Sustainable CO$_2$ Capture & Conversion Technologies

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Overview

• Introduction
• 3-stage approach
• Framework
• Application
• Conclusions
• Outlook
Global scenario

Population growth

Increasing demands (energy, food, water, etc.)

More manufacturing (chemicals, cement, etc.)

Increasing emissions and waste

Global warming

Development that meets the needs of the present without compromising the ability of future generations to meet their own needs – Brundtland report

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CO₂ reduction strategies & CCU

• Carbon capture and storage (CCS)
  + Long-term storage
  – Offers no economic incentive

• Carbon capture and utilization (CCU)
  + Value-added products
  – Mostly immature processes

• Improved energy efficiency
  + Truly emission reducing
  – Lack of technology
Motivation & objectives

• Need sustainable capture and utilization processes

• Constrained by:
  – Early stage technology → limited information
  – Limited reaction and catalyst information

• Method used here:
  – 3-stage framework to decompose problem
  – Assisted by computer-aided methods and tools
  – Sustainability analysis
3-stage approach

Stage 1: Synthesis
Objective: determine optimal processing route and product for CO₂ conversion process
Input: Objectives and problem definition (materials, locations, etc.)
Output: Optimal processing network and results
Tools: Database, generic model, Super-O, GAMS

Stage 2: Design
Objective: design and analyze CO₂ conversion process to obtain targets for improvement
Input: Optimal processing route
Output: Stream tables, equipment design, economic parameters, sustainability indicators, hot spots and targets for improvement
Tools: Database, simulation software, analysis tools

Stage 3: Innovation
Objective: to find innovative and more sustainable designs
Input: detailed design and analysis information and targets for improvement
Output: improved design with corresponding design and analysis information
Tools: Database, simulation software, analysis tools, Process Intensification method (Babi et al., 2015)

Can be stepped into at any stage depending on available information
Framework – Stage 1

Step 1.1: Problem definition
Define objectives (raw materials, products, etc.)

Step 1.2: Superstructure generation and data collection
- Generate superstructure
- Collect data
- Check consistency
- Modify model (if necessary)

Step 1.3: Solution of the optimization problem
- Generate input file, solve optimization problem, generate output file
- Perform post-optimality calculations

Stage 2
Framework – Stage 2

Step 2.1: Detailed design and simulation
Perform detailed equipment design and simulation of selected process

Step 2.2: Process optimization
Optimize process operating conditions, design parameters, etc. (if necessary)

Step 2.3: Analysis
Perform economic and sustainability analyses
Use hot spots to determine targets for improvement

Stage 3

Literature Databases Models Software tools

Optimized design, stream tables, etc.

Economic parameters, sustainability indicators, targets for improvement

Framework – Stage 3

• Use the targets from Stage 2 analysis

• Use of Process Intensification (PI) and unique process integration
  – Innovative designs
  – Improved sustainability

• PI involves phenomena-based method developed by Babi et al. (2015)

*Computers and Chemical Engineering*
Important methods and tools

• Reaction Path Synthesis (RPS) → determine all feasible reactions from CO₂ to desired products
• Database → facilitate the storage and retrieval of data
• Generic model → allow solution of a variety of problems
• Simulation library → enable easy reuse of simulations
## Tools

### Reaction Path Synthesis

<table>
<thead>
<tr>
<th>Step</th>
<th>Criteria</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C, H, O compounds, max chain length 7, max 2 functional groups</td>
<td>&gt; 100 products</td>
</tr>
<tr>
<td>2</td>
<td>All chemically feasible reactions CO2 to the target products</td>
<td>&gt; 1000 reactions</td>
</tr>
<tr>
<td>3</td>
<td>Only thermodynamically feasible reactions</td>
<td>&gt; 150 reactions</td>
</tr>
<tr>
<td>6</td>
<td>Kinetic information available in literature</td>
<td>&gt; 20 reactions</td>
</tr>
</tbody>
</table>

### Database

<table>
<thead>
<tr>
<th>Number of feedstocks</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of products</td>
<td>13</td>
</tr>
<tr>
<td>Number of steps</td>
<td>25</td>
</tr>
<tr>
<td>Number of intervals</td>
<td>91</td>
</tr>
<tr>
<td>Number of components</td>
<td>36</td>
</tr>
<tr>
<td>Number of utilities</td>
<td>3</td>
</tr>
<tr>
<td>Number of reactions</td>
<td>37</td>
</tr>
</tbody>
</table>

### Simulation Library

<table>
<thead>
<tr>
<th>Number of Simulations</th>
<th>&gt;60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Products produced</td>
<td>11</td>
</tr>
<tr>
<td>CO₂ feedstocks considered</td>
<td>4</td>
</tr>
</tbody>
</table>
Application

• Goal: sustainable CO$_2$ conversion processes
• Raw material: captured CO$_2$ (Fjellerup MSc Thesis, 2015)
• Reactions & products: determined via Reaction Path Synthesis (RPS)
Stage 1 results
## Stage 1 results

<table>
<thead>
<tr>
<th><strong>Objective function (OF)</strong></th>
<th><strong>Scenario 3</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sales – OPEX – CAPEX</td>
</tr>
<tr>
<td><strong>Number of equations (NEQ)</strong></td>
<td>4,255,204</td>
</tr>
<tr>
<td><strong>Number of variables (NV)</strong></td>
<td>4,229,505</td>
</tr>
<tr>
<td><strong>Number of discrete variables (NDV)</strong></td>
<td>426</td>
</tr>
<tr>
<td><strong>Problem type</strong></td>
<td>MIP</td>
</tr>
<tr>
<td><strong>Solver</strong></td>
<td>CPLEX</td>
</tr>
<tr>
<td><strong>Execution time (seconds)</strong></td>
<td>10.499</td>
</tr>
<tr>
<td><strong>Sales (MM USD/y)</strong></td>
<td>100.4</td>
</tr>
<tr>
<td><strong>OPEX (MM USD/y)</strong></td>
<td>65.8</td>
</tr>
<tr>
<td><strong>CAPEX (MM USD)</strong></td>
<td>20.5</td>
</tr>
<tr>
<td><strong>Profit (MM USD/y)</strong></td>
<td>32.55</td>
</tr>
</tbody>
</table>
Stage 2

**CAPEX (MM USD)**
- 54.3

**OPEX (MM USD/y)**
- 57.8

**NetCO₂ (kgCO₂/kgDMC)**
- -0.36

**Yield**
- 1.7

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**Bottleneck: energy intensive separation** → Target for improvement


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Stage 3

Address target for improvement → Process intensification (Babi et al, 2015)

Reactive distillation (RD) → excess MeOH to avoid EC/EG separation

Extractive distillation (ED) → overcome DMC/MeOH azeotrope

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Integrated capture and conversion

K. Fjellerup, MSc Thesis, DTU, 2015


<table>
<thead>
<tr>
<th></th>
<th>Capture</th>
<th>Methanol</th>
<th>DMC</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPEX (MM USD)</td>
<td>0.1</td>
<td>19.4</td>
<td>54.3</td>
<td>73.8</td>
</tr>
<tr>
<td>OPEX (MM USD/y)</td>
<td>0.9</td>
<td>2.1</td>
<td>57.8</td>
<td>60.8</td>
</tr>
<tr>
<td>NetCO₂</td>
<td>0.13 kg CO₂/kg captured</td>
<td>-0.7 kg CO₂/kg MeOH</td>
<td>-0.36 kg CO₂/kg DMC</td>
<td>-0.7 kg CO₂/kg DMC</td>
</tr>
</tbody>
</table>

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Conclusion

• 3-stage framework for the sustainable design of CO$_2$ capture and utilization processes

• Incorporates various computer-aided methods and tools

• Database and simulation library to facilitate storage and retrieval
Future work

• Consider various scenarios to understand influence of price, demand, etc.

1. Operating cost – utility cost
2. Operating cost
3. Capital cost + operating cost
4. Product price
5. Demand
6. Location
7. Price sensitivity
Future work – Scenario 4

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Outlook

• Current reduction potential of conversion technology < 10%

⇒ A combined approach to tackling CO₂ emissions is necessary

IPCC, 2014. Climate Change 2014: Mitigation of Climate Change
Thanks for listening!

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References


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KT Consortium Annual Meeting, 2017 7th June, 2017
References


S. Cignitti, 2014. Computer-aided Reaction Path Synthesis, MSc Thesis. Technical University of Denmark (DTU), Kgs. Lyngby, Denmark

K. Fjellerup, 2015. Sustainable Process Networks for Carbon Dioxide Conversion, MSc Thesis Technical University of Denmark (DTU), Kgs. Lyngby, Denmark
