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

Project Kickoff Meeting

University of Illinois at Urbana-Champaign

Trimeric Corporation

Pittsburgh PA • December 11, 2015

Acknowledgements

- This project is supported by the U.S. Department of Energy / National Energy Technology Laboratory (DOE/NETL) through Cooperative Agreement No. DE-FE0026434

- DOE/NETL Project Manager: Andrew Jones

Project Team and Key Personnel

- University of Illinois:
  - Brajendra K Sharma (PhD, Senior Chemical Engineer)
  - David Ruhter (MS, Lab Manager)
  - Hong Lu (PhD, Chemical/Environmental Engineer)
  - Joseph Pickowitz (Environmental Engineer)
  - Kevin O'Brien (PhD, Director)
  - Qing Ye (PhD Student)
  - Santanu Chaudhuri (PhD, Principal Research Scientist)
  - Shihan Zhang (PhD, Chemical/Environmental Engineer)
  - Viktoriya Gomilko (MS, Assistant Research Chemist)
  - Wei Zheng (PhD, Senior Chemist)
  - Yongqi Lu (PhD, Chemical/Environmental Engineer)

- Trimeric Corporation:
  - Andrew Sexton (PhD, P.E., Senior Chemical Engineer)
  - Austyn Douglas (Chemical Engineer)
  - Kevin Fisher (VP, P.E., Senior Chemical Engineer)
  - Ray McKaskle (P.E., Senior Chemical engineer)

Objectives

- Overall goal
  - Demonstrate technical advantages of a novel biphasic CO_2 absorption process (BiCAP) and generate engineering and scale-up data for scale up

- Specific objectives
  - Developing new biphasic solvents with desired properties
  - Generating thermodynamic and reaction engineering data
  - Demonstrating CO_2 absorption coupled with multiple stages of liquid-liquid phase separation (LLPS)
  - Demonstrating high-pressure CO_2 desorption
  - Assessing techno-economic performance

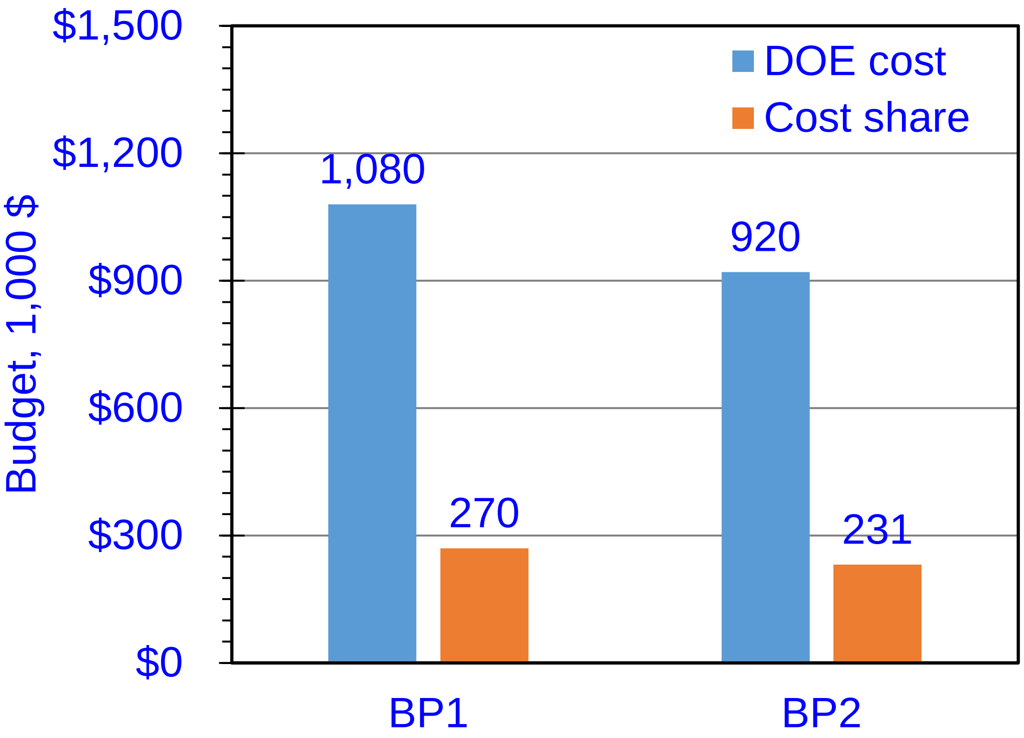
Project Budget and Duration

Project duration: 10/1/15 – 9/30/18 (36 months)

- BP1: 10/1/15 – 3/31/17 (18 months)
- BP2: 04/1/17 – 9/30/18 (18 months)

	Budget, $
DOE funding	1,999,996
UIUC	1,849,996
Trimeric	150,000
Cost share	501,052
UIUC (cash & in kind)	501,052
Total	2,501,048

(Cost share is ~20%)



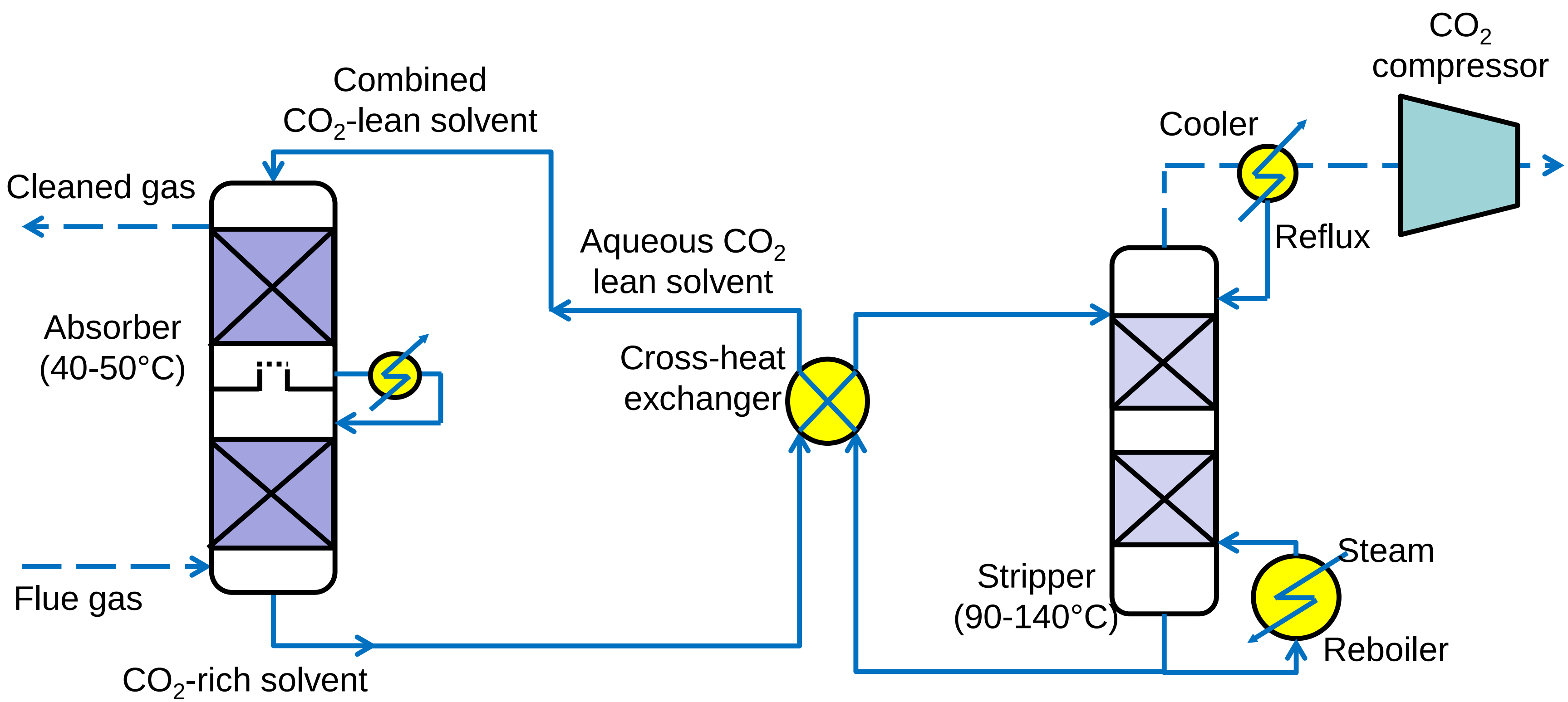
Technology Background

Project Work Flow and Organization

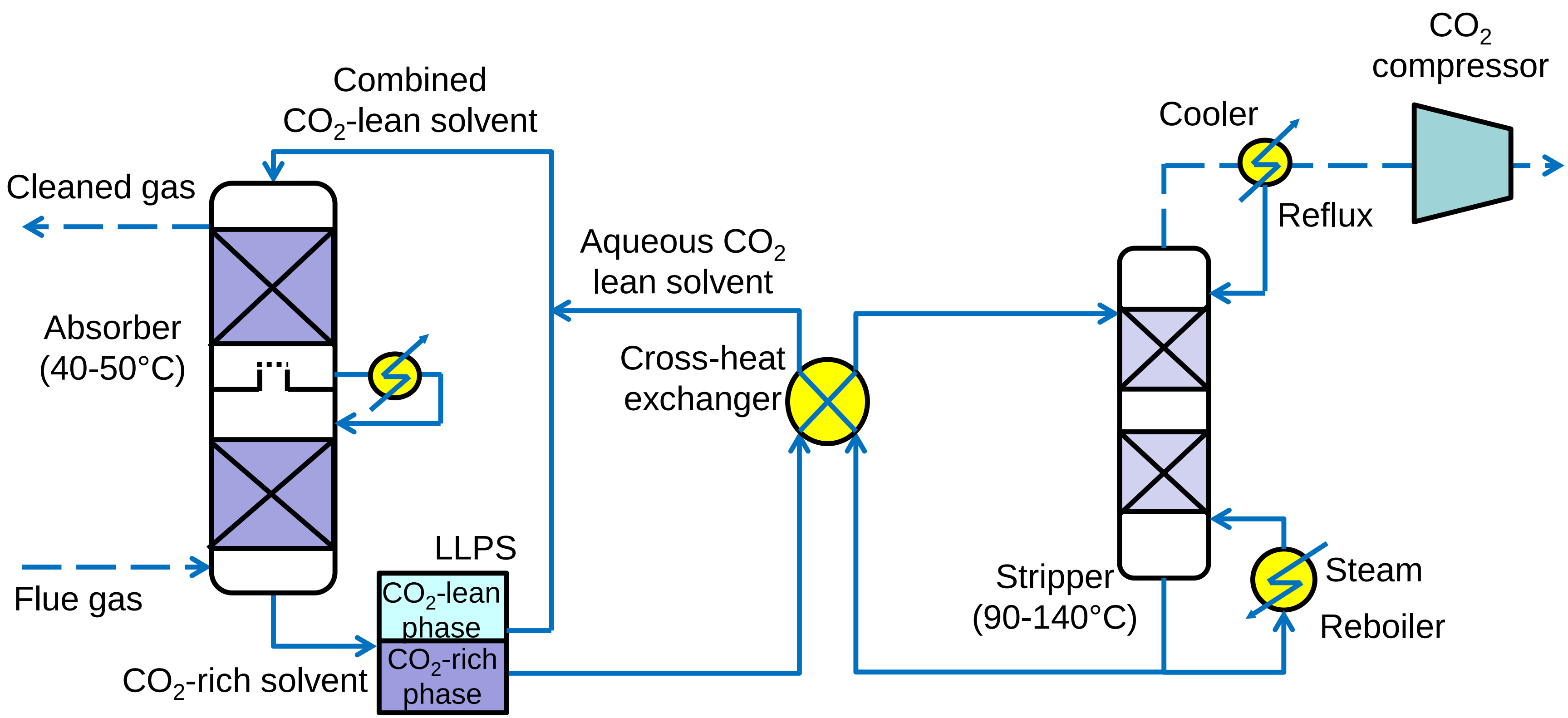
Scope of Work and Approach

Timeline, Milestones and Deliverables

Conventional Monophasic CO_2 Absorption Processes (e.g., MEA)



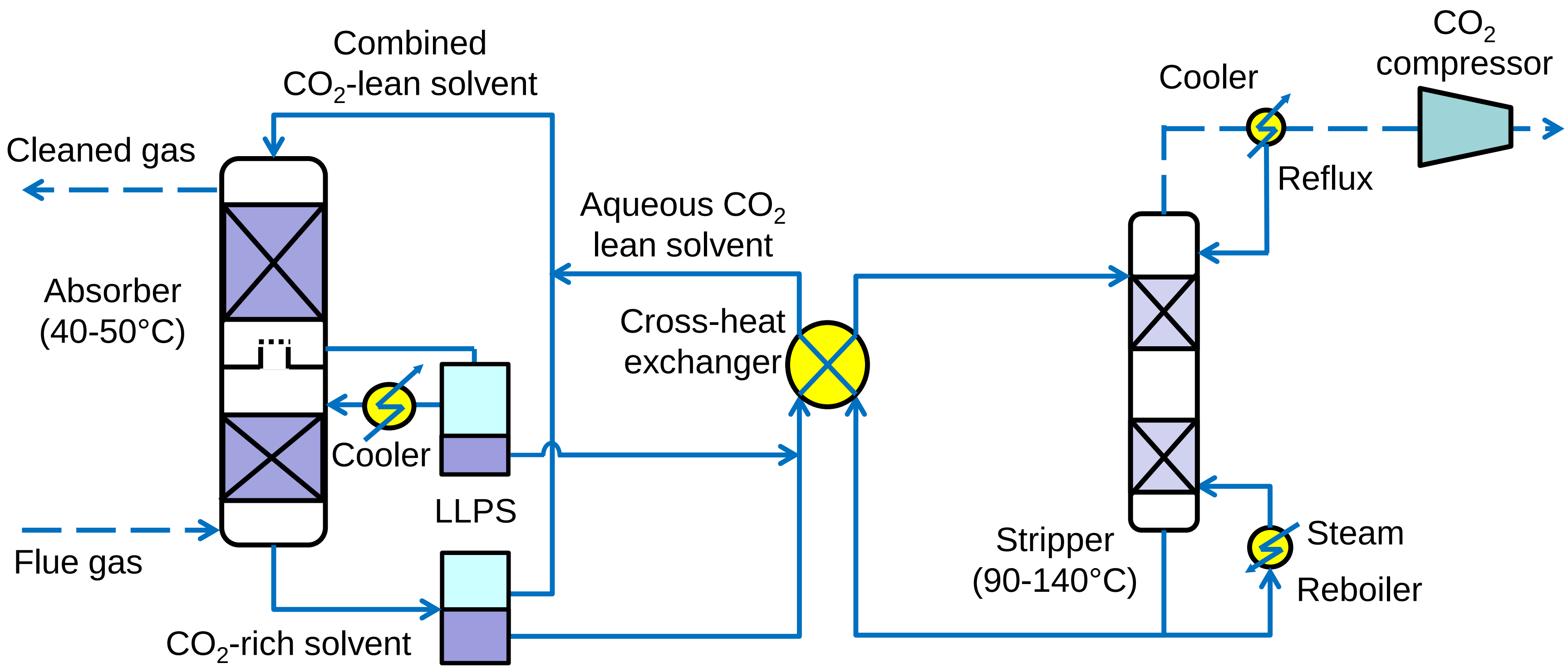
Biphasic CO_2 Absorption Processes Reported by Other Groups (e.g., IFPEN's DMX, 3H, NTNU)



Impacts on stripper:

- Reduced energy requirement due to reduced mass of solvent to be regenerated in stripper
- Reduced stripping heat and compression cost due to increased CO_2 loading in rich phase feed and increased stripping pressure

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



(Two stages of LLPS are shown in this illustration; actual number of stages can be different)

Adds impacts on absorber to the impacts on stripper:

- **Lean phase to next packed bed improves kinetics (reduced capital cost)**
- **Reduced mass of solvent to next packed bed (reduced capital cost)**
- **Reduced viscosity with rich, viscous phase separated improves mass transfer rate (reduced capital cost)**

Advantages of Multi-Stage LLPS

- Modified operating curve allows for a higher mass transfer driving force and thus a faster absorption rate
- Measurement data revealed rich phases more approach to equilibria and lean phases less approach to equilibria

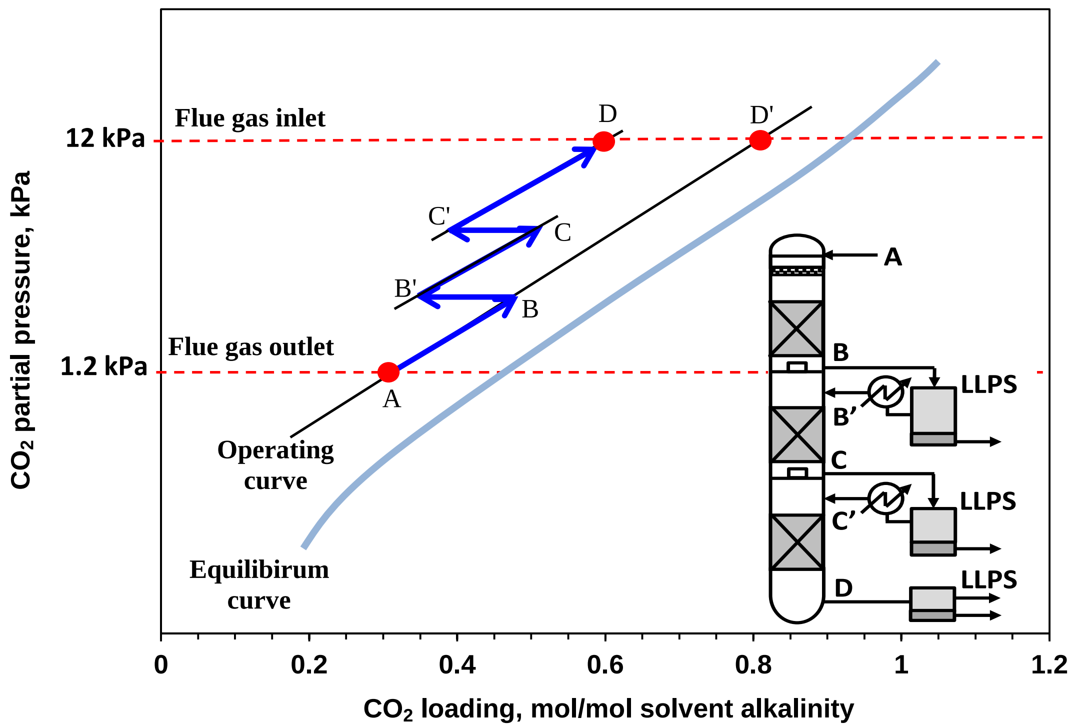


Illustration of operating and equilibrium curves with 3 stages of LLPS during CO_2 absorption
(Note: the equilibrium curve that may change after each LLPS is not displayed in this illustration)

BiCAP vs MEA and Other Biphasic Processes

Biphasic processes vs MEA

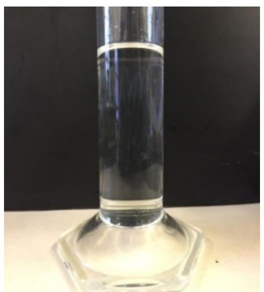
- Biphasic solvents have larger solvent capacity for CO_2 stripping due to absorbed CO_2 concentrated in one phase as feed solution to the stripper
- Reduced mass and elevated P for CO_2 stripping
  - Reduced heat duty (low sensible heat and stripping heat)
  - Reduced compression work requirement

BiCAP vs other biphasic processes

- ***Different absorption processes:*** Multi-LLPS in BiCAP allows for low CO_2 loading throughout the absorber, resulting in a faster absorption rate, lower viscosity, and reduced absorber size
- ***Different solvents***: BiCAP solvents possess larger CO_2 capacity, higher CO_2 enrichment, and tunable phase transition behavior facilitated with the use of unique solubilizers
- ***Different desorption processes:*** Desorption with a flash step to reduce compression cost

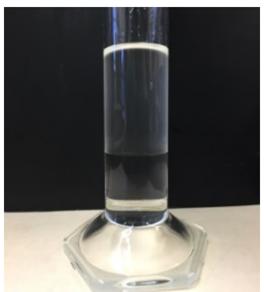
Biphasic Solvents for Multi-Stage LLPS

- Solvents screened in previous and ongoing work demonstrated multiple stages of phase transition/separation and CO_2 enrichment



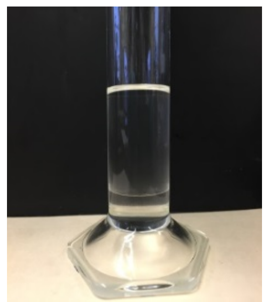
t = 0 min, before CO_2 absorption:

One single phase (homogeneous), no CO_2 loading



t = 18 min, CO_2 absorption:

Dual phases formed and CO_2 enriched in lower phase (3.39 mol/L vs 0.36 mol/L in upper phase)

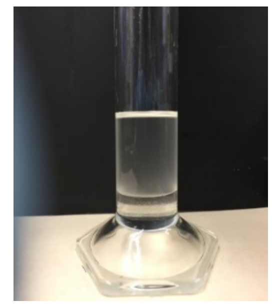


t = 18 min, LLPS:

50%vol of lower phase was removed

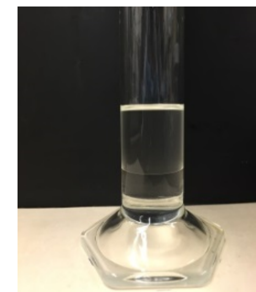
t = 39 min, CO_2 absorption:

Dual phases re-developed and CO_2 enriched in lower phase (5.98 mol/L vs 0.40 mol/L in upper phase)



t = 39 min, LLPS:

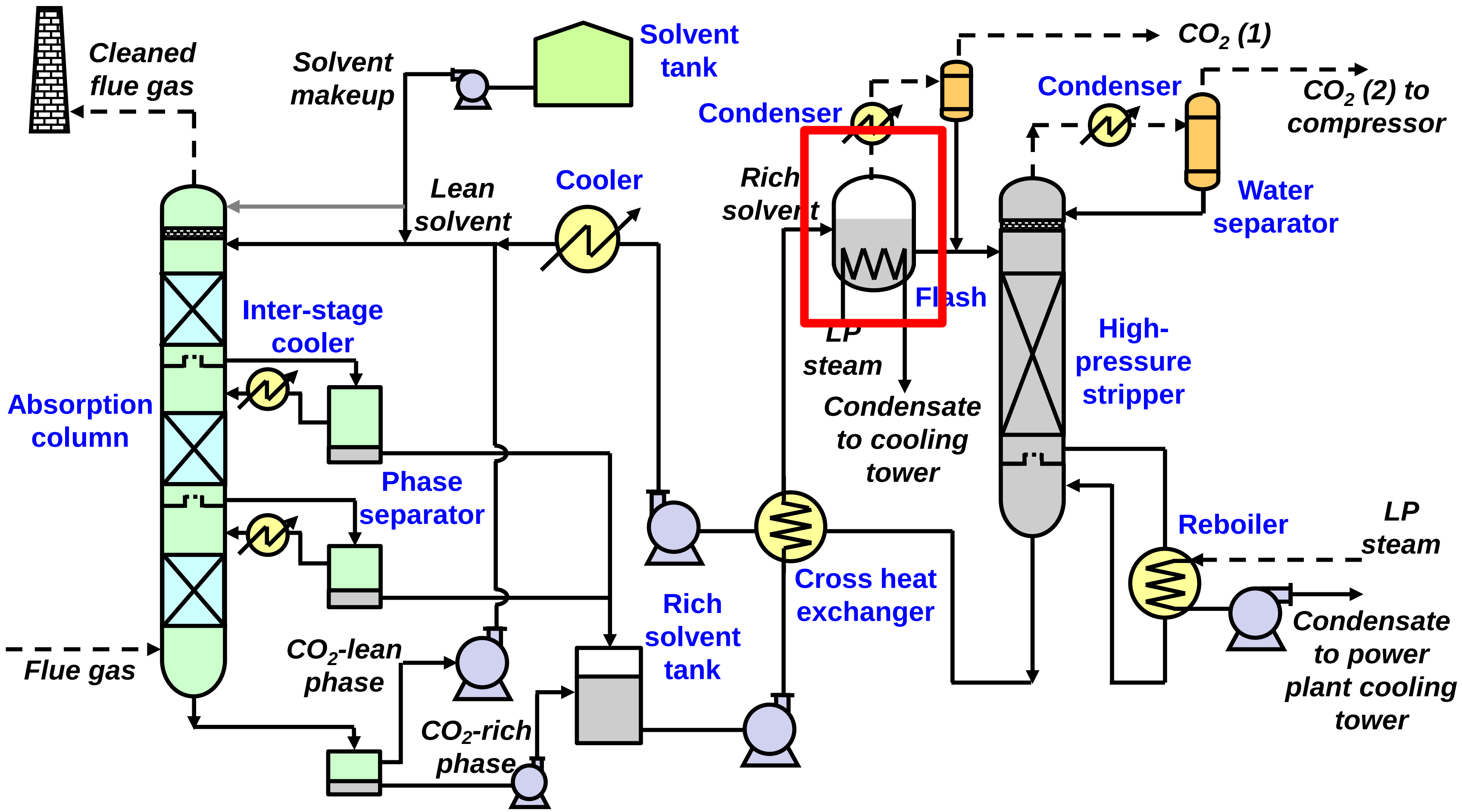
53%vol of lower phase was removed



t = 70 min, CO_2 absorption:

Dual phases re-developed and CO_2 enriched in lower phase (5.34 mol/L vs 0.45 mol/L in upper phase)

BiCAP with Flash Desorption Step



Flash step reduces compression requirements

Technical Risks and Mitigation Strategies

Description of Risk	Risk Mitigation and Response Strategies
Solvents cannot meet all criteria	1) Process analysis to identify most critical properties for energy use and cost and guide solvent selection 2) Solvent screening work extended to explore more solvents guided by MD simulation studies
Capital cost not favorable	1) Stages of CO_2 absorption and LLPS reduced 2) Issues related to process subunits/equipment analyzed/identified and vendors consulted
Targeted desorption pressure (5-10 bar) cannot be achieved	1) Solvent formula tuned to allow high desorption P 2) Flash and stripper design reconfigured (e.g.,, new integration options) and operating conditions optimized
Solvent oxidization / thermal degradation is severe or corrosion tendency is high	1) Solvents with improved stability 2) Solvent reclamation studies 3) Testing of selected commercial corrosion inhibitors
LLPS takes a longer residence time than the target (<5 min)	1) Solvent formula tuned to allow for fast LLPS 2) Study centrifugation to enhance LLPS

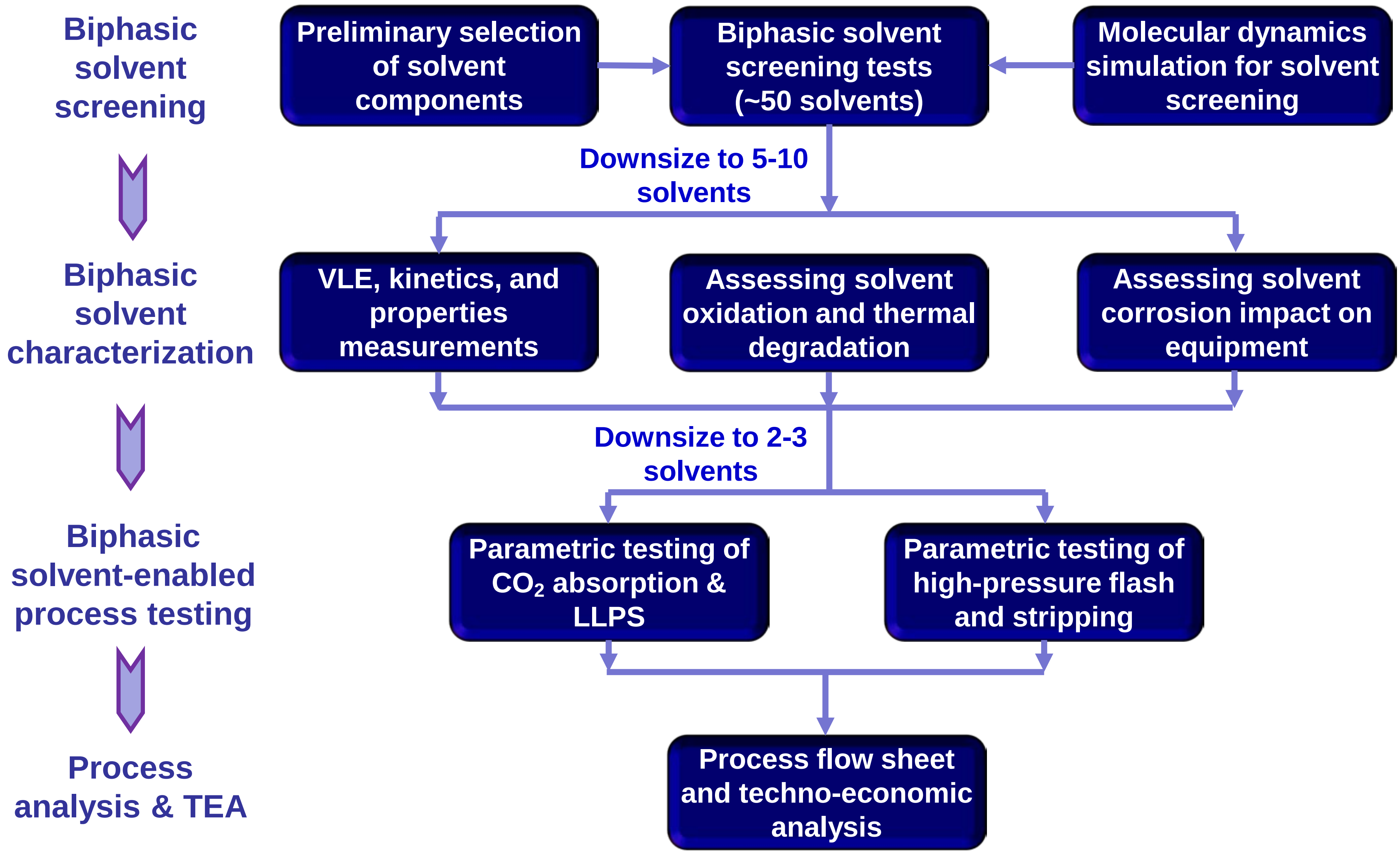
Technology Background

Project Work Flow and Organization

Scope of Work and Approach

Timeline, Milestones and Deliverables

Decision Tree of Technical Work



Project Organization and Structure

US Dept. of Energy
Contracting Officer's Representative

UIUC
PI: Dr. Yongqi Lu
Co-PI: Dr. Kevin Obrien

ISGS-UIUC
Task Coordinator, Dr. Hong Lu

- —Task 2. Screening and characterization of biphasic solvents
- —Task 3. Measuring phase equilibria, absorption kinetics, and solvent properties
- —Task 5. Testing CO_2 absorption and phase separation in a multi-stage packed-bed column
- —Task 7. Testing CO_2 desorption in a flash and stripping column

ISTC-UIUC
Task Coordinator, Dr. Wei Zheng

- —Task 4. Determining thermal & oxidation stabilities of the selected solvents
- —Task 8 Assessing the impact of solvent corrosion on equipment

ARI-UIUC
Task Coordinator, Dr. Santanu Chaudhuri

- —Task 2.3 Molecular simulation study for solvent screening

Trimeric
Subcontractor PI, Mr. Ray McKaskle

- —Task 6. Development of a process sheet and preliminary process analysis
- —Task 9. Technical and economic feasibility study

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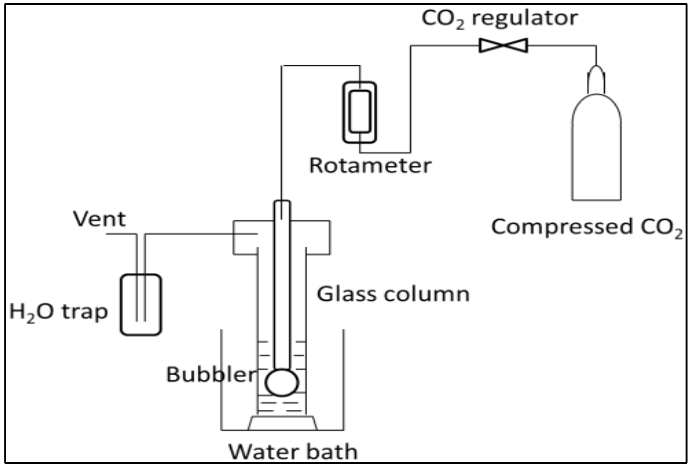
Task 2.0 Screening & Characterization of Biphasic Solvents (up to 50 solvents)

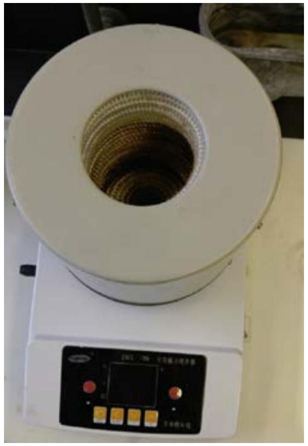
- Task 2.1 Absorption and phase transition screening
- Task 2.2 Desorption screening
- Task 2.3 MD simulations for screening

Task 2.1 / 2.2 Lab Screening Experiments

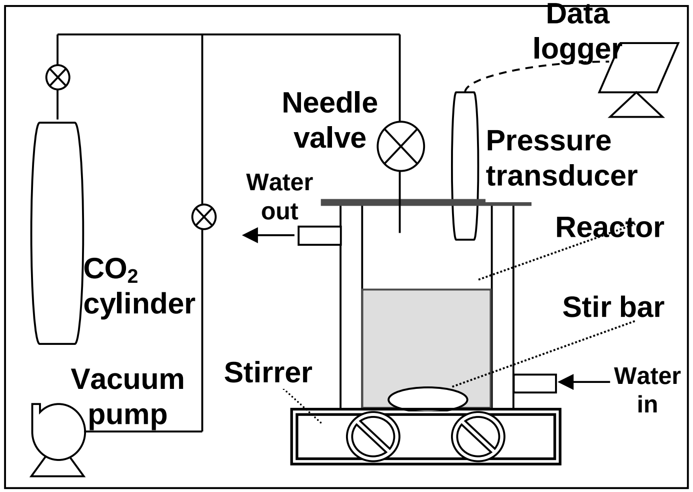
- **CO_2 absorption performance and phase transition behavior**
  - Components pre-selected based on existing work and BP, VP, MW, $, etc.
  - Testing of CO_2 absorption capacity and rate at 40°C
  - Impact of multiple LLPS (1-3)
- **CO_2 desorption performance**
  - Desorption pressure vs CO_2 loading of CO_2-enriched phase at 80-100°C



LLPS and capacity screening with gas impingers



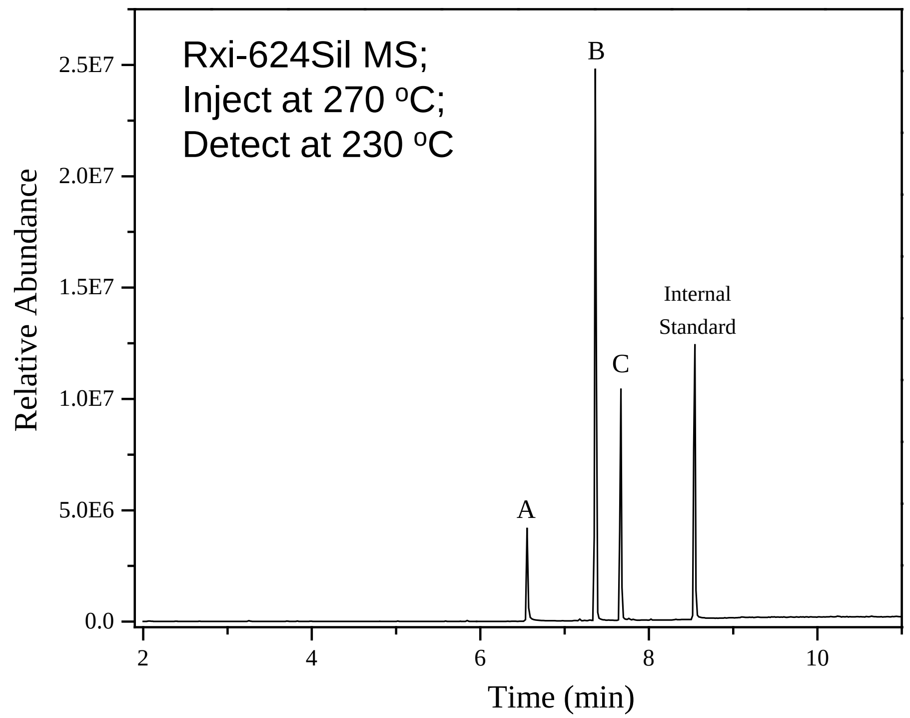
Desorption screening with high P/T reactors



kinetics screening with a STR

Task 2.1 / 2.2 Lab Screening Experiments

- **Analysis of dual phases with NMR, GC-MS, and/or ATR-FTIR**
  - GC-MS: Thermos Scientific (Trace 1300 GC and ITQ 700 MS) with TriPlus RSH autosampler
  - 13C and 1H NMR: Varian Unity Inova spectrometer 500 NB



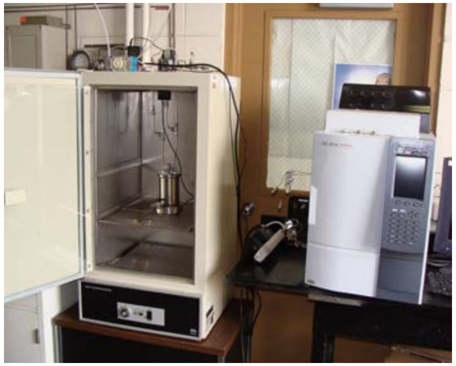
Task 2.3 MD Simulation for Solvent Screening

- **Objectives**
  - Explain dual phase separation observed for known formulations
  - Predict dual phase separation for unknown components
  - Predict equilibria, kinetics and transport properties (D, μ, σ, Cp, ΔH)

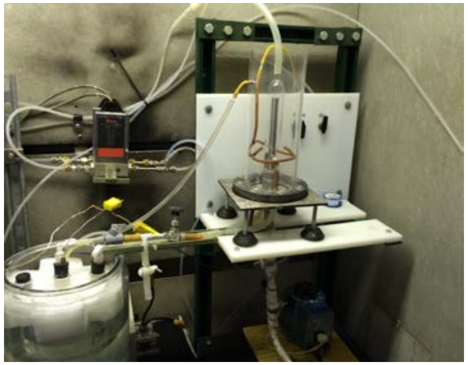
- **Approach: a combination of first-principles and ReaxFF MD simulations**
  - Step 1: Identify most effective dielectric media as favorable solvent environments for CO_2+amine reactions against water medium; potential polar solvents further screened for miscibility in water
  - Step 2: Identify impact of amines ratio on coupled reaction-diffusion
  - Step 3: Assess combined effectiveness of organic solubilizers with amines and predict phase separation energetics, diffusivity, and chemical potential of species

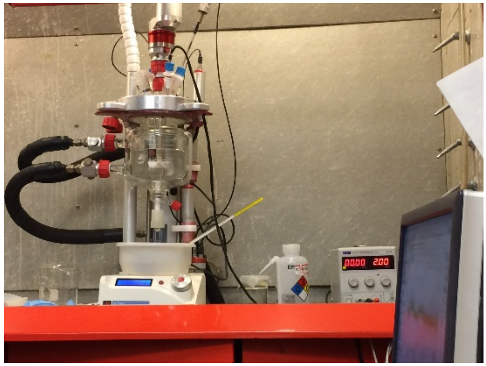
Task 3. Measuring Phase Equilibria, Absorption Kinetics, and Solvent Properties (5-10 solvents)

- **VLE measurement**
  - VLE data at 30-140°C
  - Impact of multi-LLPS
- **Absorption kinetics measurement**
  - Rate constants and mass transfer coefficients using a WWC reactor
  - Impact of multi-LLPS
- **Solvent properties**
  - Reaction enthalpy; diffusivity, viscosity, Cp, density, surface tension


Low temperature VLE cell


High P/T VLE reactor


WWC reactor for kinetics


Reaction calorimeter

Task 4. Determining Thermal and Oxidation Stabilities of the Selected Solvents (5-10 solvents)

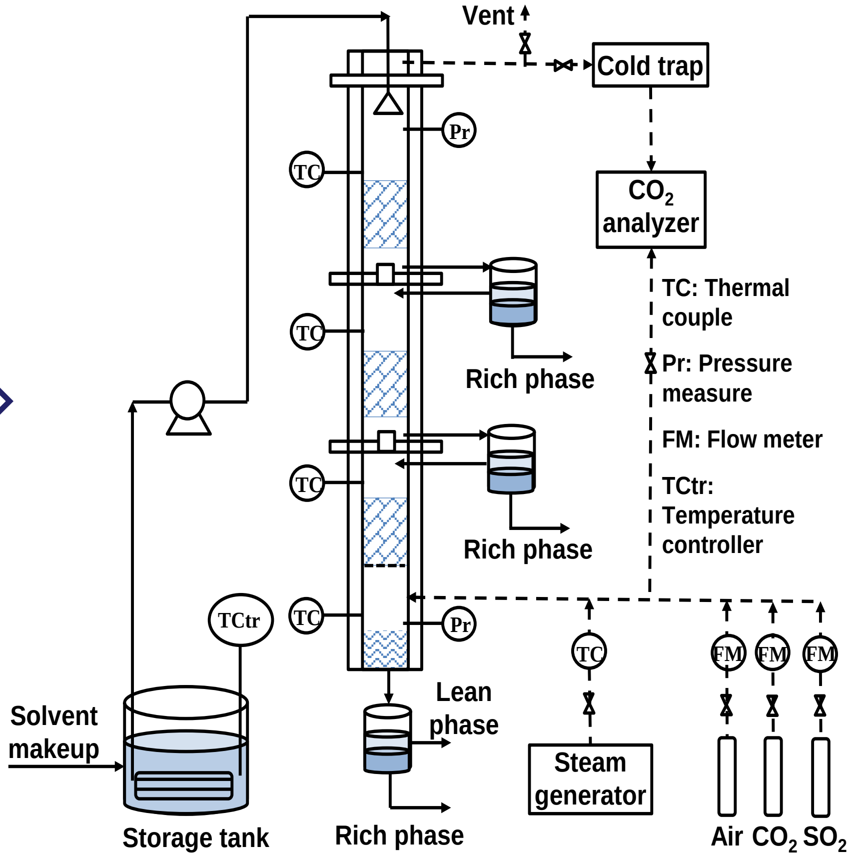
- **Oxidation stability**
  - Wet testing in an O_2–enriched atmosphere
    - O_2-enriched gas bubbling in solvents with representative CO_2 loadings at typical absorption temperatures for ~2 mon
    - Samples analysis with GC/MS and LC/MS
    - Degradation pathway and oxidative mechanisms
  - Modified Rancimat testing
    - Degradation of solvents purged with O_2-CO_2 gas assessed by continually monitoring conductivity of water in solvents

- **Thermal stability**
  - CO_2-enriched solvent samples sealed in tubes and placed in ovens at typical desorption temperatures and CO_2 loadings for ~2 mon
  - Sampling and analysis of degradation products with LC/MS, GC/MS, and/or HPLC with diode array detection
  - Degradation mechanisms/pathway and kinetics

Task 5. Testing CO_2 Absorption and LLPS in a Multi-Stage Packed-Bed Column (2-3 solvents)

- Modification of an existing absorption column to incorporate multi-LLPS
- Parametric testing on absorption efficiency and phase separation impact
- Continuous testing
- Development of a rate-based model for absorption

An existing packed-bed column



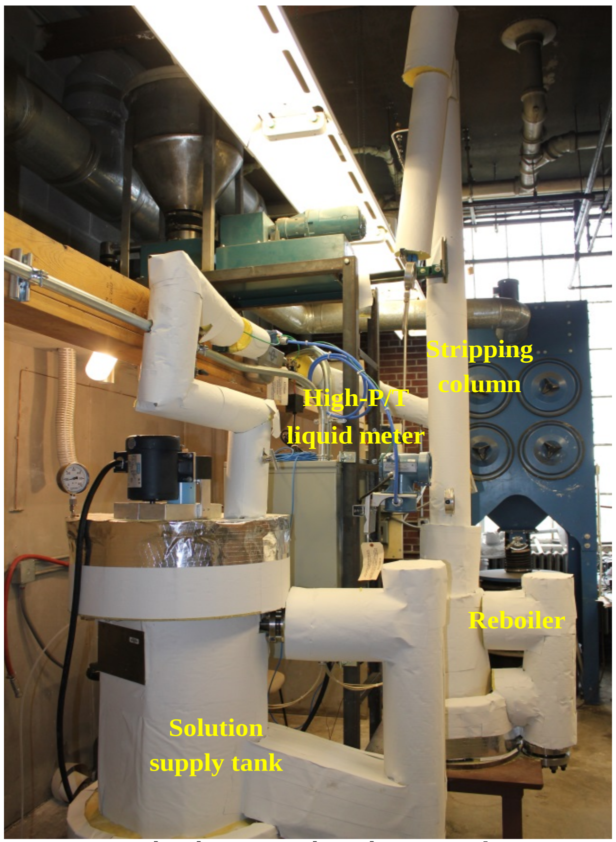
Task 6. Development of a Process Sheet and Preliminary Process Analysis

- **Development of a conceptual process flow sheet**
  - Identify all major process equipment
  - Create a conceptual process flow diagram

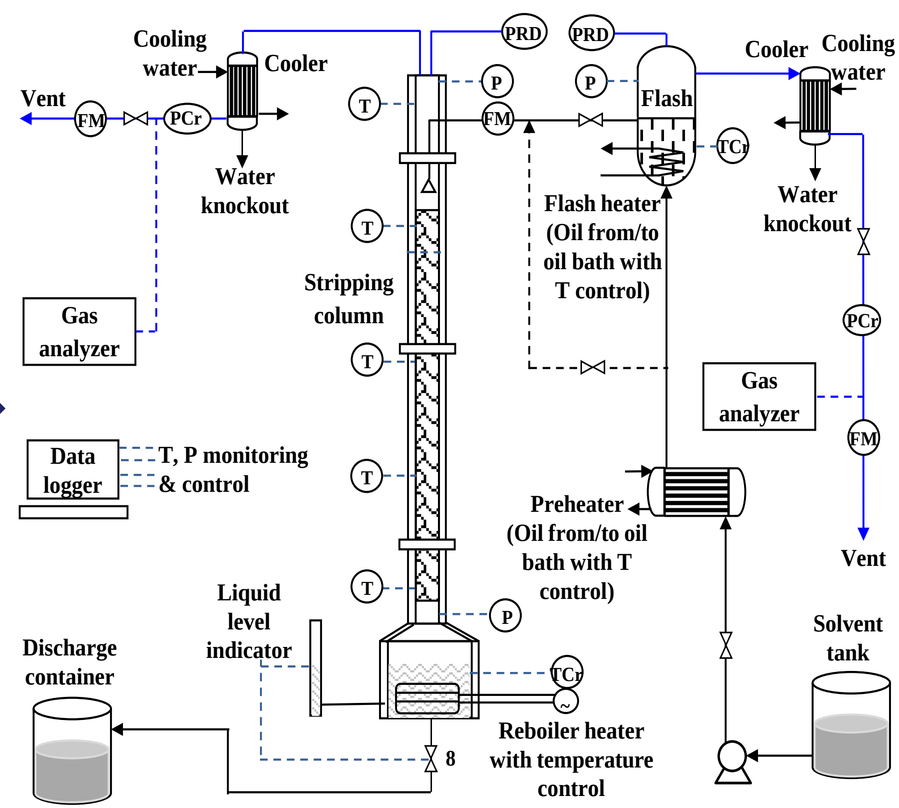
- **Preliminary process analysis**
  - Analysis and review of initial mass & energy balances (M&EBs), stream tables, and cost estimates

Task 7. Testing CO_2 Desorption in a High-Pressure Flash and Stripping Column (2-3 solvents)

- Modification of an existing packed-bed stripper by incorporating a flash
- Parametric testing on heat duty and desorption performance
- Continuous testing
- Development a desorption model for CO_2 flash and stripping



An existing stripping column rated at 200°C /500 psia



T: Thermocouple; P: Pressure transducer; FM: Flow meter
TCr: Temperature controller; PRD: Pressure rupture disk; PCr: Pressure regulator

Task 8. Assessing the Impact of Solvent Corrosion on Equipment (2-3 solvents)

- **Solvent corrosion testing on two equipment materials**
  - Carbon steel (CS) simulating absorbers
  - Stainless steel (SS) simulating strippers

- **Weight loss-based testing**
  - Weight loss of test specimens in solvent samples vs time
  - Samples of representative solvent compositions (loading and concentration) at typical adsorption/desorption temperatures

- **Modified Rancimat testing**
  - Testing environments with multiple combinations of O_2-CO_2 gas streams and solvent compositions at typical adsorption/desorption temperatures

Task 9. Technical and Economic Feasibility Study

- Process simulation and mass & energy balance (M&EB) calculations
  - Process simulation and optimization
  - M&EBs developed for BiCAP system

- Technical and economic feasibility study
  - Selection and sizing of major process equipment
  - Estimation of equipment capital costs
  - Estimation of major fixed and variable operating & maintenance (O&M) costs
  - Evaluation of economic metrics for BiCAP process
  - Sensitivity of economic performance to critical process and cost variables

Technology Background

Project Work Flow and Organization

Scope of Work and Approach

Timeline, Milestones and Deliverables

Project Timeline: 3 Years with 2 Budget Periods

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

Project Milestone Log – BP1

ID	Task	Milestone Description	Planned Completion	Delivered by	Verification Method
a	2.1/2.2	Down-select 5-10 biphasic solvents *(CO_2 capacity ≥ 5M MEA; able to form dual phases and ≥ 80% of absorbed CO_2 enriched in one phase; CO_2 desorption pressure ≥ 5 bar)*	06/30/16	UIUC	Results reported in the quarterly report
b	2.3	Complete molecular dynamics simulations and predictions	06/30/16	UIUC	Results reported in the quarterly report
c	3	Down-select 2-3 biphasic solvents *(VLE results indicate 90% CO_2 absorption and ≥ 5 bar CO_2 desorption; CO_2 absorption kinetics ≥ 5M MEA; ΔH=1,400-2,000 kJ/kg CO_2, viscosity of CO_2-lean phase ≤20 cP)*	09/30/16	UIUC	Results reported in the quarterly report
d	5.1	Complete modification of the existing packed-bed absorption column to include 2-3 LLPS stages	09/30/16	UIUC	Description & photos provided in the quarterly report
e	4	Complete assessment of biphasic solvent oxidation and thermal stabilities	12/31/16	UIUC	Results reported in the quarterly report
f	5.2	Complete simulated flue gas testing of 2-3 biphasic solvents using the modified absorption column *(CO_2 capacity and kinetics ≥ 5M MEA)*	03/31/17	UIUC	Results reported in the quarterly report
g	6	Complete preliminary process analysis and develop a conceptual process flow sheet	03/31/17	Trimeric	Results reported in the quarterly report

Cont'd – BP2

ID	Task	Milestone Description	Planned Completion	Delivered by	Verification Method
h	7.1	Complete modification of the existing CO_2 stripping column with incorporating a flash unit	09/30/17	UIUC	Description & photos provided in the quarterly report
i	8	Complete comprehensive assessment of solvent corrosion impacts	12/31/17	UIUC	Results reported in the quarterly report
j	7.2	Complete simulated flue gas testing of 2-3 solvents using the modified CO_2 stripping (*stripping pressure ≥5 bar and total energy use (including compression) ≤0.22 kWh//kg CO_2 captured)*	03/31/18	UIUC	Results reported in the quarterly report
k	9	Preliminary technical and economic feasibility study completed	09/30/18	Trimeric	Results reported in Final Report
QR	1	Quarterly report	Each quarter	All	Quarterly Report files
FR	1	Draft Final report	10/31/2018	All	Draft Final Report file

Success Criteria

Decision Point	Basis for Decision/Success Criteria
Completion of BP1	
	Identify 2-3 top-performing solvents based on VLE, CO_2 capacity, absorption kinetics, ΔH, viscosity, and phase transition and CO_2 enrichment behavior
	Complete simulated flue gas testing of 2-3 solvents in an absorption column with multi-LLPS: CO_2 capacity and kinetics $\geq$5 M MEA; each LLPS stage ≤ 5 min; $\geq$ 80% CO_2 enrichment in the rich liquid phase
	The multi-stage absorption and LLPS configuration demonstrates reliable operability during lab-scale testing and the number of LLPS stages optimized
	Submission of a preliminary process analysis & conceptual process flow sheet
	Submission and approval of a Continuation Application
Completion of BP2	
	Operating conditions identified: ≥5 bar stripping pressure, working capacity ≥2 times that of 5M MEA during CO_2 desorption, and total energy use (including compression) of $\leq$0.22 kWh//kg CO_2 captured
	Initial techno-economic feasibility study shows significant progress toward achievement of the overall DOE performance goals
	Submission of an updated state-point data table based on lab-scale testing
	Submission of a Final Report

Project Deliverables

- Project Management Plan
- Quarterly progressive reports
- BP1-BP2 continuation application
  - Preliminary process analysis & conceptual PFD
  - Continuation Application
- Final technical report
  - Summary of all development, analysis, testing, design, and techno-economic analysis, as defined in contract
  - An updated state-point data table
- Other reports
  - Financial, property, annual contractors', and close-out reporting, as defined in contract

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