowledgements

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- **University of Illinois:**
  - Kevin O'Brien (Co-PI; PhD, Director)
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  - Brajendra K Sharma (PhD, Senior Chemical Engineer)
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  - Joe Pickowitz (Environmental Engineer)
  - Santanu Chaudhuri (PhD, Principal Research Scientist)
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  - Ray McKaskle (Subaward PI; P.E., Senior Chemical engineer)
  - Andrew Sexton (PhD, P.E., Senior Chemical Engineer)
  - Kevin Fisher (VP, P.E., Senior Chemical Engineer)