Development of a Practical Hydrogen Storage System based on Liquid Organic Hydrogen Carriers and a Homogeneous Catalyst

Craig M. Jensen, Daniel Brayton
Hawaii Hydrogen Carriers, LLC

Scott Jorgensen
General Motors, LCC

US DOE Annual Merit Review Meeting
May 17, 2012

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
• Start Date: June 2011
• End Date: May 2013
• 40% complete

Budget
• Total project funding: $617,977
• DOE share: $494,142
• Contractor share: $123,835

Barriers
A. System Weight and Volume
B. System Cost
C. Efficiency
E. Charging/Discharging Rates
H. BOP Components
F. Thermal management
R. Regeneration Processes

Partners
• General Motors, LLC
• Oregon State University
Liquid Organic Compounds as Hydrogen Carriers

- Contain 6.6- 8.8 wt% H$_2$ available
- Cheap, abundant, producible in massive quantities
- Elimination of thermal management problems associated with solid-state hydrogen absorbing materials.
- Infrastructure used to make and deliver gasoline is appropriate for LOCS can be thought of as “recyclable gasoline”
- Use of well-established class of materials reduces cost, risks, and time to market.

Relevance
1. Identify the LOHC/pincer catalyst combination of that give the best combination of high cycling capacity, rapid dehydrogenation kinetics \textit{without} LOHC degradation upon cycling.

2. Design of a space, mass and energy efficient tank and reactor system to house the LOHC and facilitate hydrogen release that can be easily interfaced with a fuel cell.
Dehydrogenation of Cycloalkanes to Arenes

- Considered as a hydrogen source since the 1930s.
- High loading of heterogeneous precious metal catalyst required for reasonable rate of hydrogen delivery.
- Thermal dynamic constraint of high $\Delta H$ ($\sim300 \, ^{\circ}C$ for plateau pressure of 1 atm) requires “off-equilibrium” approaches such as PdAg filter tubes.

LOCs have remained a tantalizing but impractical possibility for the past 60 years”


\[
\text{Pt or Pd on C or Al}_2\text{O}_3 \xrightarrow{300-320 \, ^{\circ}C} \text{Cycloalkane} + 3 \, \text{H}_2
\]
Homogeneous Ir PCP “Pincer” Dehydrogenation Catalysts

- First homogeneous aliphatic dehydrogenation catalyst
- 3 orders of magnitude higher activity than heterogeneous catalyst temperatures as low 100 °C
- Two-way catalyst

• Introducing heteroatoms and/or functionalization into the ring system lowers $\Delta H_{\text{dehy}}$ (values in kJ/mol).

• Combinations of LOHCs (ie N-ethylperhydrocarbazole) and heterogeneous catalysts (ie Rh on C or Pd on Al$_2$O$_3$) previously investigated – G.P. Pez: A.R. Scott: A.C. Cooper: H. Cheng US Patent Appl. 2005/0002857
Dehydrogenation of N-ethylperhydrocarbazole using homogeneous Ir PCP pincer catalyst gives higher rates of dehydrogenation at 2 orders of magnitude lower loadings than heterogeneous catalysts.

Approach

LOC Selection
key physical properties: sub-ambient melting points, high boiling points, and appropriate $\Delta H_{\text{dehyd}}$

\[
\text{perhydrodibenzofuran, 4} \quad \text{perhydroindole, 5} \quad \text{N-methyl perhydroindole, 6} \\
\text{4,4’-bipiperidine, 7} \quad \text{4-(aminomethyl)-piperidine, 8} \quad \text{aminomethylcyclohexane 9}
\]

<table>
<thead>
<tr>
<th>LOC</th>
<th>Limitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perhydrodibenzofuran</td>
<td>thermodynamics</td>
</tr>
<tr>
<td>4,4’-dipiperidine</td>
<td>polymerization</td>
</tr>
<tr>
<td>Aminomethylcyclohexane</td>
<td>condensation products</td>
</tr>
</tbody>
</table>

Evaluation of baseline and alternative reactors designs will yield improved system performance

- 16 alternate reactor concepts generated
- Evaluation progresses using simplified operation and geometry for speed
- Downselect to 2 or 3 concepts for detailed and dynamic evaluations
BOP concept designed – improvements will reduce mass, volume, and cost

- Use existing automotive or other ultra high volume parts where possible
- Leverage existing DOE work where possible (HSECoE)
- Make nonstandard parts compact and efficient
Task 1. Optimization of Catalyst/LOHC Hydrogen Cycling Performance

Subtask 1.1. Isothermal kinetics studies of the dehydrogenation candidate LOHCs.
Subtask 1.2. Differentiation of thermodynamic vs. kinetic limitations by studies of transfer dehydrogenation in cases where incomplete dehydrogenation is observed.
Subtask 1.3. Investigate additive intervention of side reactions.
Subtask 1.4 Cycling Studies. Determine if LOHC/catalyst combinations that have acceptable dehydrogenation kinetics and capacity will undergo cycling without degradation. Investigation of re-hydrogenation reaction efficiencies.
Task 2. Design and Modeling of Reactor

Subtask 2.1. Model Development. 1) notional model: 2) detailed reactor modeling using COMSOL; 3) validation of fluid mechanics, heat transfer, and reaction dynamics; and 4) basic cost estimate.

Subtask 2.2. Function evaluation at: 1) full flow condition; 2) idle; 3) mid-speed/mid-load; and conditions.

Subtask 2.3. System Optimization. Based on lessons learned about system function, change will be made in the reactor and/or balance of plant where efficiency and/or cost effective changes are possible.

Subtask 2.4. Final Simulations. Steady state and transient simulations will both be done with multiple reaction paths.
Approach/Milestones

M1 – Complete kinetics studies PHMI based systems (month 3)
M2 – Complete kinetics studies of PHI based systems (month 6)
M3 – Complete transfer dehydrogenation experiments (month 9)
M4 – Complete kinetics and studies of AMC based systems with and without additives (month 12)
M5 – Complete kinetics studies on alternative LOHCs (month 18)
M6 – Complete cycling studies (month 24)

Go/No go decisions on PHMI, PHI, and AMC (month 12)

M1 – First version of software complete, including detailed reactor design(s) and notional BOP (month 2)
M2 – Validated version of reactor model(s) (month 4)
M3 – Characterization of steady state with one chemistry path (month 7)
M4 – Transient performance with one chemistry path (month 8)
M5 – Multipath selectivity (month 9)
M6 – Final simulation model generated and validated (month 13)
M7 – Report to Prime (HHC) on design and modeling (month 18)
Ethylperhydrocarbazole (EPHC)

dehydrogenation of 5 membered ring requires heating to 180°C

Methylperhydroindole (MPHI)

dehydrogenation of the 5-membered ring at 160°C
Accomplishments

Isothermal Kinetic Studies

<table>
<thead>
<tr>
<th></th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$ ($M^{-1}s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPHI</td>
<td>133</td>
<td>$9.457 \times 10^{10}$</td>
</tr>
<tr>
<td>EPHC</td>
<td>111</td>
<td>$1.2603 \times 10^{8}$</td>
</tr>
</tbody>
</table>

Arrhenius

$y = -16020x + 22.97$

$R^2 = 0.9961$
Dehydrogenation of amine group and alpha carbon to nitrile only. => downselected

Dehydrogenation of only 5 membered ring indicated in preliminary study
More effective heat transfer in helical reactor improves packaging

- Helical reactor, among others, is an improvement on baseline counter-flow
- Better heat transfer allows a short, easy to package, reactor
- Smaller reactor reduces heat loss
MPHI gives higher throughput

- Fixed reactor geometry and conditions
- Require near 100% conversion
- 5x improvement in H₂ production
Collaborations

Reactor Design

General Motors, LLC – Subcontractor. Dr. Scott Jorgensen

Oregon State University – Sharing results obtained from other US DOE funded liquid hydrogen carrier project. Prof. Kevin Drost
Future Work

LOC screening
• Complete kinetic studies of perhydro-indolizidine dehydrogenation
• Complete kinetic studies of methylperhydro-indole dehydrogenation
• Complete kinetic studies of alternative LOCs.
• Carry out cycling studies on methylperhydro-indole and/or better performing alternative LOC.

Reactor Design
• Downselect reactor(s) and calculate dynamic performance to select best option
• Trade off analysis of hydrogen-hydrocarbon separator
• Determine properties required to meet different DOE targets
Summary

- Pincer catalyst is effective for the dehydrogenation of aminoethyl-cyclohexane only to cyclohexylnitrite at relevant temperatures and thus AMC has been down-selected as a viable LOC.
- The Methylperhydro-indole/pincer catalyst system is the most promising LOC identified to date.
- Modeling studies show that heat transfer is most effective in a helical reactor.
- Better heat transfer allows a short, easy to package reactor.
- Smaller reactor reduces heat loss
- Reduction of enthalpy and conservation of waste heat from both the reactor and other sources on the vehicle are key to a high hydrogen capacity system.