Integrated Electrochemical Processes for CO$_2$ Capture and Conversion to Commodity Chemicals

Project Number: DE-FE0004271

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Presentation Outline

• Motivation, Goals, Objectives
• Background
• Cyclic Carbonate Synthesis via Catalytic Coupling of CO$_2$ and Epoxides
• Cyclic Carbonate Synthesis via oxidative carboxylation using CO$_2$ and Olefins
• Conclusions
Benefit to the Program

• Identify the Program goals being addressed.
  – Develop technologies to demonstrate that 99 percent of injected CO₂ remains in the injection zones.
• The research project is developing a novel approach to capturing and converting CO₂ into commodity chemicals, which may thus reduce the burden on CO₂ storage sites, in addition to providing a means to reduce anthropogenic CO₂ emissions and an inexpensive method for producing useful materials from CO₂.
Project Overview: Goals and Objectives

- To develop and demonstrate a novel chemical sequestration technology that utilizes CO$_2$ from dilute gas streams generated at industrial carbon emitters as a raw material in order to produce useful commodity chemicals.
  - **Single** electrochemical system for CO$_2$ capture and chemical conversion
  - **Coupled** system for CO$_2$ capture and chemical conversion
Project Overview: Goals and Objectives

• To develop and demonstrate a novel chemical sequestration technology that utilizes CO₂ from dilute gas streams generated at industrial carbon emitters as a raw material in order to produce useful commodity chemicals.
  – Single electrochemical system for CO₂ capture and chemical conversion
  – Coupled system for CO₂ capture and chemical conversion
Technical Status
Accomplishments to Date

– A novel catalytic method for the continuous chemical conversion of CO$_2$ has been developed and thoroughly investigated mechanistically.

– A mechanism-guided design of sequential continuous flow systems has been developed to achieve a variety of carbonates using CO$_2$ and olefins.
  • Detailed mechanistic exploration.
  • Several advantages over existing methods.
  • Springboard for development of several other classes of CO$_2$ conversion.
Motivation for CO₂ Capture, Sequestration, and Conversion

• Anthropogenic carbon dioxide (CO₂)
  • considered a primary cause of global climate change
  • coal-fired power plants, and the petroleum and natural gas industries account for 86% of anthropogenic CO₂
  • we will continue to depend on non-renewable fossil fuels for the next several decades

• The CO₂ cycle is not balanced
  • 3.9% excess (caused by anthropogenic CO₂) with respect to the yearly CO₂-flow in the natural “carbon cycle”
  • Only 30-35% of the chemical energy content associated with anthropogenic CO₂ emissions is converted into various forms of energy.
  • 65-75% is lost as heat to the Earth’s atmosphere.

Carbon Dioxide as a Chemical Feedstock

- What is the motivation for producing chemicals from CO$_2$?

- CO$_2$ is an inexpensive, non-flammable, non-toxic feedstock that is stable, easy to store, and readily available.
- It can be used to replace toxic chemicals such as phosgene and isocyanates.
- CO$_2$ is a renewable resource, as compared to oil or coal; the future supply of fossil fuels is considered limited.
- The use of CO$_2$ in new routes to existing chemical intermediates and products could be more efficient and economical than current technologies.
- The production of chemicals from CO$_2$ could have a small but likely significant positive impact on the global carbon balance.
- CO$_2$ is an exceptionally inexpensive source of carbon, at ~0.1¢/mol.
- For comparison: Ethylene, ~3¢/mol (1.5¢/mol of C atoms); propylene, (~5¢/mol, 1.5¢/mol of C atoms).

Gas/Liquid Continuous Flow Chemistry

Traditional batch reactions:
- Low interaction and mass transfer
- Interfacial area of ca. 100-300 m²/m³<sub>liq</sub>
- High capital and infrastructure costs
- Associated safety factors

Continuous flow synthesis:
- Exceedingly high surface-to-volume ratio
- Efficient heterogeneous mass-transfer
- Excellent reproducibility
- Reduced equipment footprint and labor work
Conversion of CO$_2$ Using Epoxides

Bromine-catalyzed conversion of CO$_2$ and epoxides to cyclic carbonates:

\[
\begin{align*}
\text{CO}_2, \text{DMF, 120 °C} & \quad \rightarrow \quad \text{5 mol %} \\
\text{Ph} & \quad \text{5 mol %} \\
\text{Ph} & \quad \text{(benzoyl peroxide = BPO)} \\
\end{align*}
\]

Batch Results (6 h): 75 % yield
Flow Results (30 min): 90-98 % yield

- polar aprotic solvents
- electrolytes in lithium ion batteries
- constituents in oils and paints
- antifoam agents for antifreeze and plasticizers
- raw materials for the synthesis of polycarbonates and polyurethanes

 Slug flow reduces dispersion; provides efficient mass transfer contact
Well-controlled conditions for evaluation of reaction kinetics and mechanisms
Kinetic Study

\[ \frac{d[\text{Epoxide}]}{dt} = -\left( k_{10}^{\text{exp}} + k_1^{\text{exp}} [BPO]_0[NBS]_0 \right)[\text{Epoxide}] \]
Proposed Mechanism Based on Kinetics Investigations

\[ r_{overall} = \frac{k_4 k_{r4} [k_{10} + k_1 [BPO]] [NBS] [Epoxide]}{2(k_4^2 - k_{r4}^2)} \]
Capture of CO₂ Using Simple Olefins

Mechanism-guided flow design to avoid reagent incompatibility:

Originally designed multi-stream flow

- Low reaction rate (especially for aliphatic olefins)
- Reagent incompatibility (such as DBU and NBS)

Low solubility of olefins in DMF/H₂O
Interaction between NBS and DBU
(DBU = 1,8-diazabicycloundec-7-ene)
Dibromide formation promoted by DBU; form bromohydrins before addition of DBU

Mechanism-guided design of flow

- Significantly enhanced rate
- Minimized by-products
- High yield
- Wide substrate scope
Possible Reaction Pathways

Ph\(\rightarrow\)NBS (1 equiv), DBU (1.6 equiv)
\(\rightarrow\)H\(_2\)O (1.5 M), CO\(_2\) (300 psi)
3 h, Parr reactor
92% conversion

DBU activated CO\(_2\)

Path a: NBS
Path b: DBU activated CO\(_2\)
Path c: water induced bicarbonate anion
Path d: Bromohydroxylation pathway

Bromohydrin generated from olefins and NBS in water.
Mechanistic Study

- Water was necessary
- DBU significantly decreased the rxn rate (indicated formation of DBU-NBS complex)
- CO₂ increased the reaction rate (indicated DBU-CO₂ complex formation)
- DMF helped formation of epoxide.

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<th>yield of A</th>
<th>other products</th>
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<td>100%</td>
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<td>87% C</td>
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<td>2</td>
<td>NBS + H₂O + DBU</td>
<td>26%</td>
<td>0%</td>
<td>15% D</td>
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<td>3</td>
<td>NBS + H₂O + DBU + CO₂</td>
<td>84%</td>
<td>55%</td>
<td>8% D</td>
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<td>4</td>
<td>NBS + DMF + DBU + CO₂</td>
<td>50%</td>
<td>0%</td>
<td>45% B</td>
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</table>

\(^a\) Conversion and yield are based on analysis of crude \(^1\)H NMR spectra using trichloroethylene as the external standard.
Initial Two-Stream Gas/Liquid Flow Setup

Stream 1: Gas
- 
  - CO₂
  - mass flow controller
  - pressure gauge
  - packed-bed reactor
  - 6-way valve
  - sample loop
  - slow bleed
  - bomb (bulk collection)
  - N₂

Stream 2: Liquid
- reagents
- syringe (EtOAc)
- sample collection

Reactions:
- NBS (1.2 equiv), DBU (1 equiv), DMF/H₂O (2:1, 0.4 M)
- CO₂ (130 psi), V₉/V₁ = 1:1,
- 100 °C, 7.5 min

Results:
- Ph : 100% conversion, 85% yield
- PhO : 15% conversion, 10% yield

Packed-bed flow reactor
Sequential Transformations in Flow

NBS (1.2 eq) in acetone for 30 min, 40 °C

NBS (1.2 eq) in acetone for 30 min, 40 °C

H₂O + DBU (1.3 eq) for 10 min, 100 °C

NH₄OAc (0.1 eq) in H₂O

75%

72%

43%

71%

79%

82%

85%

73%

80%

85%

72%

72%

89%

49%

52%

87%

85%

88%

48%
Sequential Flow Setup
Comparison of sequential transformations between batch and flow:

**Batch**
- NBS (1.2 equiv), NH₄OAc (0.1 equiv), acetone/H₂O (2:1), 40 °C, 30 min
- DBU (2.5 equiv), H₂O, CO₂ (250 psi), Parr reactor, 100 °C, 30 min
- 100 % conversion
- 15% epoxide products
- 45% carboxylic acid

**Flow**
- NBS (1.2 equiv), NH₄OAc (0.1 equiv), acetone/H₂O (2:1), 40 °C, 30 min
- DBU (2.5 equiv), H₂O, CO₂ (120 psi), 100 °C, 10 min
- 100 % conversion
- No epoxide products
- 73% carboxylic acid

Sequential Transformation in Flow
Sequential Transformation in Flow

**Feature**
- sequential reactions
- excellent surface-to-volume ratio
- packed-bed reactor
- acetone as co-solvent
- elevated temperature and pressure
- no headspace

**Function**
- significantly enhances the reaction rate; avoids reagent incompatibility
- increases the reaction rate; suppresses byproduct formation
- increases the reaction rate; more steady flow
- avoids phase-transfer-reagents
- provides rate enhancement
- reduced equipment footprint (safety)
An Integrated Capture and Conversion System

Organocatalytic Route - with decoupled capture and conversion units

Carbon Conversion Unit

Organocatalytic Route - with decoupled capture and conversion units

Carbon Capture Unit

“Electrochemically-Mediated Amine Regeneration”
Absorber
Syringe Pump
EMAR Pump
Power Supply
Gas/Liquid Separator
EMAR Cell
Coil Reactor
Heated Water Bath
Summary

– Key Findings
  • A novel mechanism of epoxide activation was discovered, and its impact may be very broad.
  • A sequential flow system works best for the conversion of CO$_2$ using olefins due to the incompatibility between DBU and NBS.

– Lessons Learned
  • Continuous processing is superior to batch for elucidation of conversion mechanisms and kinetics
Acknowledgments

– MIT
  • Dr. Jie Wu
  • Dr. Jennifer A. Kozak
  • Xiao Su
  • Dr. Fritz Simeon
  • Prof. Timothy F. Jamison
  • Prof. T. Alan Hatton

– Siemens (Life Cycle Analyses)
  • Dr. Elena Arvinitis
  • Dr. Noorie Rajvanshi
  • Dr. Amit Kapur

– DOE-NETL
  • Dr. Bill O’Dowd
Appendix

– These slides will not be discussed during the presentation, but are mandatory
Gantt Chart
Department of Energy

Project Management:
Prof. T. Alan Hatton (MIT)
(Technical Point of Contact)

Technology Development:
Prof. T. Alan Hatton (MIT)
Prof. Timothy F. Jamison (MIT)

Team Members:
Dr. Fritz Simeon (MIT)
Dr. Jennifer A. Kozak (MIT)
Dr. Jie Wu (MIT)
Su Xiao (MIT)

Life Cycle Assessments:
Dr. Elena Arvanitis (Siemens)
Dr. Noorie Rajvanshi (Siemens)
Dr. Amit Kapur (Siemens)
<table>
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<tr>
<th>Sub-Task</th>
<th>Project Milestone Description</th>
<th>Project Duration: 10/01/2010-09/30/2013</th>
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<td>Investigate the impact of quality of CO₂ gas stream on the chemical conversion process</td>
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<td>Evaluate the activity of recycled catalyst in flow micro-reactor</td>
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Publication:


Conference Presentation:


## Gantt Chart (continued)

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