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
  - Develop new biphasic solvents
  - Demonstrate process concept via lab/bench column testing
  - Generate engineering and scale-up data
  - High-level process and techno-economic analysis (TEA)

- ☐ Project duration
  - BP1: 10/1/15 to 06/30/17 (21 months)
  - BP2: 07/1/17 to 12/31/18 (18 months)

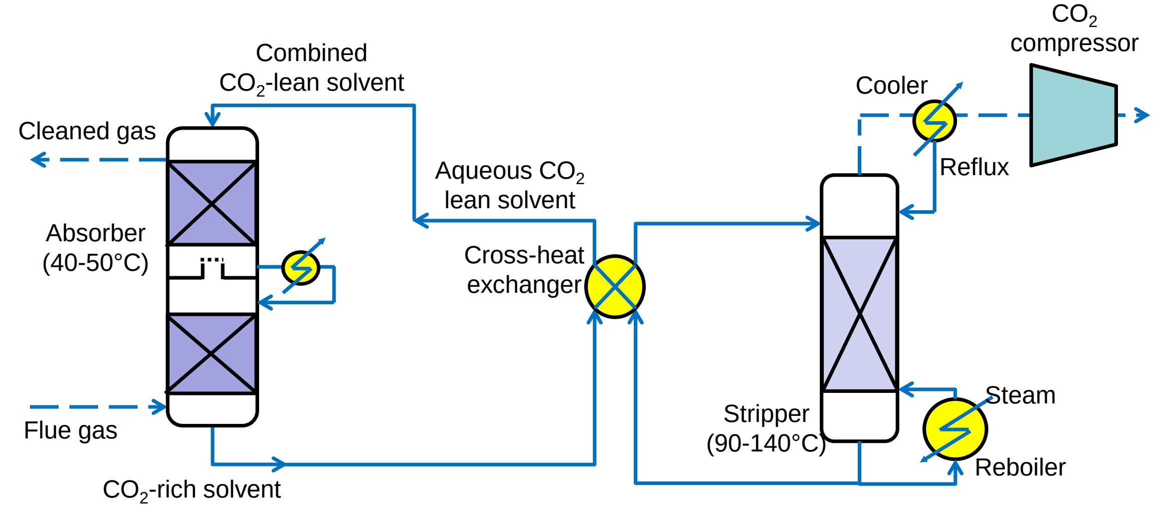
- ☐ Funding profile

DOE funding	**1,999,996**
BP1	1,079,663
BP2	920,333
Recipient cost share	**501,052**
BP1	269,920
BP2	231,132
Total	**2,501,048**

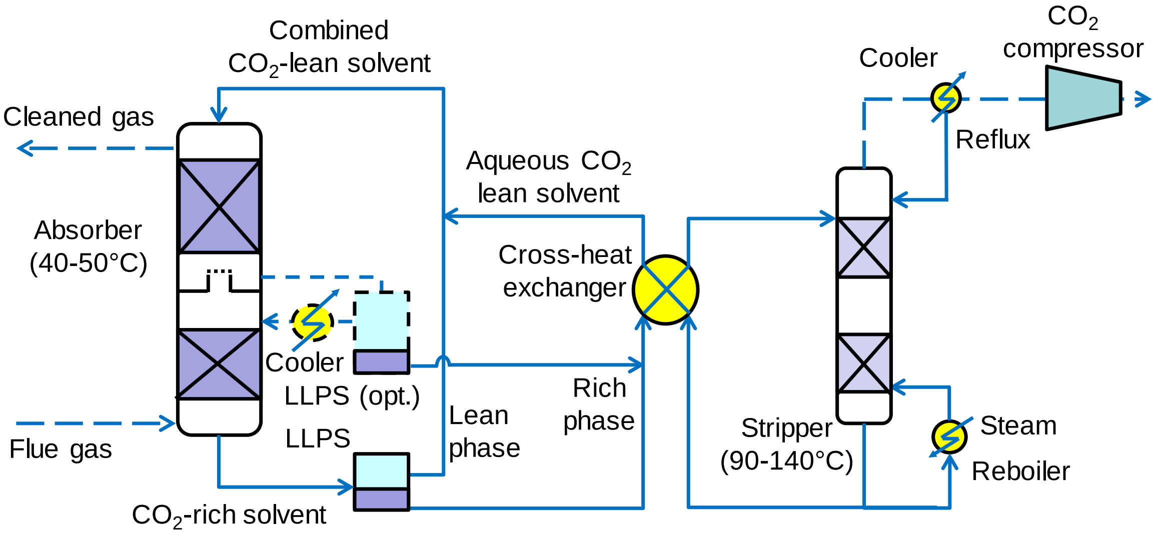
Project Participants

- **University of Illinois**
  - **Illinois State Geological Survey**
    - Solvent development
    - Solvent equilibria, kinetics, and properties measurements
    - Absorption and desorption column testing
    - Process modeling
  - **Illinois Sustainable Technology Center**
    - Assessment of solvent stability and corrosion impacts
  - **Applied Research Institute**
    - Molecular dynamics simulation study for solvent screening
- **Trimeric Corporation**
    - Process feasibility and high-level TEA

Biphasic vs. Conventional Absorption Process



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



Biphasic Absorption Process

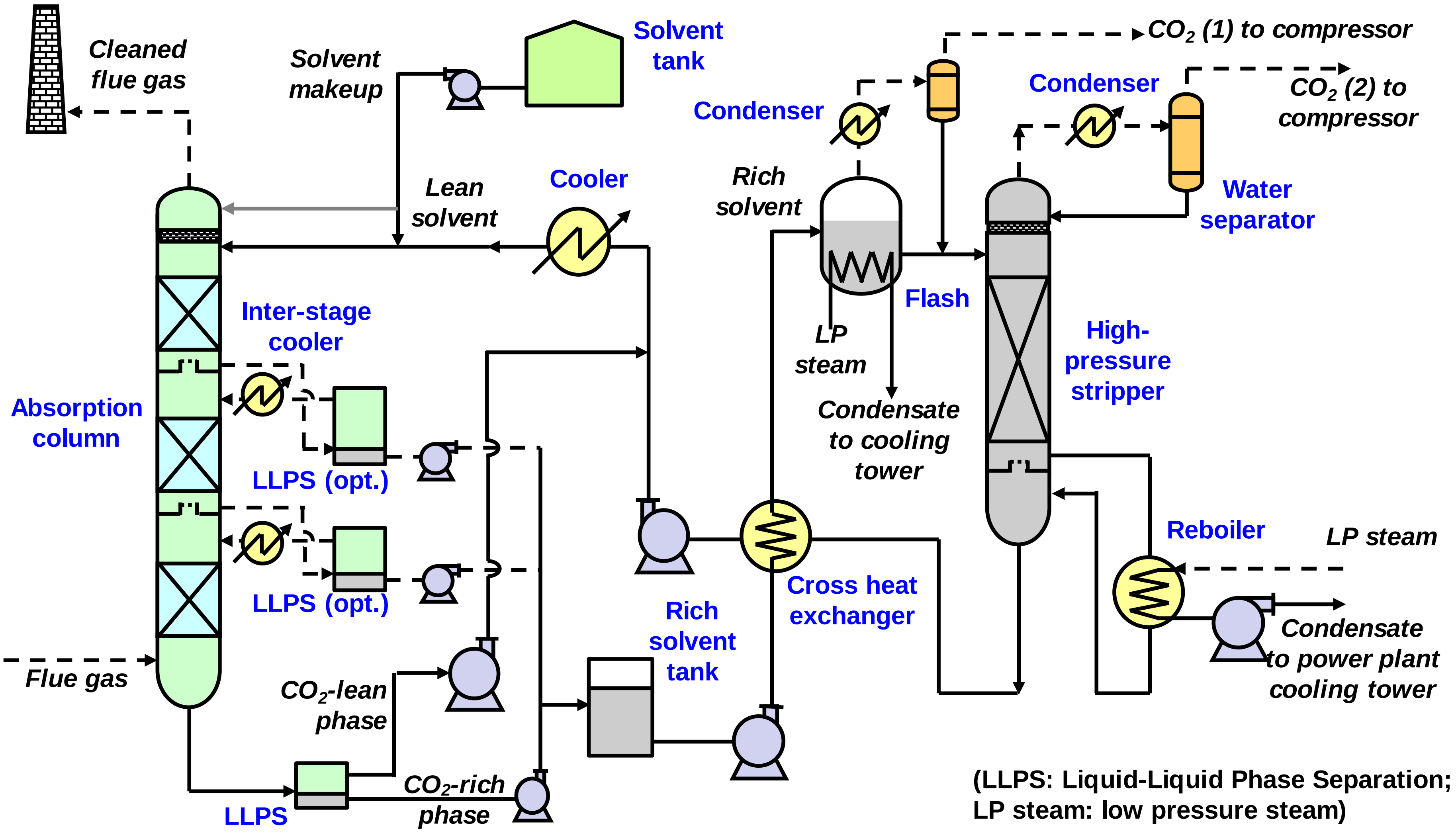
Benefits of biphasic process in stripper:

- Reduced equipment size due to reduced mass of solvent to be regenerated
- Reduced energy use and compression requirement due to reduced mass of solvent, high CO_2 loading, and elevated stripping pressure

Benefits in absorber via phase separation and biphasic solvent development:

- Reduced viscosity with separation of rich, viscous phase improves mass transfer rate and allows use of viscous solvents
- Reduced equipment size

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



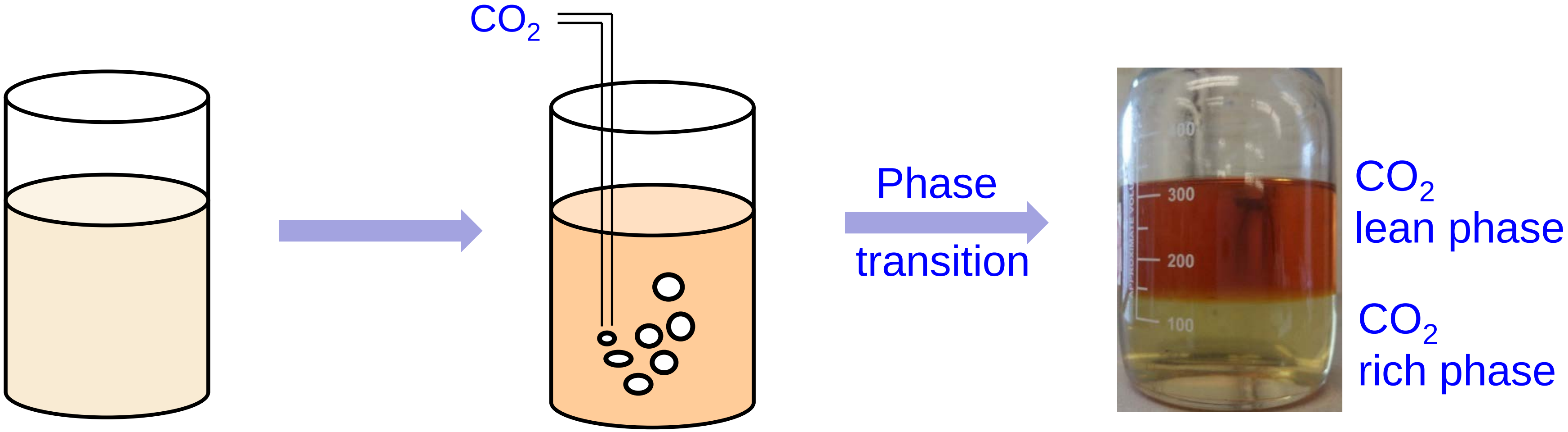
(LLPS: Liquid-Liquid Phase Separation;
LP steam: low pressure steam)

Proposed Biphasic CO_2 Absorption Process (BiCAP)

Novel Biphasic Solvents

Amine-based solvent blends:

- Tunable phase transition behavior with a new group of solvent formulations
- Consider multi-criteria (capacity, rate, CO_2 enrichment %, desorption pressure, stability, corrosion, viscosity, and availability/cost)
- Allow multiple steps of phase separation
- In aqueous form suitable for humid flue gas application



Lean solvent in a single phase

Phase transition induced by CO_2 loading

Two-phase system (w/ tunable phase vol.%)

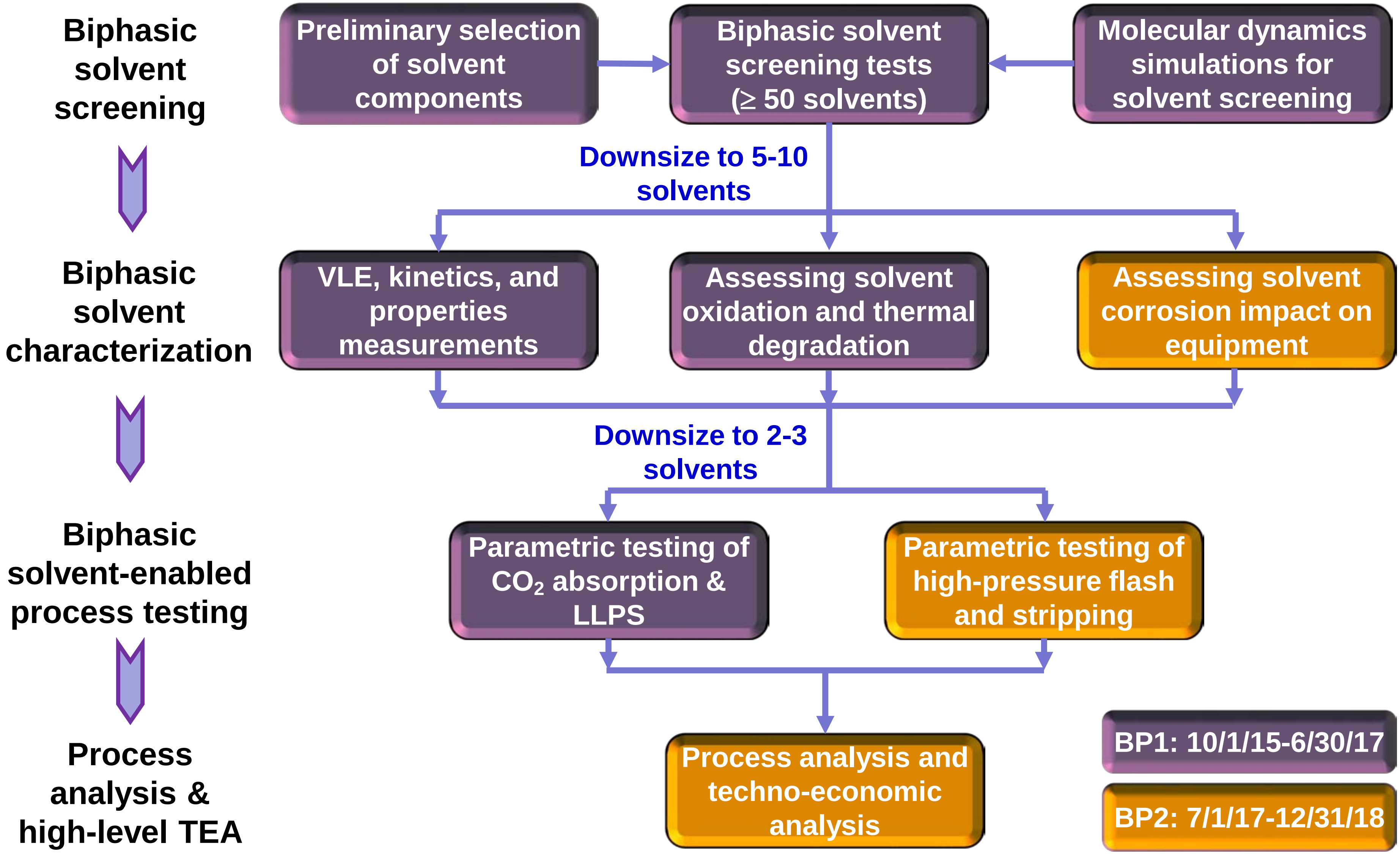
Advantages of BiCAP for Post-Combustion CO_2 Capture

- **BiCAP Solvents:**
  - Phase transition behavior tunable based on a unique solvent formulation (proprietary), allowing for a wider selection of solvent blends
  - Stable with oxygen and at high temperature (e.g., 150 °C)

- **Absorption process:**
  - Multiple phase separators reduce solvent viscosity and CO_2 loading by removing the more viscous rich-phase solvent during absorption, allowing for use of relatively high viscosity solvents

- **Desorption process:**
  - High working capacity due to the absorbed CO_2 enriched in one phase as feed solution to the stripper
  - Reduced mass of solvent for regeneration and elevated CO_2 stripping pressure result in lower heat duty and compression work requirements

Project Work Plan



Biphasic solvent screening

Preliminary selection of solvent components

Biphasic solvent screening tests ($\geq$ 50 solvents)

Molecular dynamics simulations for solvent screening

Downsize to 5-10 solvents

Biphasic solvent characterization

VLE, kinetics, and properties measurements

Assessing solvent oxidation and thermal degradation

Assessing solvent corrosion impact on equipment

Downsize to 2-3 solvents

Biphasic solvent-enabled process testing

Parametric testing of CO_2 absorption & LLPS

Parametric testing of high-pressure flash and stripping

Process analysis & high-level TEA

Process analysis and techno-economic analysis

BP1: 10/1/15-6/30/17

BP2: 7/1/17-12/31/18

BP1 Planned Tasks Completed on Schedule

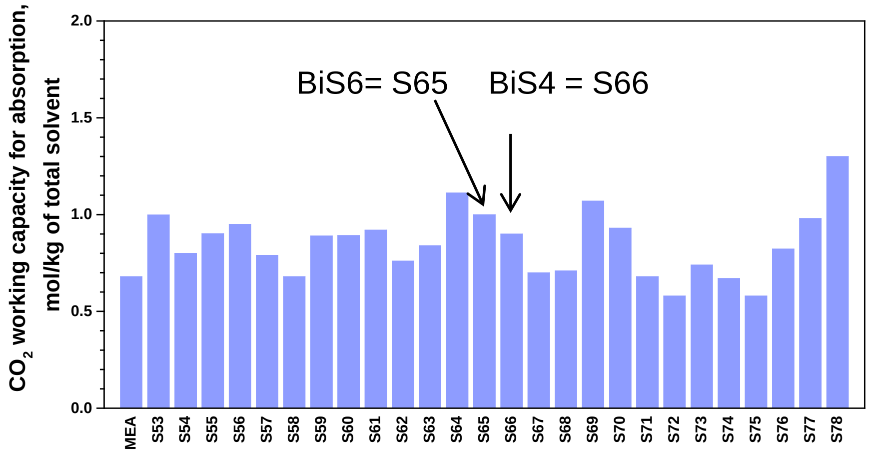
Project Tasks	Progress to date
Task 1. Project planning & management	
2. Screening & characterization of biphasic solvents (~50 solvents) • Screening on CO_2 absorption & phase transition Screening on CO_2 desorption pressure • Molecular dynamics simulation studies	Complete (>80 formulations evaluated)
3. Phase equilibria, absorption kinetics, and solvent properties (5-10 solvents) • VLE measurement • Absorption kinetics measurement • Solvent properties measurement	Complete (VLE for 10 solvents; kinetics for 6 solvents; viscosity/density for ~80 solvents, heat capacity for 11 solvents; heat of absorption for 10 solvents)
4. Determining thermal & oxidation stabilities of solvents (5-10 solvents) • Oxidation stability • Thermal stability	Complete (Oxidation stability tests for 6 solvents for 2 weeks; thermal stability tests at 120-150 °C for 10 solvents for ~8 weeks)
5. Testing CO_2 absorption & phase separation in a multi-stage packed-bed column (2-3 solvents) • Fabrication of experimental system • Parametric testing	Complete (Tested 2 selected biphasic solvents)
6. Development of a process sheet and preliminary techno-economic analysis • Conceptual process flow sheets • Preliminary techno-economic analysis	Complete (Flow sheets developed and preliminary TEA completed)

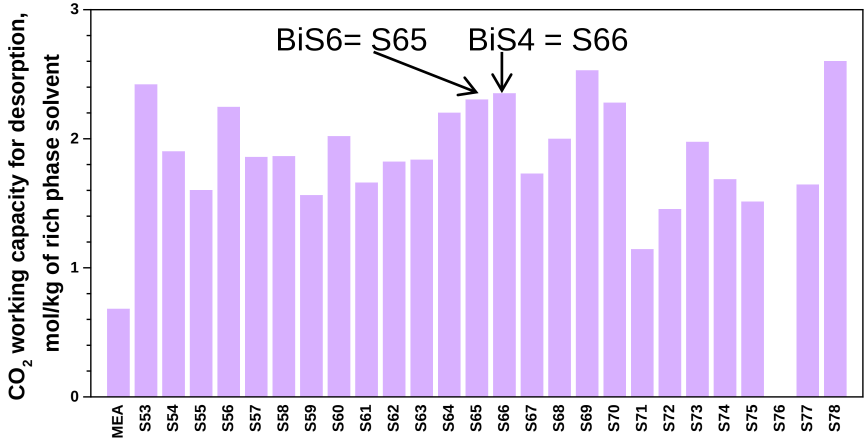
All BP1 Milestones (7) and Success Criteria (3) Succeeded

- 3 technical Success Criteria for BP1:

BP1: 10/1/15 – 6/30/17 (by Q7):
Identify 2-3 top-performing solvents (based on phase transition and 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-phase separations: CO_2 capacity and kinetics ≥ 5 M MEA; Each LLPS stage ≤ 5 min residence time; ≥ 80% CO_2 enrichment in the rich liquid phase
Demonstrate reliable operability of the multi-stage absorption & phase separation configuration during lab-scale testing

Task 2: Solvent Screening





Working capacity of biphasic solvents:

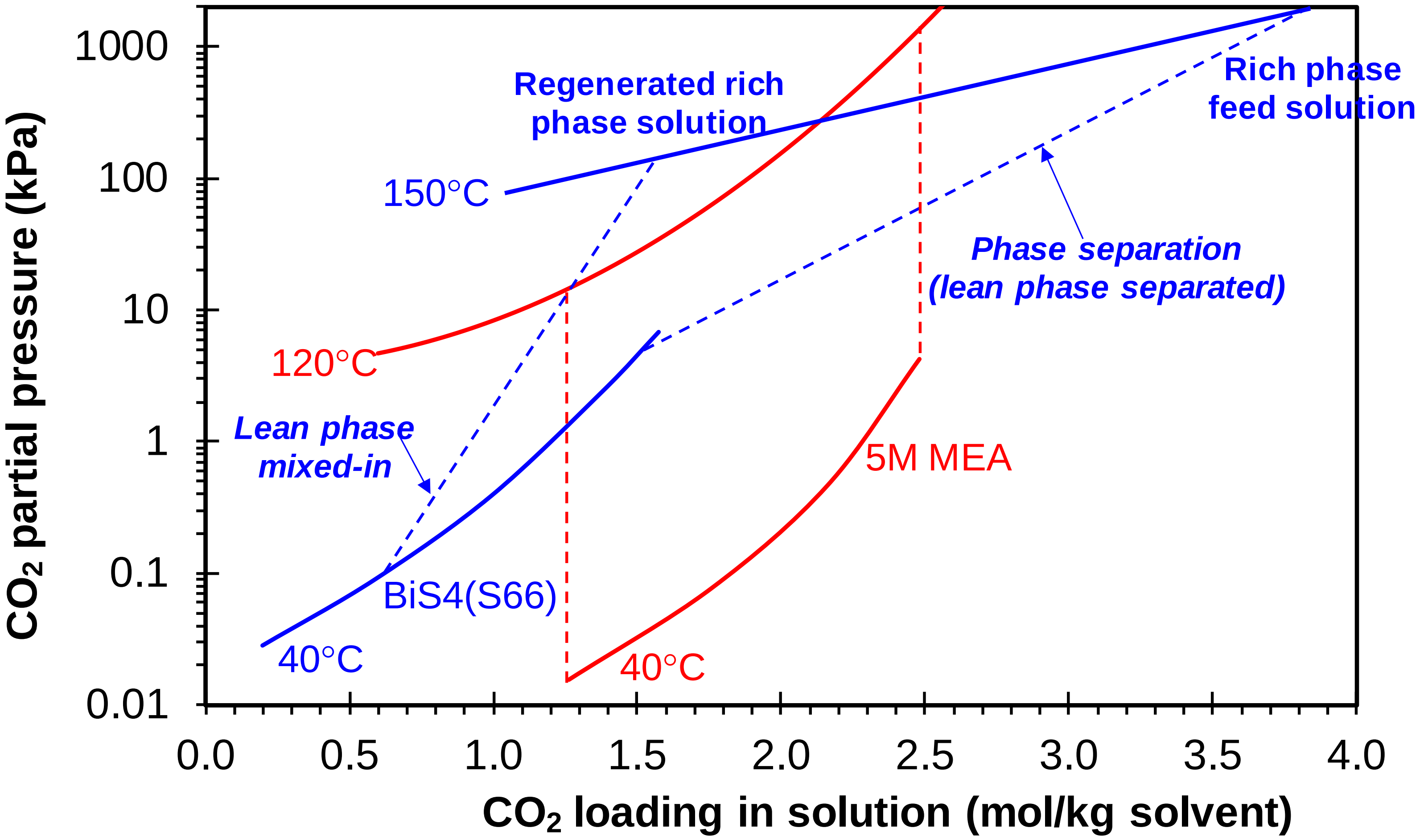
- ❑ Phase separation ***decouples*** the <u>absorption</u> and <u>desorption</u> steps, resulting in their different solvent working capacities[1)]
- ❑ For comparison purposes, assuming lean and rich CO_2 loadings equivalent to 0.1 and 5 kPa CO_2 equilibrium pressures at 40°C:
  - ➢ Absorption working capacity: ≥ MEA[2,3)]
  - ➢ Desorption working capacity: 2-4 times > MEA[2,3)]
- ❑ ~98% of absorbed CO_2 concentrated in rich phase liquid for most solvents

Notes:

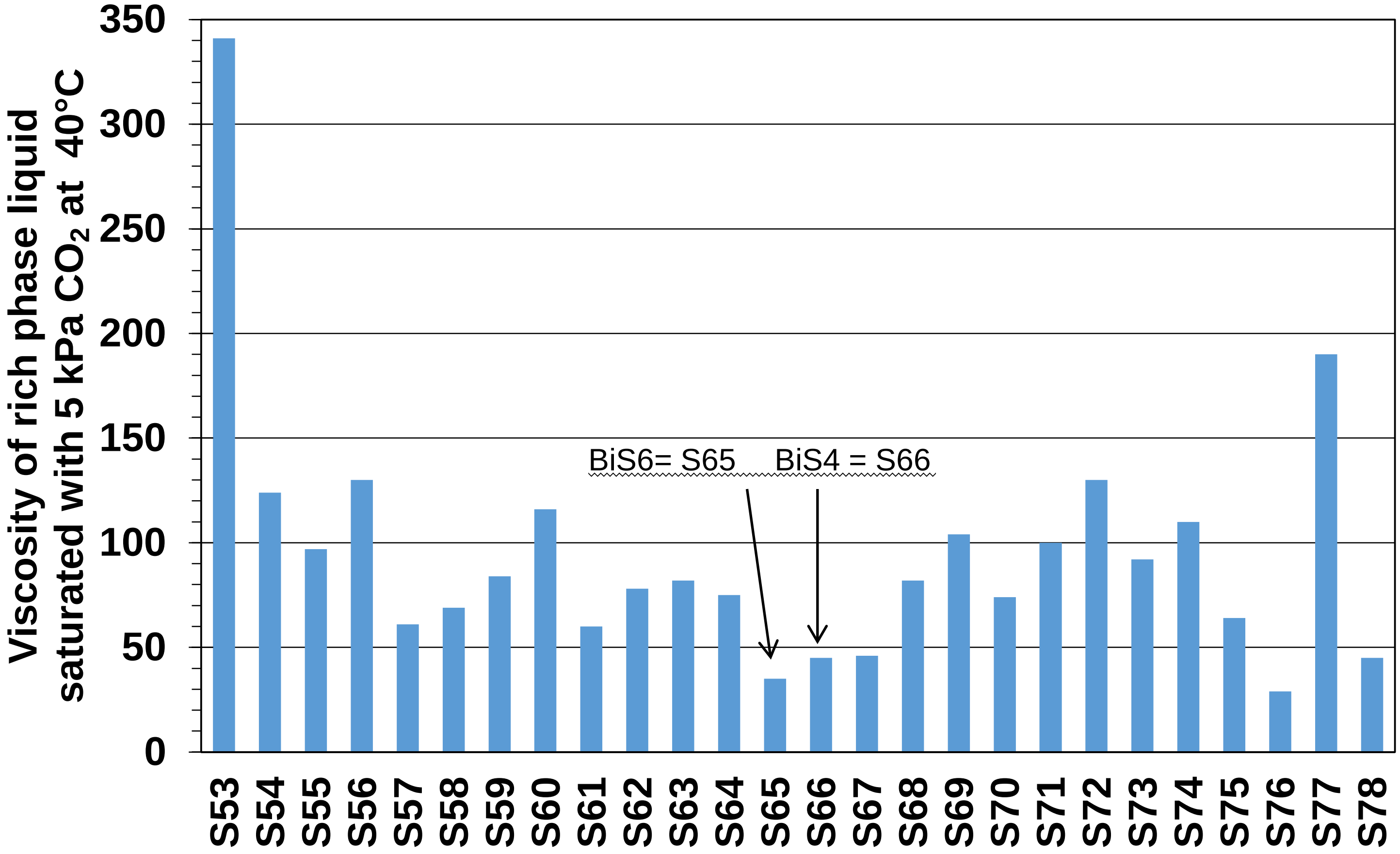
1) CO_2 working capacity for absorption: difference between CO_2 loadings at absorber top and bottom;
   CO_2 working capacity for desorption - difference between CO_2 loadings at desorber top and bottom)
2) Working capacity is estimated based on maintaining lean and rich CO_2 loadings equiv. to 0.1 and 5 kPa CO_2 equilibrium pressures at 40 °C at the top and bottom of absorber or stripper
3) CO_2 working capacity for 5M MEA equiv. to 0.1 and 5 kPa CO_2 equilibrium pressures at 40 °C is estimated at 0.68 mol/kg. Practical MEA lean loading is lower (<0.1 kPa CO_2) and its practical working capacity amounts to 1-1.25 mol/kg

Task 3: Phase Equilibria, Absorption Kinetics & Solvent Properties: VLE Measurements

- VLE data measured under both absorption conditions (30–50 °C) and desorption conditions (100-160 °C)



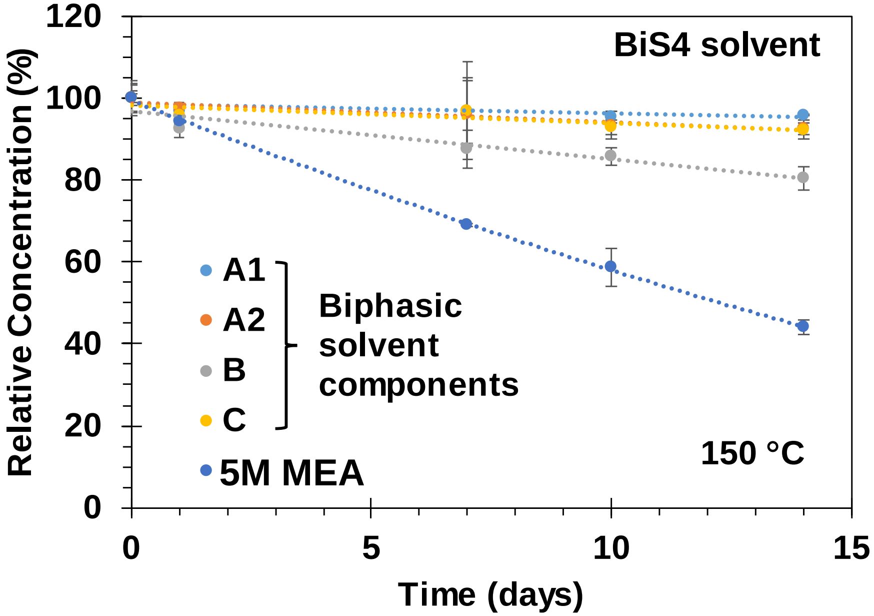
Viscosity Optimization and Reduction



- ☐ Most recent solvents have viscosity of CO_2-saturated rich-phase solution <100 cP at 40°C (< 50 cP solvents selected for further testing)
- ☐ Lean phase viscosity < 9 cP (data not displayed)

Task 4. Stability of Biphasic Solvents: Thermal Stability

- Thermal degradation tested (1) at 150 °C for 2 weeks and (2) at 120 and 135 °C for 8 weeks

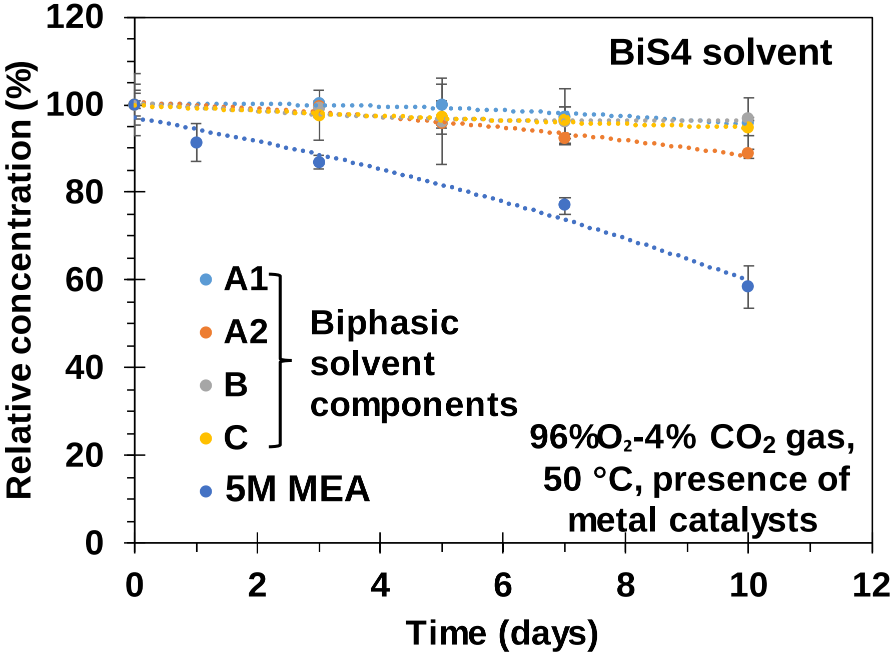


BiS4 solvent (S66, saturated in 5 kPa CO_2) as an example:

- Stability of BiS4 after 2 weeks at 150 °C
  - 4 - 19% of BiS4 components degraded vs. 56% MEA loss at 150 °C
  - <u>Stability of BiS4 at 150 °C similar to 5M MEA at 120 °C</u>
- Degradation at 120 and 130 °C for 8 weeks (not shown in figure) revealed a slower but otherwise similar trend to 150 °C

Biphasic Solvent Oxidative Stability

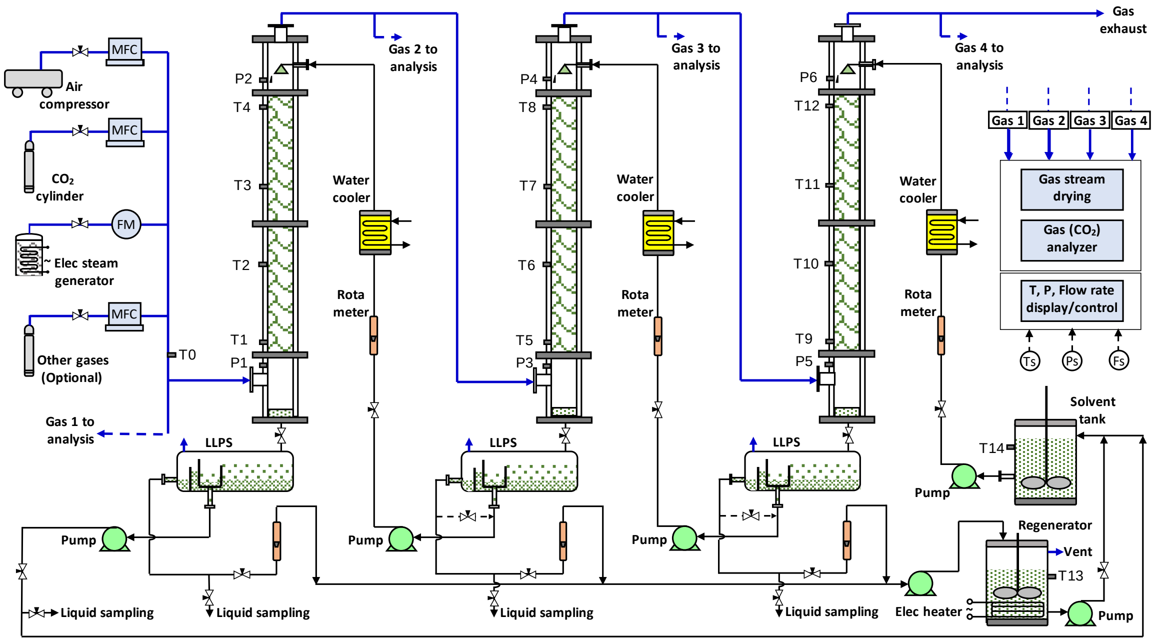
- ❑ Oxidative degradation tested (1) in 96% O_2-4% CO_2 gas (rich loading) and (2) in 96% O_2-400 ppm CO_2 gas (lean loading) in presence of metal catalysts for 10 days at 50 °C



BiS4 solvent (S66) in 96% O_2-4% CO_2 gas mixture as an example:

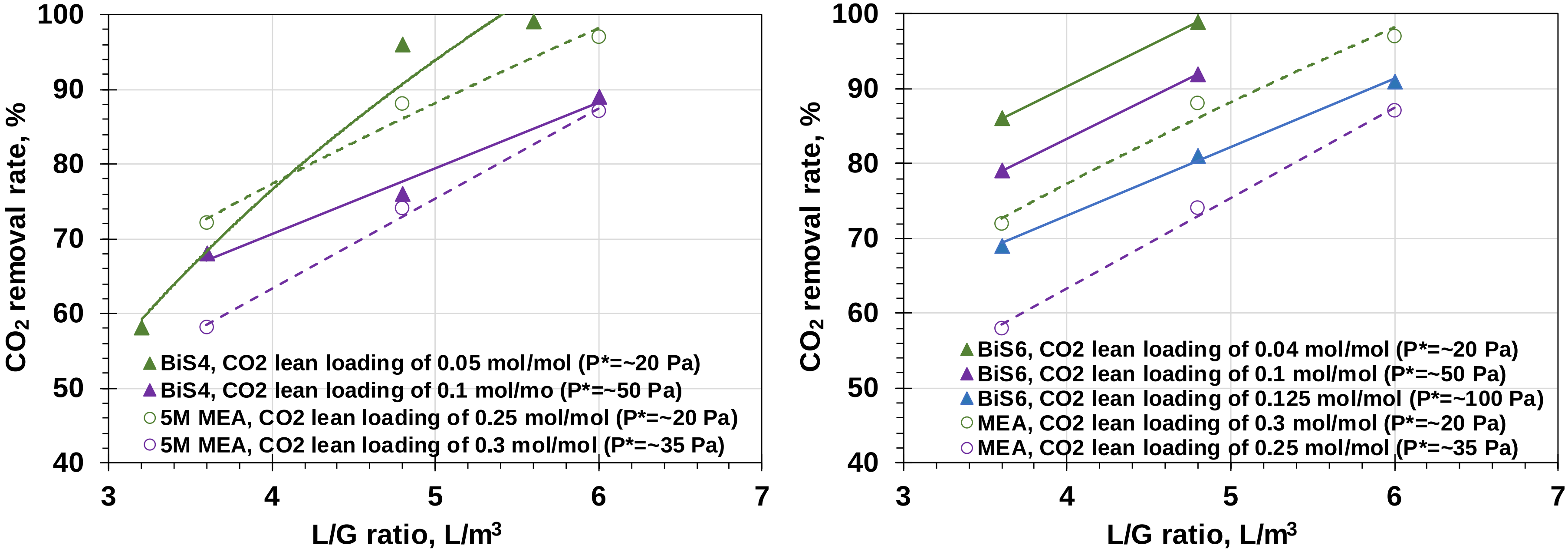
- ❑ <11% solvent components degraded after 10 days at 50 °C vs. 41% MEA loss <u>(Oxidation rate is <27% of MEA)</u>

Task 5. Laboratory Absorption System with 3-Stages of Packed Beds and LLPS Vessels Fabricated and Tested



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

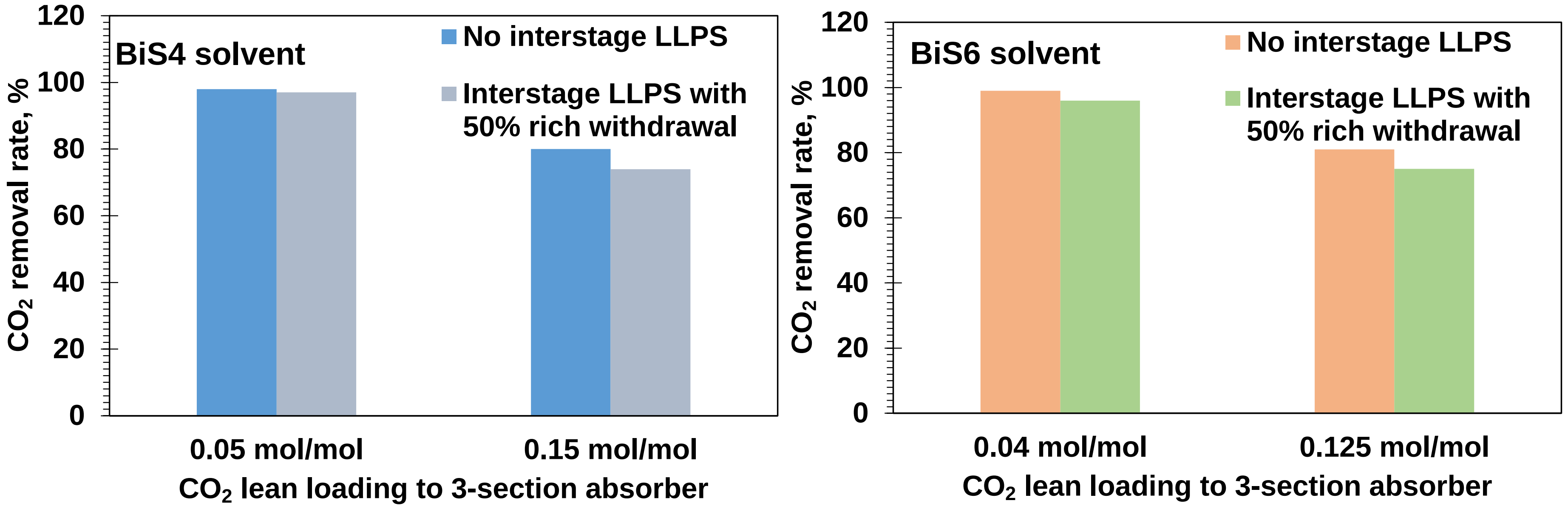
Column Testing of 2 Selected BiCAP Solvents



(3-stages of CO_2 absorption tests with 13 vol.% CO_2 in air at 35 - 40°C)

- CO_2 removal rate and loading capacity in the absorption step for the 2 selected solvents (BiS4 and BiS6) exceeded or comparable to 5M MEA under the same L/G and comparable CO_2 lean loading (i.e., corresponding to the same equilibrium P^*_{CO2} at 40°C)

Effect of Inter-Stage Rich Phase Withdrawal

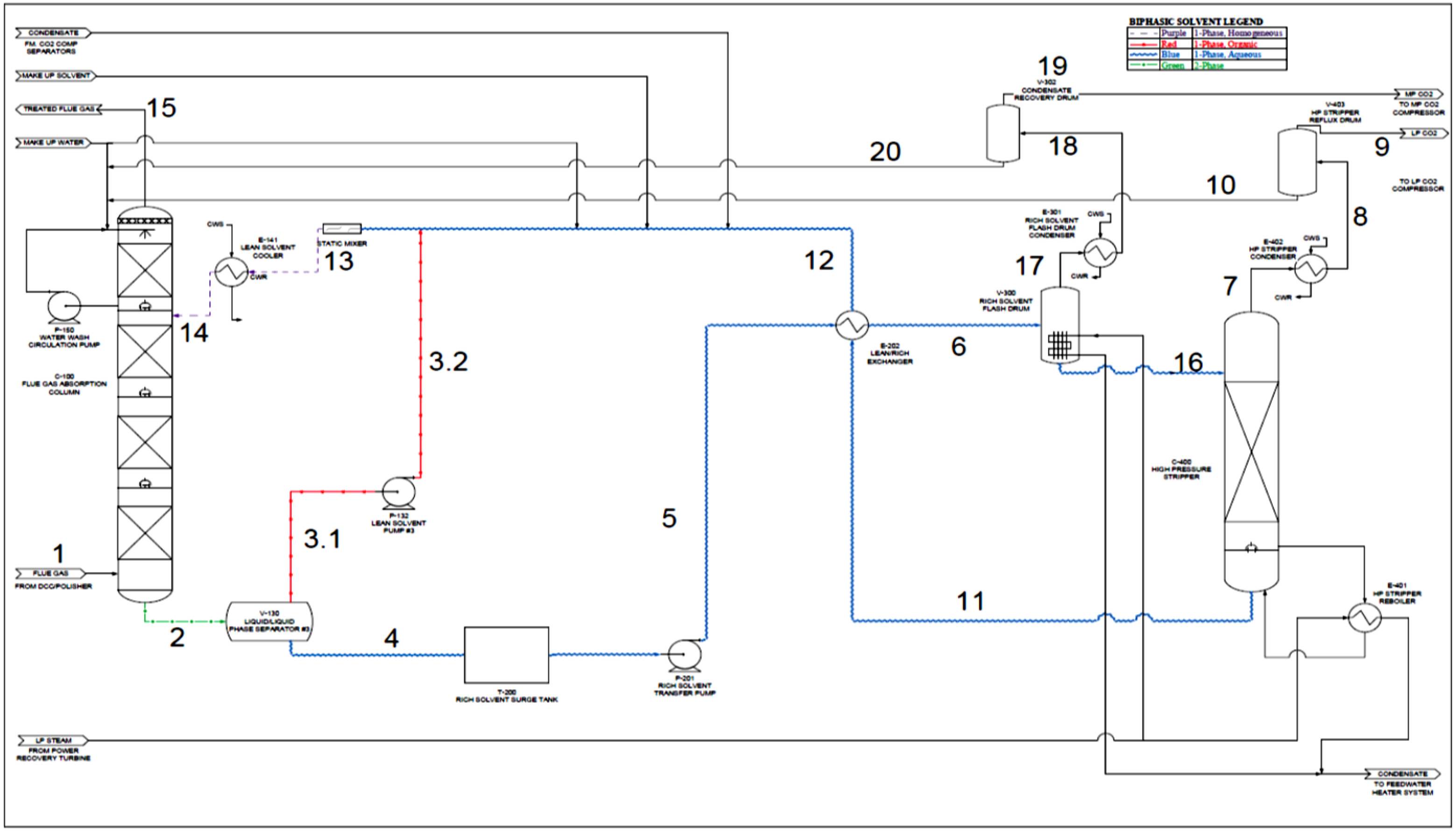


(CO_2 absorption tests at L/G=4.8 L/m^3, 13.6 vol.% CO_2 in air, and 35 – 40 °C)

- Slightly higher CO_2 removal rate achieved with 1-stage LLPS compared to 3-stage LLPS
- Viscosity of CO_2-saturated rich phase solvent is 45 cP for BiS4 and 35 cP for BiS6; Inter-stage rich phase withdrawal expected to perform better for higher viscosity solvents (e.g., >100 cP)

Task 6. Preliminary Process Analysis

- Aspen Plus model developed by ISGS to simulate BICAP process and generate mass and energy balance data
- Preliminary Process Analysis conducted by Trimeric for a 550 MWe (net) power plant integrated with BiCAP process



Preliminary Estimation of Derating & Parasitic Power Use

		BiCAP	DOE Case 12
Gross Generating Capacity	**MWe**	**726**	**802**
Total Steam Derate	**MWe**	**103**	**139**
Reboiler/Flash Heat Duty	MWth	369	542
Thermal to Electric Energy	MW_e/MW_{th}	0.256	0.256
Power Value of Steam	MWe	95	139
Penalty/Power Recovery	MWe	7.6	N/A
Direct Electrical Derate	**MWe**	**39.1**	**75.2**
Compression Duty	MWe	25.8	44.9
Other (Pumps, Fans, etc.)	MWe	13.3	30.3
Total Derate for CO_2 Capture	**MWe**	**142**	**214**
Total parasitic use for entire plant	**MWe**	**176**	**252**
Net Electricity Produced	**MWe**	**550**	**550**

- ❑ Capture parasitic power use: 20% of gross output (142/726) for BiCAP process vs. 27% (214/802) in DOE Case 12
- ❑ Total derate for CO_2 capture with BiCAP is 34% lower than Case 12

Preliminary Economic Comparison: BiCAP vs. DOE Case 12

2007$ (x1,000$)	BiCAP	DOE Case 12 [2]	Difference vs. Case 12
Total Plant Cost	**$1,130,000**	**$1,600,000**	**-29%**
CO_2 Capture and Compression	$378,000	$469,000	-19%
Total Fixed Operating Costs	**$39,900**	**$53,200**	**-25%**
Total Variable Operating Costs	**$30,300**	**$35,700**	**-15%**
Solvent Make-Up Costs Due to Degradation	$2,061	$1,017	103%
Total Fuel Costs	**$72,800**	**$80,400**	**-10%**
Coal Flowrate (lb/hr)	512,000	566,000	-10%
COE[1] (mills/kWh, 2007$)	**83**	**107**	**-22%**
Cost of CO_2 Captured[1] ($/tonne, 2007$)	**$28**	**$49**	**-43%**
Cost of CO_2 Avoided[1] ($/tonne, 2007$)	**$35**	**$70**	**-50%**

[1] Includes Transportation, Storage, and Monitoring;

[2] DOE/NETL-2010/1397, Revision 2, Nov. 2010; Revision 2a, Sep. 2013

- Compared with DOE Case 12, BiCAP process can achieve:
  - 22% reduction in COE~~;~~
  - 43% reduction in cost of CO_2 captured
  - 50% reduction in cost of CO_2 avoided

Future Work Plan for This Project

Parametric testing of high-pressure flash and stripping (by 6/30/18)

- **Task 7. Testing CO_2 desorption in a high pressure flash and stripping column (2 - 3 solvents)**
  - Fabrication of a flash and stripper system
  - Parametric testing of CO_2 flash and stripping
  - Modeling of CO_2 flash and stripping

Assessing solvent corrosion impact on equipment (by 3/31/18)

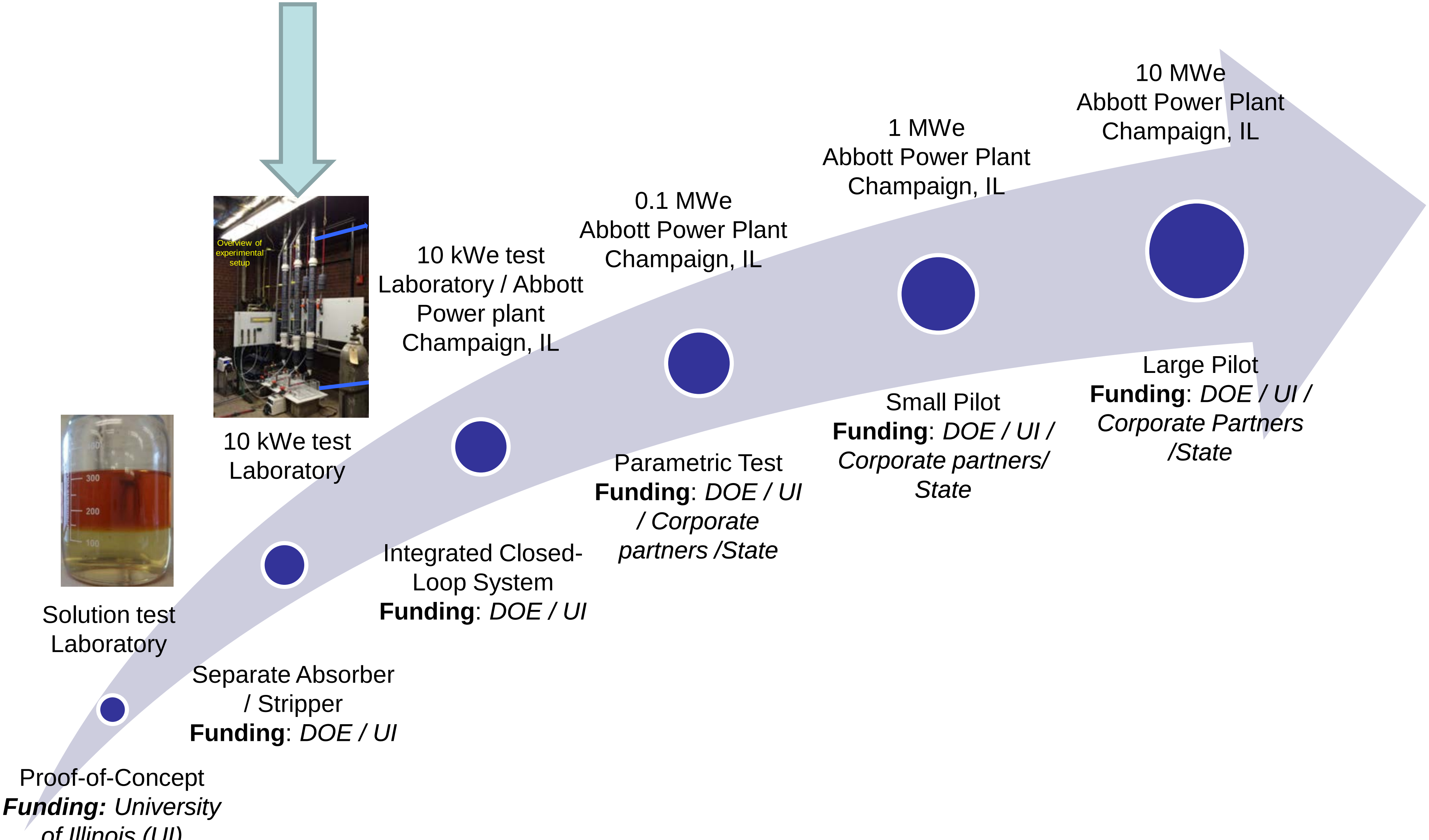
- **Task 8. Assessing the impact of solvent on equipment corrosion (2 - 3 solvents)**
  - Under absorption conditions
  - Under desorption conditions

Process analysis and techno-economic analysis (by 12/31/18)

- **Task 9. Final Techno-Economic Analysis**
  - Updated process simulation and mass and energy balance calculations
  - High-level cost and sensitivity analysis

BiCAP Technology Development Vision

Currently



Solution test Laboratory

Proof-of-Concept
***Funding:** University of Illinois (UI)*

10 kWe test Laboratory

Separate Absorber / Stripper
Funding: *DOE / UI*

10 kWe test Laboratory / Abbott Power plant Champaign, IL

Integrated Closed-Loop System
Funding: *DOE / UI*

0.1 MWe
Abbott Power Plant
Champaign, IL

Parametric Test
Funding: *DOE / UI / Corporate partners /State*

1 MWe
Abbott Power Plant
Champaign, IL

Small Pilot
Funding: *DOE / UI / Corporate partners/ State*

10 MWe
Abbott Power Plant
Champaign, IL

Large Pilot
Funding: *DOE / UI / Corporate Partners /State*

Summaries

Biphasic Solvents

- ☐ Phase transition behavior tunable with unique solvent formulation
- ☐ Working capacity for CO_2 desorption: >2 times > MEA process
- ☐ Desorption pressure: 3-4 times > MEA process
- ☐ Stable with O_2 and at high temperature
- ☐ Acceptable viscosity of CO_2-loaded rich-phase solvent (≤ 50 cP)

BiCAP Process

- ☐ Reduces total parasitic power use for CO_2 capture by 34% compared with DOE Case 12
- ☐ Reduces COE by 22% and cost of CO_2 capture by 43% compared with DOE Case 12

Thank you!

Questions / Comments?