Monolithic Piston-Type Reactor for Hydrogen Production through Rapid Swing of Reforming/Combustion Reactions

Project ID #PD111

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Pacific Northwest National Laboratory
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This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline

- Start – November 2014
- End – October 2017
- 15% Complete

Budget

- Total Project Budget – $2,755K
- Total Recipient Share – $555K
- Total Federal Share – $2,200K
- Total DOE funds spent* – $350K
  *as of 3/31/15

Barriers

- Barriers addressed:
  - Plant capital cost and efficiency (unit scale of economy)
  - Operations and Maintenance (O&M)

- Target:
  - Cost of distributed $\text{H}_2$ from bio-mass to <$4$/Kg $\text{H}_2$

Partners

- Cormetech
  - Monolith support
  - Catalyst/sorbent commercialization
- Washington State University
  - Reforming catalysis and kinetics
- Dason Technology
  - Integrated test apparatus
  - Process development
Relevance - H2A analysis (HPTT feedback)

Impacts of production technology innovations on H₂ cost

- $0.98/gal; 1 kg H₂ / 9 kg bio-oil
- 28% lower capital via simplified processing
- 50% reduced operation costs via efficient energy integration
- 49% lower bio-oil cost

* PNNL-23053, NREL/TP-5100-61178
** S Czernik et al, 2010 AMR, Washington, D.C., NREL/PR-560-48066
*** NREL/TP-510-37779
Relevance
Facilitating DOE’s H₂ Cost Goal = $4/gge

Bio-oil reforming technology advancements being pursued in this work

1. Reduced Capital Costs of Plant
   - Minimizing unit operations (e.g., no furnace requirements)
   - Smaller PSA, smaller (or possible elimination of) WGS, no air separation
   - Process simplification minimizes BOP components

2. Increased Energy Conversion Efficiency
   - In situ CO₂ capture, push thermodynamics of reforming to higher conversion
   - In situ heat exchange between reaction & regeneration to minimizes heat loss
   - 80% energy conversion efficiency achievable (versus 71.4% for methane reforming, 2011 status)

3. Increased Durability
   - Reduced O&M (operations & maintenance) requirements
   - Directly addresses coking & catalyst deactivation
   - Modular, compact reactors to make unit turn-around easier
Approach – our process innovations
Reduce unit process steps and intensify heat/mass transfer

Typical commercial processes for centralized H₂ production

- Hydrocarbon (methane) + steam
- Air
- Fuel
- Flue gas
- High-T furnace
- Steam-reforming reactor
- Water-gas-shift reactor
- Pressure swing adsorption (PSA)
- CO₂ mix
- Pure H₂

Present process

- Bio-oil + steam
- Air
- Reduce unit process steps
- Integrated reforming/CO₂ sorption reactor
- PSA
- CO₂ mix
- Pure H₂
- Enriched H₂

Project focuses:

- Compact, high throughput, low-cost reactor
- Effective and stable catalyst and sorbent materials
- High system energy efficiency

Rapid swing reactor operation

- Address catalyst deactivation & sorbent saturation by periodic regeneration
- Make in-situ heat transfer
Approach – monolith reactor innovation for rapid (1-10 min) swing operation

**Reforming conditions:**
- $T < 600^\circ\text{C}$, $P < 24$ bar
- Endothermic steam-reforming reaction
- Coking & de-oxygenation reaction
- Exothermic carbonation reaction

**Regeneration conditions:**
- $T < 750^\circ\text{C}$, $P \sim 1$ bar
- Exothermic coke combustion
- Endothermic carbonate decomposition

**Design features:**
- Place catalyst/sorbent at the same spot to achieve rapid mass and heat transfer
- Have straight flow channels to minimize dead space and pressure drop
- Fix the sorbent and catalyst to avoid attrition and hydrodynamic erosion
**Approach - materials innovation for integrated steam-reforming and CO₂ carbonation**

**Composite catalyst of synergistic functions**
- Provide redox and acidic sites for concerted cracking and reforming and reactions
- Be activated by air calcination

\[
\begin{align*}
    H_2O & \rightarrow H_2, CO_2, R_i \\
    C_nH_mO_k & \rightarrow H_2 + R_2-CH_2-R_1 \rightarrow R_2-CH_3 + HR_1 \\
    H_2O + [-cat] & \rightarrow [O]-cat + H_2
\end{align*}
\]

**CO₂ sorbent with tailored properties**
- Work under the reforming conditions
- Provide adequate working capacity, rapid kinetics, and stability

\[
\begin{align*}
    HC + [O]-cat & \rightarrow CO_2 + H_2O + [-cat] \\
    H_2O + [-cat] & \rightarrow [O]-cat + H_2
\end{align*}
\]

- Reforming catalysts are designed based on team’s previous experiences and synergistic catalyst design model
- CO₂ sorbents are formulated based on previous CO₂ capture studies at PNNL

Approach - milestones addressing three critical challenges

**Milestone 1 (FY15) – material innovations**: development of optimum reforming catalysts and in-situ CO₂ sorbents under proposed operation conditions (*single-tube reactor tests at gram levels*)
- H₂ productivity (0.6 [kg-H₂/h]/kg of catalyst)
- CO₂ capture productivity >0.2 [kg-CO₂/h]/kg of sorbent

**Milestone 2 (FY16) – monolithic reactor innovation**: demonstration of in-situ CO₂ capture for pure H₂ production and catalyst/sorbent stability (*single-tube & integrated reactor tests in tens of g level*)
- >100 cycles of reforming/regeneration tests with production of >90% pure H₂ at GHSV >10,000 v/v/h
- Update techno-economic analysis

**Milestone 3 (FY17) – process innovation**: Demonstration of an integrated reactor system with technical readiness level ≥ 4 (*tests in hundreds of g level*)
- H₂ production capacity =2 kg/day, >90% H₂ in reactor, >99% H₂ after PSA
- ≥10 wt% H₂ yield
- A mobile testing skid for continuous swing reactor operation
Collaboration and technology transfer

Prof. Yong Wang
Washington State Univ.
- Fundamental understandings and discovery of new reforming catalysis
- Catalyst characterization and kinetics studies

Dr. Chris Bertole
Cormetech
- Development of monolith support of tailored properties

PNNL
- New technology innovations (material, reactor, process)
- Critical process or product concept studies

Dr. Bang Xu
Dason Technology
- Reactor system tests and process development

Scale-up, manufacture, and commercialization of monolith support & catalyst

Process design, engineering and field tests for process commercialization

Future

Future
Accomplishment & Progress

**Versatile laboratory-bench system built for reaction/sorption tests**

**Single-tube reactor**

- Different sizes of reactor tubes
- Particle-packed and monolith-inserted beds
- Rapid temperature or pressure swing
- Multi-cycle operation
- Tests of new materials and new process concepts

**Schematic of test apparatus**

**Control system**
### Accomplishment & Progress

**CO₂ sorbents prepared in-house and screened by TGA tests**

<table>
<thead>
<tr>
<th>Material + promoters</th>
<th>Working capacity measured with multiple cycles of CO₂ sorption/air purge, wt% [sorption↔regeneration temperature]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>360°C↔450°C</td>
</tr>
<tr>
<td>MgO</td>
<td>60% 1ˢᵗ cycle &lt;1% cycles 2+</td>
</tr>
<tr>
<td>MgO +Na₂CO₃</td>
<td>15% stable</td>
</tr>
<tr>
<td>CaO</td>
<td>Temperature too low for regeneration</td>
</tr>
<tr>
<td>Decomposed dolomite</td>
<td>5-8% stable</td>
</tr>
</tbody>
</table>

**Promising sorbent materials and respective operating temperatures are identified in GREEN**

- Promoted MgO-Na₂CO₃ and dolomite sorbents prepared for packed bed testing
- Packed bed tests are ongoing
- Design and preparation of new sorbents is ongoing
Accomplishment & Progress

Temperature variation due heat of CO₂ sorption in a particle-packed bed

- Pronounced temperature variations shown in such a small particle-packed bed (1/2” OD tube)!
- Efficient heat transfer is important
- The results affirm present approaches:
  - In situ coupling of endothermic reforming reaction with exothermic CO₂ capture
  - In situ coupling of exothermic coke combustion with endothermic CO₂ desorption

Degree of temperature rise-up decreased by reducing p_CO₂ from 1.0 to 0.2 bar
Presence of steam promotes working capacity of a MgO-based sorbent

- Rapid sorption/desorption kinetics is shown
- Sorbent can be regenerated by either PSA or TSA
- Presence of steam slightly stabilizes the sorbent performance, promising for usage under steam-reforming conditions

**Adsorption conditions:** 390°C, 1 bar, 20% CO₂, GHSV = 4,200 l/h

**Regeneration conditions:** 450°C, 1 bar, air

**Break-through curves with dry gas**

**Break-through curves with 30% H₂O**
A metal oxide nano-composite catalyst showed significant reforming activity at 400°C.

Deactivation by coking occurred rapidly and activity could not be restored by raising temperature.

Catalytic performances are drastically affected by bio-oil flow distribution.
Accomplishment & Progress

**TiO$_2$ monolith support prepared and catalyzed for reforming reaction**

**Core-drilled 20mm x 120mm monolith (~300cpsi) for 1-inch reactor**

- Monolith integrity and porous structures are maintained at high calcination temperature.

- Significant amounts of the catalyst can be loaded with uniform textures.

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![Image of monolith](image1.png)

Approximately 1-mm channel

0.36mm wall thickness

![Image of TiO$_2$ monolith](image2.png)

TiO$_2$ monolith channel wall impregnated with reforming catalyst

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**Graph 1:**

- BET surface area vs. Calcination temp, °C

**Graph 2:**

- BET surface area vs. Catalyst loading, wt%

- Pore volume vs. Catalyst loading, wt%
Accomplishment & Progress
Integrated testing system designed and being built

**Process flow diagram finalized for integrated testing unit**

![Process Flow Diagram](image)

**Scale of Development**

- **H₂ production, kg/day**
  - Year 1 – 0.51
  - Year 3 – 2.54
  - Commercial – 1525

- **Reactor dimension**
  - Year 1 – 1 in.
  - Year 3 – 2 in.
  - Commercial – ~40 in.

- **Reforming catalyst**
  - Year 1 – 20 grams
  - Year 3 – 40 grams
  - Commercial – 60 kg

- **CO₂ sorbent**
  - Year 1 – 162 grams
  - Year 3 – 808 grams
  - Commercial – 485 kg

**Design specifications:**

500°C [reforming] ↔ 600°C [regeneration]

- 10wt% CO₂ sorbent working capacity
- 10 [g/hr]/g-catalyst bio-oil SV
- 2:1 H₂O:bio-oil
- 80% single pass conversion
- 80%/20% carbon yield to reforming/coke
- 90% CO₂ capture

- **Capability to recycle un-converted bio-oil**

**Progress:**

- Designs of key equipment are completed
- Vendor quotes are acquired and procurement is ongoing
## Remaining barriers and challenges, and proposed future work

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Challenges</th>
<th>Proposed approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-T, regenerative reforming catalyst</td>
<td>Bio-oil flow distribution</td>
<td>FY15: New designs of distributor and reactor bed package</td>
</tr>
<tr>
<td></td>
<td>Regeneration and stability, and activity enhancement</td>
<td>FY15: More catalyst designs and preparation, more reforming/regeneration tests</td>
</tr>
<tr>
<td>In-situ CO₂ sorbent</td>
<td>Matching of CO₂ sorption/regeneration conditions with steam-reforming</td>
<td>FY15: Tailoring CO₂ sorbent properties and more sorption process parametric tests</td>
</tr>
<tr>
<td>Monolith reactor integration</td>
<td>Material integration of reforming catalyst and CO₂ sorbent into TiO₂ monolith structures</td>
<td>FY16: Tailoring and understanding of monolith properties as a sorbent and catalyst support</td>
</tr>
<tr>
<td></td>
<td>Synchronization of reforming reaction and CO₂ capture processes in the monolith structure</td>
<td>FY16: Operation of the integrated reactor testing system and parametric process tests</td>
</tr>
</tbody>
</table>
# Summary

<table>
<thead>
<tr>
<th>Material preparation &amp; characterization</th>
<th>First group of TiO₂ monoliths prepared</th>
<th>Cormetech</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A few groups of new reforming catalysts prepared and tested, including monolith-supported ones</td>
<td>WSU &amp; PNNL</td>
</tr>
<tr>
<td></td>
<td>Review of recent literature on CO₂ sorbent and bio-oil reforming completed</td>
<td>PNNL</td>
</tr>
<tr>
<td></td>
<td>Two promising CO₂ sorbents identified by TGA tests for respective low-T and high-T sorption</td>
<td>PNNL</td>
</tr>
<tr>
<td>Adsorption &amp; reaction tests</td>
<td>Single-tube reactor testing capabilities built</td>
<td>PNNL</td>
</tr>
<tr>
<td></td>
<td>Rapid kinetics and initial stability of the low-T CO₂ sorbent in presence of H₂O confirmed by packed bed tests</td>
<td>PNNL</td>
</tr>
<tr>
<td></td>
<td>Two promising low-T reforming catalysts identified by respective model compound and actual bio-oil reforming tests</td>
<td>WSU &amp; PNNL</td>
</tr>
<tr>
<td>Process research and development</td>
<td>A provisional patent application was filed “An integrated reactor unit for H₂ production”</td>
<td>PNNL</td>
</tr>
<tr>
<td></td>
<td>Design of integrated test unit finalized and procurement of major components in progress</td>
<td>Dason Technology</td>
</tr>
</tbody>
</table>
Technical Back-Up slides (optional)
**Exothermic coke combustion for catalyst regeneration:**
\[ C_{n-2k}(coke)-cat + 0.5(2.5n-k)O_2 \rightarrow 0.5(n-2k)H_2O + nCO_2 + \Delta H(<0) \]

**Endothermic carbonate decomposition:**
\[ MCO_3 \rightarrow CO_2 + MO + \Delta H(>0) \]

**Endothermic steam-reforming (SR) reaction:**
\[ C_nH_mO_k + (2n-k)H_2O \rightarrow (0.5m+2n-k)H_2 + nCO_2 \]

**Coking & de-oxygenation reaction:**
\[ C_nH_mO_k + Cat \rightarrow C_nH_{n-2k}(coke)-cat + kH_2O \]

**Exothermic carbonation reaction:**
\[ CO_2 + MO \rightarrow MCO_3 \]

**Reforming conditions:**
- T < 500°C
- P < 300 psi (24 bar)

**Regeneration conditions:**
- T < 600°C
- P ~ 1 bar

**In situ coupling of endothermic steam reforming with exothermic carbonation**

**In situ coupling of exothermic coke combustion with endothermic carbonate decomposition**

**Thermal momentum transfer between reactors**
Co2 sorbent materials reported in the literature:

<table>
<thead>
<tr>
<th>CO2 sorbents that may work under reforming conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>• CaO-based: MgO-CaO, TiO2-CaO, Li2CO3-CaO</td>
</tr>
<tr>
<td>• MgO-based: K2CO3-MgO, Cs2CO3-doped MgO, KNO3-MgO, alkaline and alkaline earth-promoted MgO</td>
</tr>
<tr>
<td>• Other compounds: Na2Mg(CO3)2, Li8SiO6 mixed with (K-, Na-carbonates), lithium silicate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CH4 steam reforming with in-situ CO2 capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>• CeZrOx-CaO + Ni/hydrotalcite</td>
</tr>
<tr>
<td>• Mg1-xAlx(OH)2(CO3)x or Lithium zirconate +Rh/Ce,aZr1-aO2</td>
</tr>
<tr>
<td>• commercial K2CO3-promoted HTC from SASOL + Ni/alumina</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bio-oil steam reforming with in situ CO2 capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Dolomite + Ni/La2O3-Al2O3</td>
</tr>
</tbody>
</table>

- CaO-based sorbents typically require regeneration above 700°C, and the sorbent tends to deactivate with cycle.
- A stable CO2 sorbent with fast kinetics has not been shown yet through sorption/regeneration cycles.
**Accomplishment & Progress**

**Bio-oil reforming catalyst background studies and preparation**

Literature review conducted to understand pros/cons of different catalysts studied, and to address critical needs in this project work

<table>
<thead>
<tr>
<th>Commercial catalyst</th>
<th>Z417, C11-NK and NREL#20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni on different support</td>
<td>Ni/alumina, Ni/La-alumina, Ni/CaAl$_2$O$_4$, Ni/CeO$_2$–ZrO$_2$; Ni/HZSM-5(Si/Al=25), Ni/CNFs catalyst</td>
</tr>
<tr>
<td>Ni (+ additive)</td>
<td>Ni (+ additive)/ Al$_2$O$_3$, NiCu/MgCe/Al mixed oxides</td>
</tr>
<tr>
<td>Previous metal</td>
<td>Ru/MgO/Al$_2$O$_3$, 1%Pt/Al$_2$O$_3$, Rh or Ir/CaAl$_2$O$_4$</td>
</tr>
<tr>
<td>Mixed metal oxide</td>
<td>Ni–Al modified with Mg and Ca 2CaO -7Al$_2$O$_3$ doped with Mg, K or Ce</td>
</tr>
</tbody>
</table>

- Most catalysts are studied at reaction temperatures > 500°C.
- Catalyst deactivation is common problem. Coke formation is the major cause, more pronounced in the Ni-based catalysts.
- No regeneration and stability of the catalysts have been reported.
Technical Accomplishments – Task 1
thermodynamic analysis of CO$_2$ sorbent design

- MgO is in the lower working temperature range for present application
- CaO is in the higher end
- Compounds are likely needed to shift the CO$_2$/MgO equilibrium toward higher temperature

![Diagram showing thermodynamic analysis of CO$_2$ sorbent design](image-url)
Technical Accomplishments – Task 1

*MgO/Na$_2$CO$_3$ (in-house) and CaO sorbent performances*

\[ \text{MgO} + \text{CO}_2 + \text{Na}_2\text{CO}_3 \leftrightarrow \text{Na}_2\text{Mg(CO}_3)_2 \]

- A stable sorbent at 400/500ºC working/regeneration temp.

\[ \text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 \]

500ºC ↔ 600-750ºC

- >700ºC regen required
- Addition of carbonates
  - decreased working capacity
  - did *not* lower regeneration temperature
Technical Accomplishments – Task 1

Performances of dolomite-derived CO$_2$ sorbent at high $T$

Dolomite-derived sorbent
MgO + CaO + 2CO$_2$ $\leftrightarrow$ MgCa(CO$_3$)$_2$

- Only CaO component works at high temperature!

Dolomite-derived sorbent with addition of promoter
- did not lower regeneration temperature
- *Increased* working capacity
Technical Accomplishments – Task 1
Performances of dolomite-derived CO$_2$ sorbent at low $T$

Dolomite-derived sorbent with promoter at lower temperatures

$$
\text{MgO} + \text{CaO} + 2\text{CO}_2 \leftrightarrow \text{MgCa(CO}_3\text{)}_2
$$

- Only MgO component works at low temperatures!
Accomplishment & Progress

Promising reforming catalysts identified from model reaction tests

- Identified catalyst composition which gives about 70% yield to H₂ using phenol as a model compound for pyrolysis oil
- Catalysts are stable for >30 mins and no activation is required.

Reaction Conditions:
\[ T = 500 \, ^\circ\text{C}, \, S/C=10, \, P_{\text{PhOH}} = 0.81 \, \text{mol\%}, \, SV= 3000 \, \text{hr}^{-1} \]