An Advanced Catalytic Solvent for Lower Cost Post-combustion CO_2 Capture in a Coal-fired Power Plant

Award # DE-FE0012926

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Center for Applied Energy Research

- **Power Generation & Utility Fuels**
- Biofuels & Environmental Catalysis
- Carbon Materials
- Electrochemical Power Sources
- Clean Fuels and Chemicals
- Environmental Remediation

Catalyst Development
- Post-combustion CO_2 capture (gasification)
- Natural gas sweetening
- CO_2 utilization

Pilot Plant
- Coal-derived flue gas
- Solvent & process testing

Solvent Development
- Blends & exotic amines
- ASPEN modeling
- Structure-property relationships
- Degradation
- Kinetics
- Thermodynamics

Corrosion
- Traditional cell
- Electrochemical methods determination

Membrane Separations
- Zeolite membranes
- Solvent enrichment

Electrochemistry
- Solvent enrichment
- Water treatment

Analytical Methods Development
- IC-MS, GC-MS, LC-MS (TOF-ESI)
- Degradation analysis
- Nitrosamine identification

Project Overview

Overall Objective: Develop a Post-combustion integrated hybrid (membrane/solvent) process with an advanced catalyzed solvent.

Project Details

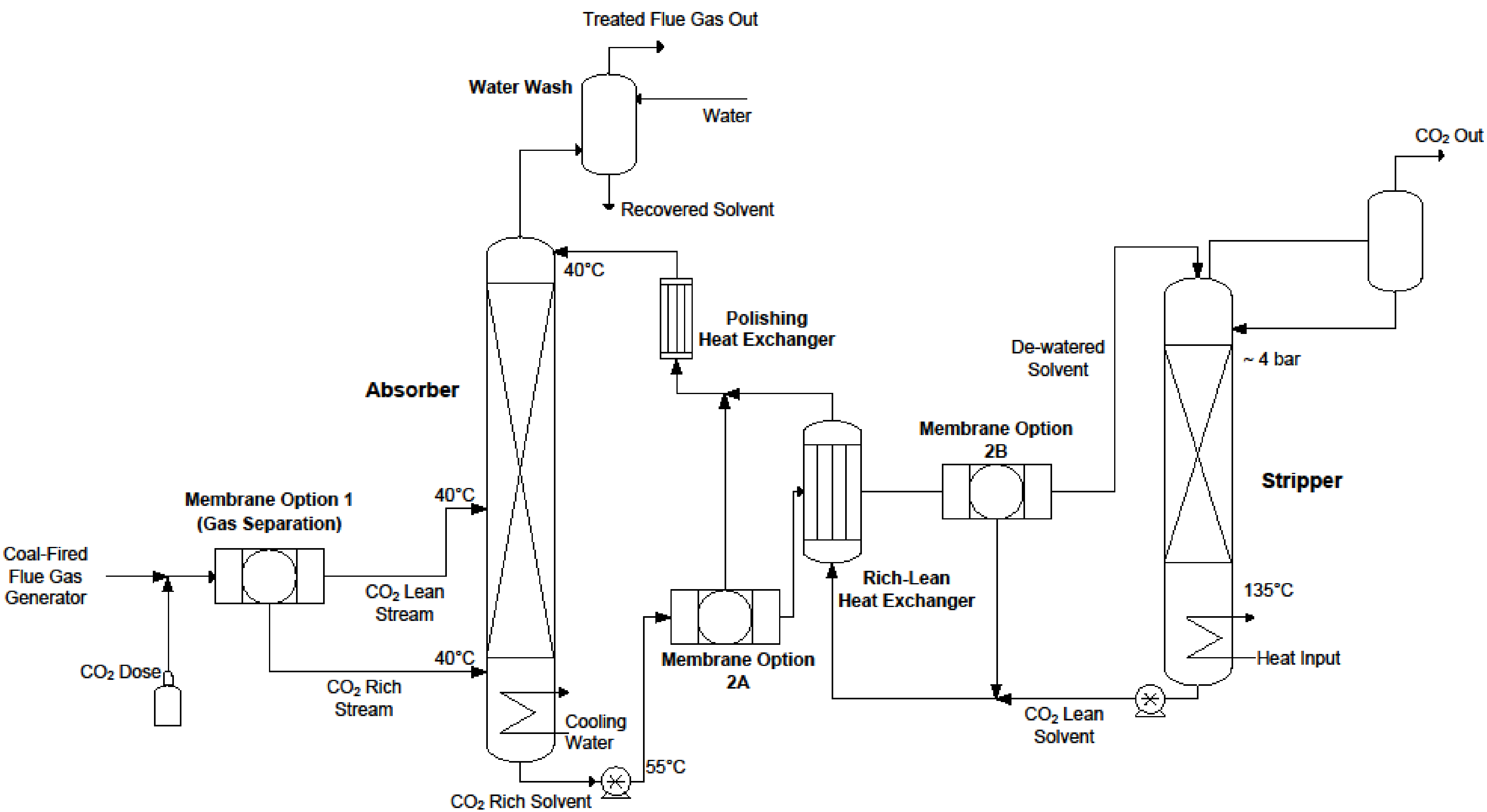
- **Benefit from multiple CAER technologies: solvent; catalyst, membrane, process**
- **Project cost:**
    - **DOE share:$2.97M**
    - **Cost share:$742K**
- **Period performance:** 10/1/2013 – 9/30/2016

Project Objectives

- Develop a low-cost CO_2 capture system via Integration of multiple CAER technologies to verify an advanced catalytic solvent with integrated membrane dewatering for solvent enrichment in our 0.1MW pilot plant (Proof of concept)

CAER	CMRG	SMG	WorleyParsons
• Project management • Catalytic solvent testing • ASPEN modeling • Membrane synthesis	• Technical support	• PPE recommendation • EH&S analysis	• Front-end engineering support • Techno-Economic Evaluation

Catalytic Solvent Process



Technology Fundamentals

- k_{obs} impacts PFO calculation

$$k_{obs} = k[amine] + k'[cat]$$

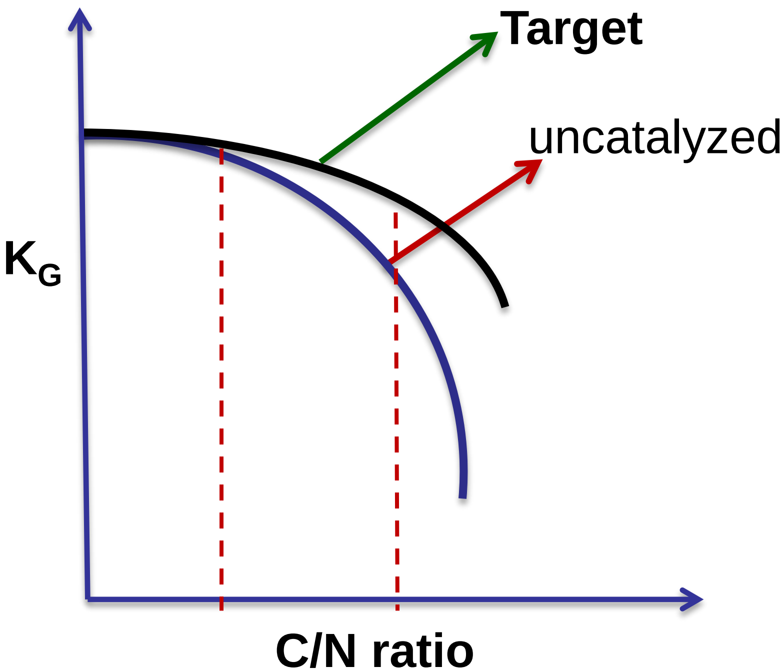
$$k_{g,PFO}' = \frac{\sqrt{D_{CO2}.k_{obs}}}{H_{CO2}}$$

$$k_{g,PFO}' \alpha \sqrt{k_{obs}}$$

Higher the value of k_{obs} higher the mass transfer rate

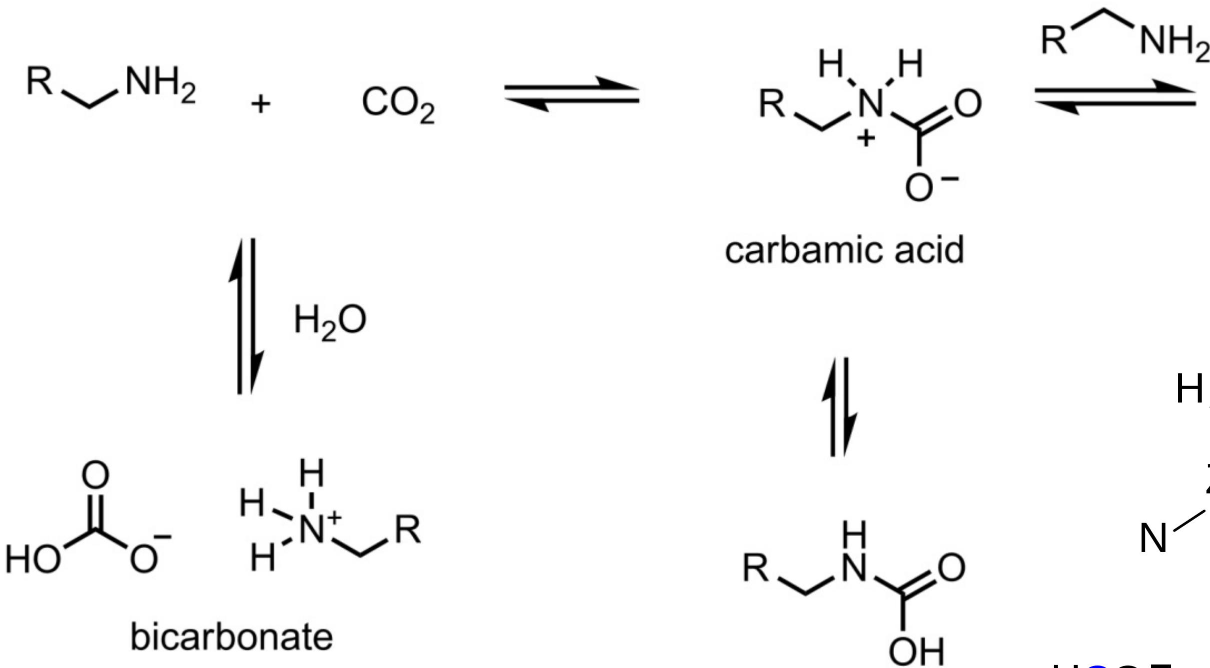
Pseudo first order approximation

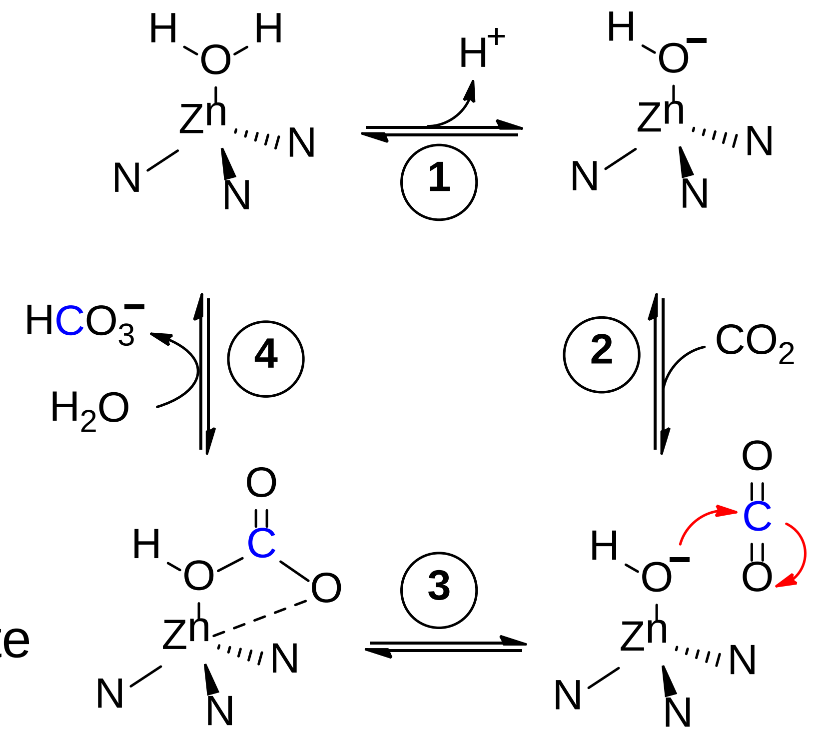
$$k_{g,PFO}' = \frac{\sqrt{D_{CO2}.k_2.[amine]}}{H_{CO2}}$$



Achieve rate enhancement at higher carbon loadings

CO_2 Capture Chemistry





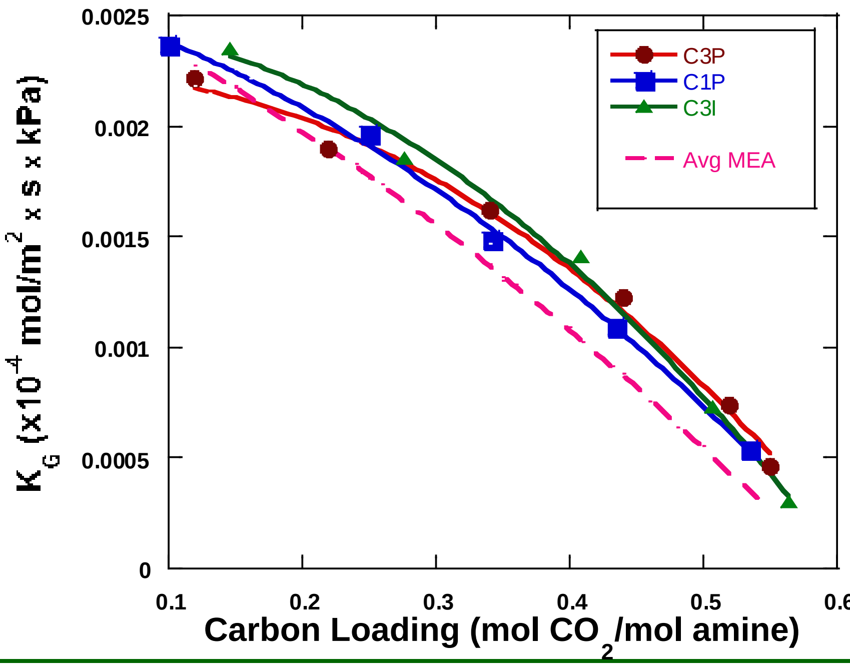
- Parallel process:
  - ➢ Typical amine-based chemistry
  - ➢ Catalytic CO_2 hydration to bicarbonate

Development Efforts: Catalysts

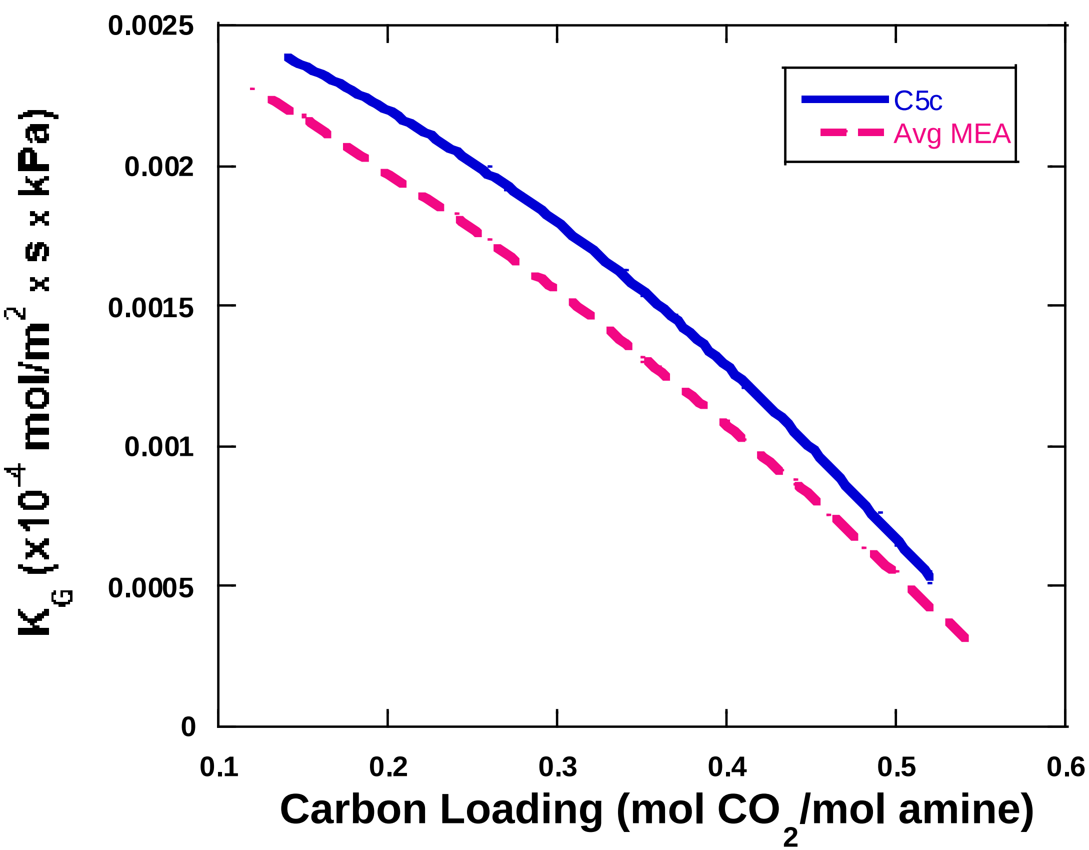
Catalyst	pH	K_{cat} ($M^{-1}s^{-1}$)	Solvent	Method
CA (Zn)	7	1,100,000	Carbonate buffer	Stop-Flow
CA(Co(III))	7	305,000		
Zn-Cyclen	7.5	564	HEPES	Stop-Flow
	8.5	2154	AMPSO	Stop-Flow
	9.11	3012	CHES	Stop-Flow
Zn-Cyclam	7.5	24	HEPES	Stop-Flow
	9	126	AMPSO	Stop-Flow
	9.8	172	CHES	Stop-Flow
Zn-NTBSA	9.5	3300	Carbonate buffer	Stop-Flow

CAER Catalyst Development

- Incorporate key features of CA without the limitations: Nucleophilic hydroxo, facile bicarbonate dissociation, Lewis acidic metal center
- Aqueous-amine soluble and stable
- Function under "real" conditions (14% CO_2, concentrated amines)



Development Efforts: Catalysts



Improved Catalyst

- Increased activity in MEA (~30% enhancement)
- Retains activity after heating at 145 °C for 150h
- Simple catalyst preparation; suitable for scale-up (~25% more $ than MEA)

Development Efforts: Catalysts

Catalyst	Solvent	ºC	Time (hour)	% Activity Lost
-	MEA	100	6	~5
C1P	MEA	100	6	~5
C3P	MEA	100	6	~100
C3I	MEA	100	5	~100
C5c	**MEA**	**145**	**150**	**~5**

Improved Catalyst

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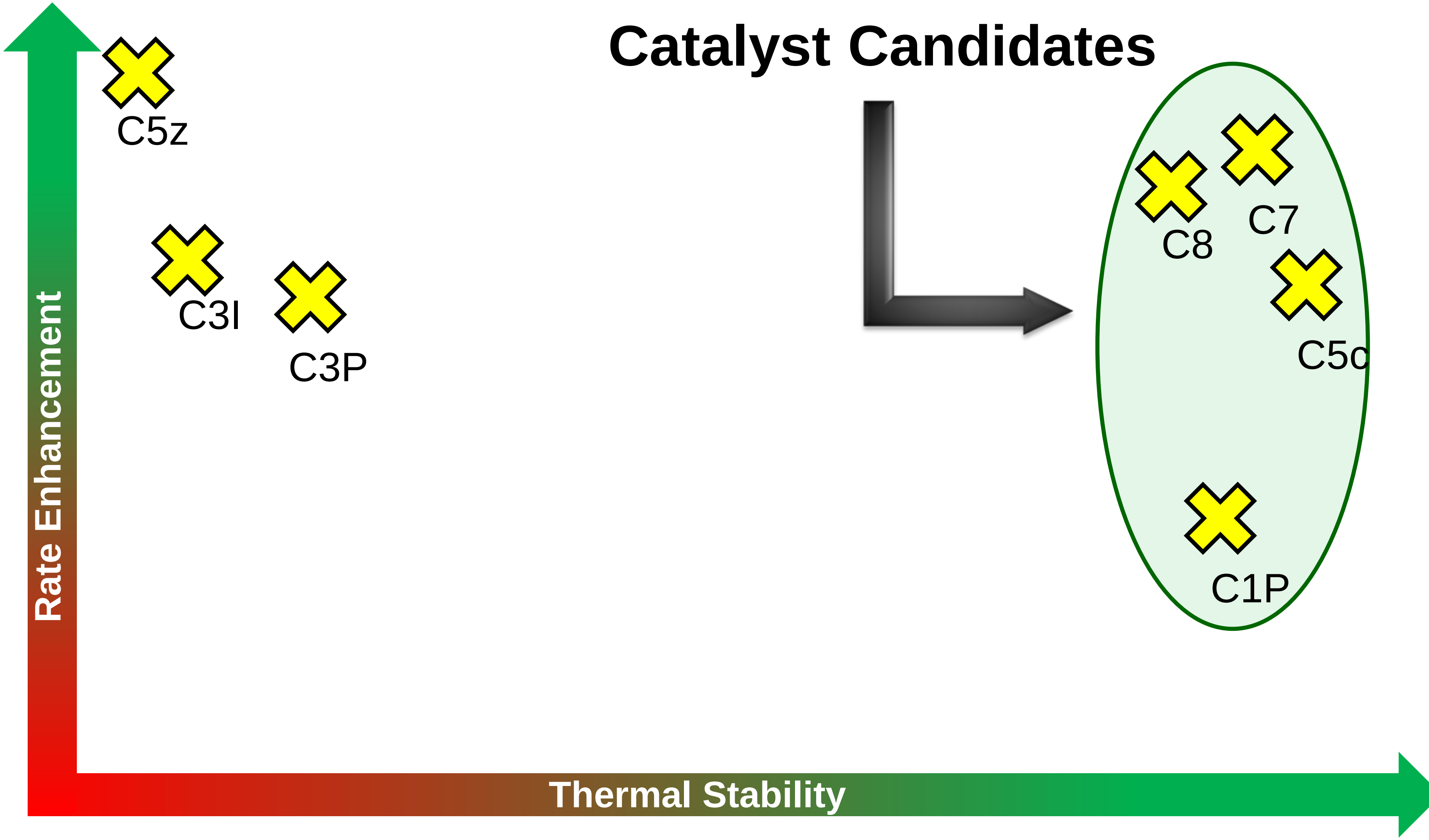
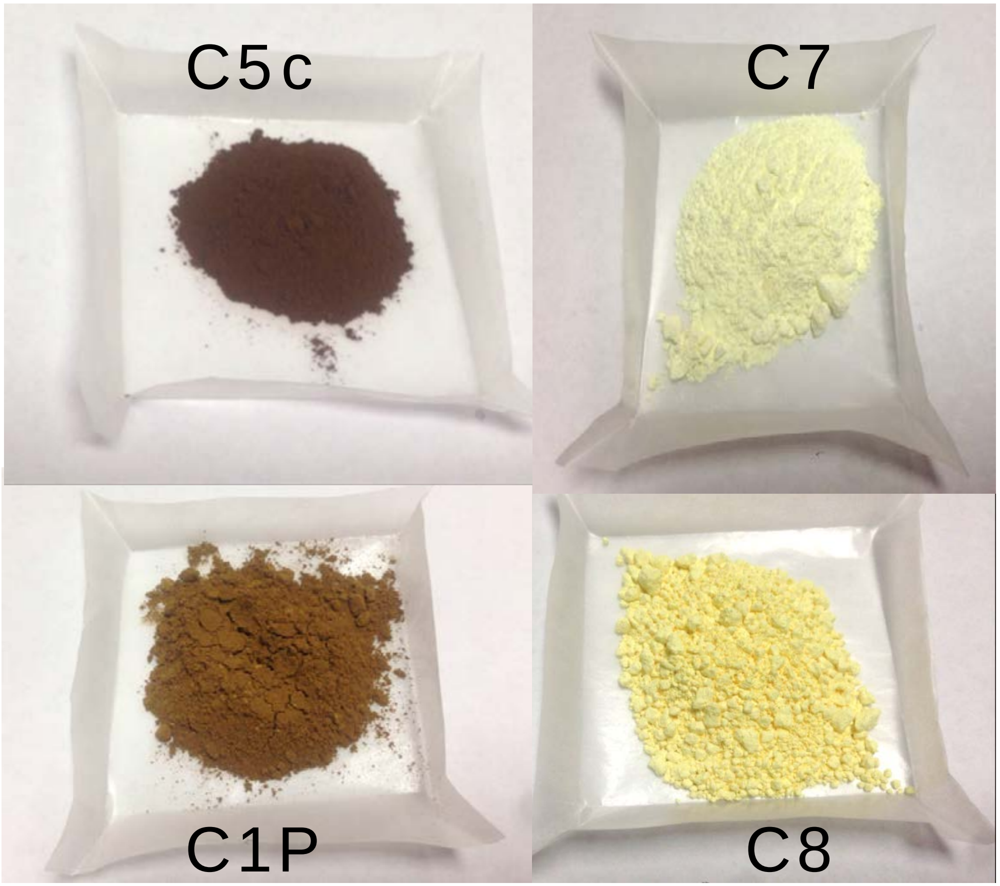
Catalysts Properties in MEA



Catalytic Solvent CO_2 Capture



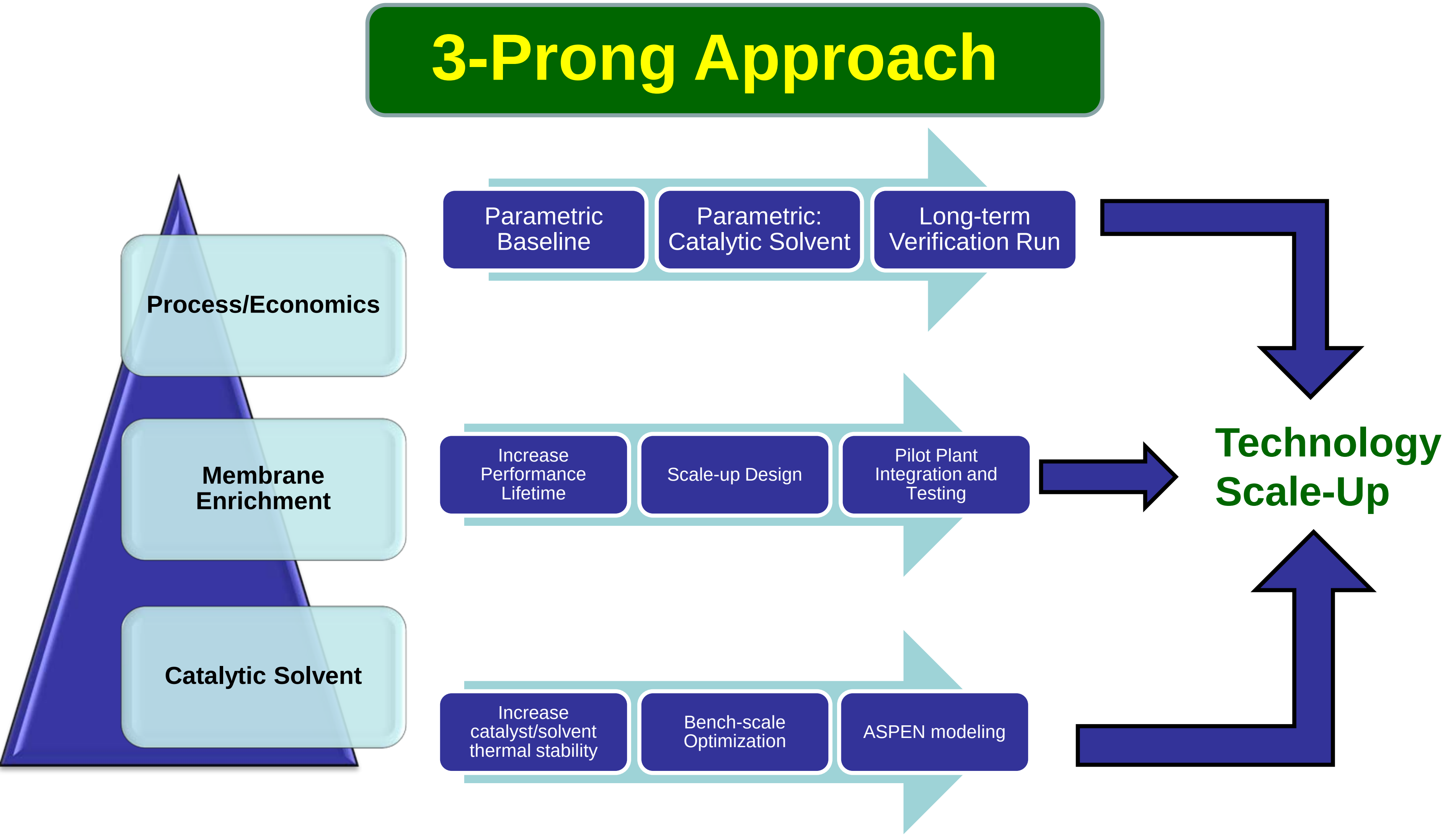
Advantages

- Potential for reduced capital cost for post-combustion CO_2 capture
  - Increased scrubber kinetics (smaller absorber)
- Potential for reduced energy consumption compared to reference case (MEA)
  - High α; cyclic capacity
  - High stripper temperatures/pressure
  - Less solvent make-up rate

Challenges

- Transition from lab- to bench-scale process under real flue gas conditions
- Solvent oxidation via catalyst addition
- Integration with multiple technologies

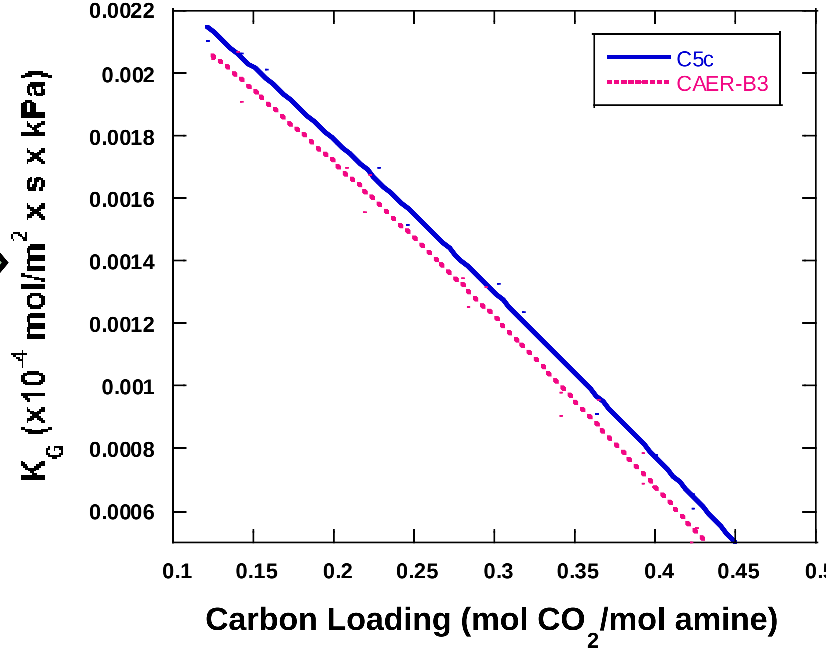
Design and Work Plan

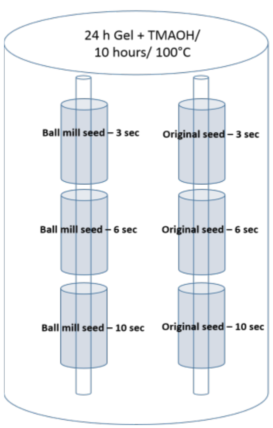


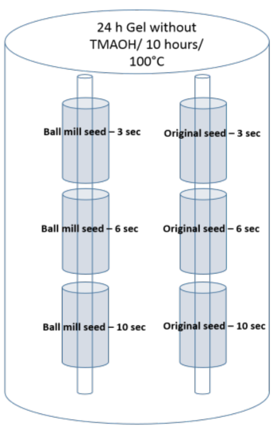
Progress and Current Status

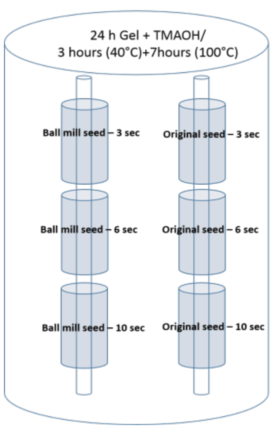
1) Catalyst synthesis (50g/batch)

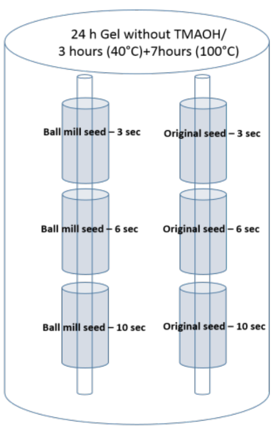
2) K_G analysis

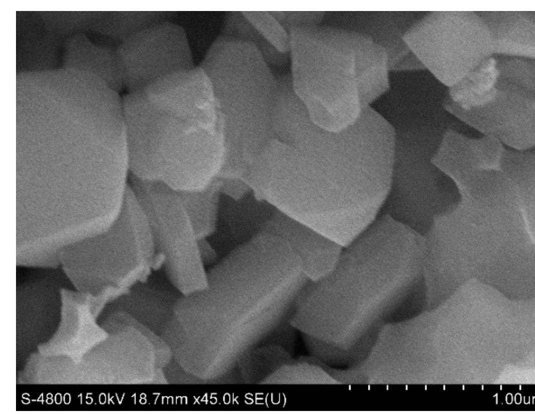












Membrane Separations

MTR Gas Membrane:

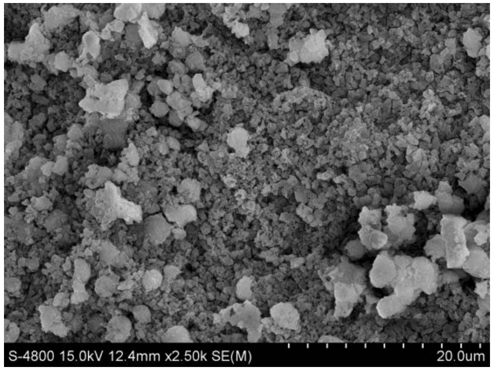
- MTR gas membrane separation unit has been sourced and delivered on June 30, 2014
- Membrane unit is being installed with shake-down testing slated for August 2014

Membrane Dewatering:

Trisep X-20		Zeolite membrane	
Time/ min	Percent Dewatered	Time/hours	Percent Dewatered
0	> 20	1	53%
10	> 20	2	8%
20	> 20	-	-
30	> 20	-	-

Conditions	**Trisep X-20**	**Zeolite**
Temperature (°C)	25	100
Pressure (psi)	1000	70
Flow rate (ml/min)	30	30

The TriSep X-20 anti-fouling membrane (containing an uncharged surface layer) successfully dewatered the CAER-B3 solvent. Extended dewatering lifetime is currently under investigation.



CAER zeolite surface after failure

Project Schedule and Milestones

	Previous work	Current Project				Future Developemt	
Yr	2011-2013	2013	2014	2015	2016	2017-2020	>2020
BP	-	1	1/2	2/3	3	-	-

Fundamental Development of concept by CAER

Slipstream ~2MW

~20 MW

Laboratory Validation and Scale-up

- **Solvent Optimization**
- Milestone: VLE and model regression

- **Membrane Enrichment**
- Milestone: 5% enrichment over 5hr

- **Catalyst Scale-up**
- Milestone: Develop method to produce 50g/batch

•*Milestone*: PPE recommendation & front-end engineering analysis

Parametric Testing on 0.1 MWth Unit

- **Catalyst Production**
- Milestone: 500g produced

- **Parametric Testing**
- Milestone: 100hr runs with and without catalyst completed

- **Membrane Enrichment**
- Milestone: 10% enrichment over 100hr and module design

Verification Testing on 0.1 MWth Unit

- **Verification Run**
- Milestone: 500hr verification run

- **Membrane Enrichment**
- Milestone: Unit integrated and 20% dewatering observed

- **Techno-Economic Analysis**
- Milestone: Favorable TEA

- **EH&S**
- Milestone: Favorable EHS assessment

Budget Periods and Tasks

BP	Task	Name
	1.0, 7.0, 12.0	Project Management and Planning
	2	Collection of Physical Properties and Solvent Optimization
	3	Carbon Enrichment Performance Evaluation with Selected Solvent
1	4	Catalyst Scale-up
	5	Front-end Engineering Analysis
	6	Assessment for PPE Requirement

Budget Period	Task No.	Milestone Description	Planned	Actual	Verification Method
1	1	*1A. Updated Project Management Plan*	3/31/14	10/30/13	PMP file
1	1	*1B. Kickoff Meeting*	11/14/13	12/4/13	Presentation file
1	2.2	*Solvent kinetic data collected for modeling including: no less than 30 data points collected for VLE regression verification*	6/30/14	5/31/14	Quarterly report
1	2.3-4	*Completion of mass transfer and kinetic data collection on CAER-B3 solvent*	9/30/14		Quarterly report
1	3.1	*Membrane shown to dewater CAER-B3 solvent by at least 5% over 5 hours*	8/31/14		Quarterly report
1	3.2	*Completion of experiment of MTR module for higher CO_2 loadings and lower stripper energy costs shown in 30 wt % MEA and CAER-B3 system in 0.1 MWth bench-scale test unit.*	8/31/14		Quarterly report
1	3.3	*Examination of alternative polyamide membranes from TriSep for post scrubber solvent enrichment*	9/30/14		Quarterly report
1	4	*Methodology developed for synthesis of > 50 g/batch of catalyst.*	1/31/14	1/31/14	Quarterly report
1	4	*At least 5% enhancement in mass transfer verified compared to the uncatalyzed*	9/30/14		Quarterly report
1	5	*Technical support and input from WP received regarding cost of chemicals, membrane, and flow diagram received.*	7/31/14		Quarterly report
1	6	*Completion of preliminary health and safety analysis on proposed solvent*	4/30/14	4/30/14	Topical report to DOE

CAER CENTER FOR APPLIED ENERGY RESEARCH

Acknowledgements

UK

The work presented here was made possible through funding by:

- The U.S. DOE/ National Energy Technology Laboratory
- Carbon Management Research Group: Duke Energy, EPRI, LGE&KU, DEDI, AEP

DOE	CAER Center for Applied Energy Research	CMRG	SMG	WorleyParsons resources & energy
• Lynn Brickett • Mike Matuszewski •Jose Figueroa	•Heather Nikolic •Jesse Thompson •Lisa Richburg •Rachael Burrows •C. Brandewie •Naser Matin •Collin Dunn •Reynolds Frimpong •Payal Chandan	• John Moffett • David Link • Michael Manahan • Brandon Delis • John Rogness • Abhoyjit Bhown • Curtis Sharp	• Clayton Whitney • Sarah Carty	• Mike Bartone •Vlad Vaysman


Thank You