

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



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ST 098

# Overview

## **Timeline**

- Start Date: June 1, 2011
- End Date: May 31, 2013
- 85% 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

# Relevance

## **Liquid Organic Compounds (LOC) as Hydrogen Carriers**

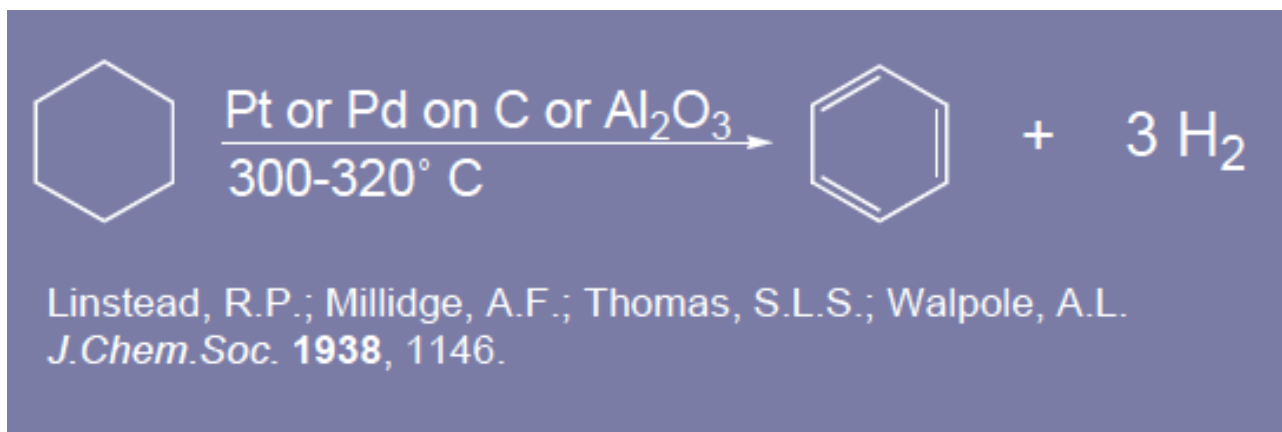
- Contain 6.6 - 8.8 wt% H<sub>2</sub> available
- Cheap, abundant, producible in massive quantities
- Elimination of thermal management problems associated with solid-state hydrogen absorbing materials
- Infrastructure used to make and deliver gasoline is appropriate for LOCs can be thought of as “recyclable gasoline”
- Use of well-established class of materials reduces cost, risks, and time to market.

# Objectives

1. Identify the Liquid Organic Hydrogen Compound (LOHC)/pincer catalyst combination that gives the best combination of high cycling capacity, rapid dehydrogenation kinetics **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.

# Approach

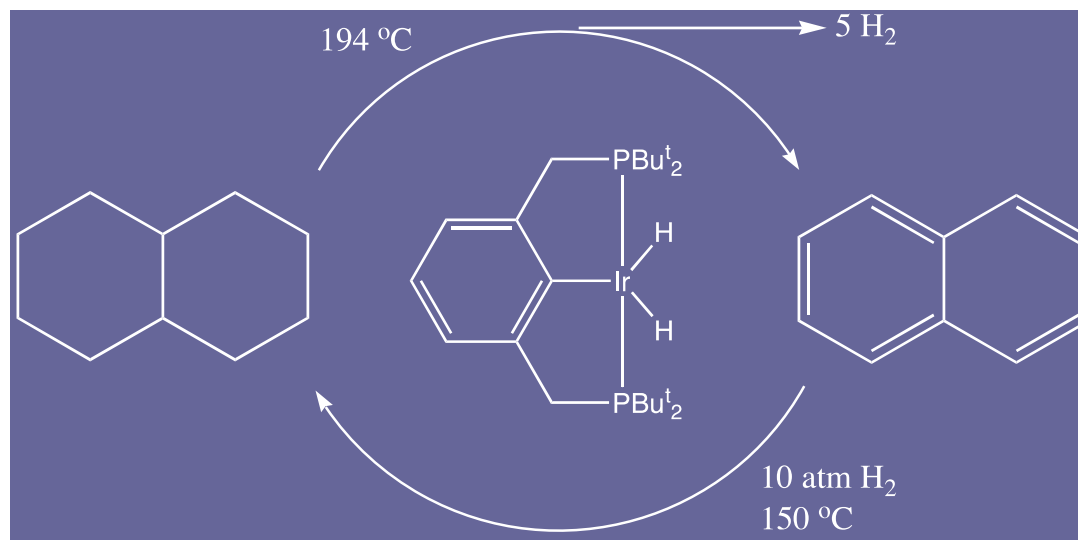
LOCs have remained a tantalizing but impractical possibility for the past 60 years.



## 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
- Thermodynamic constraint of high  $\Delta H$  (~300 °C for plateau pressure of 1 atm) requires “off-equilibrium” approaches such as PdAg filter tubes.

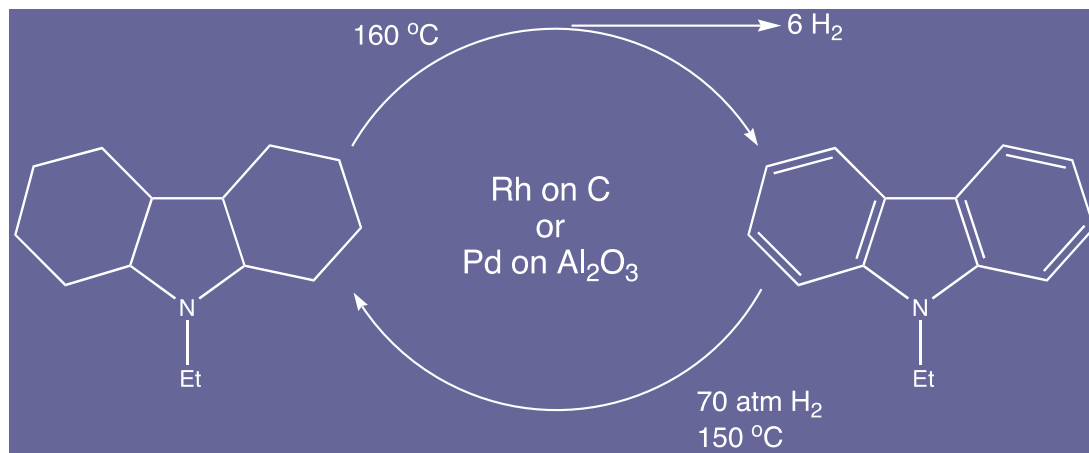
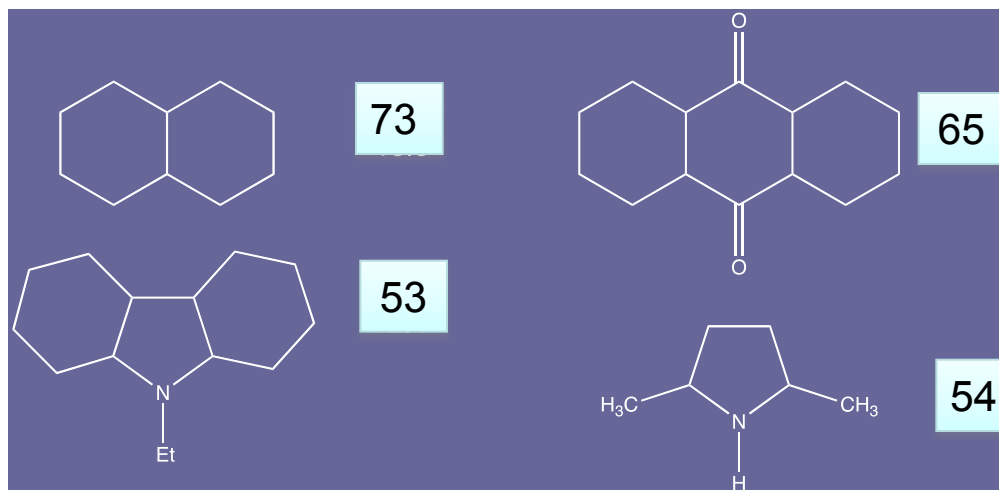
# Homogeneous Ir PCP“Pincer” Dehydrogenation Catalysts



- First homogenous aliphatic dehydrogenation catalyst
- 3 orders of magnitude higher activity than heterogeneous catalyst at temperatures as low  $100^\circ\text{C}$
- Two-way catalyst

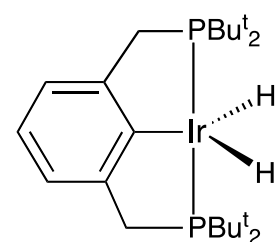
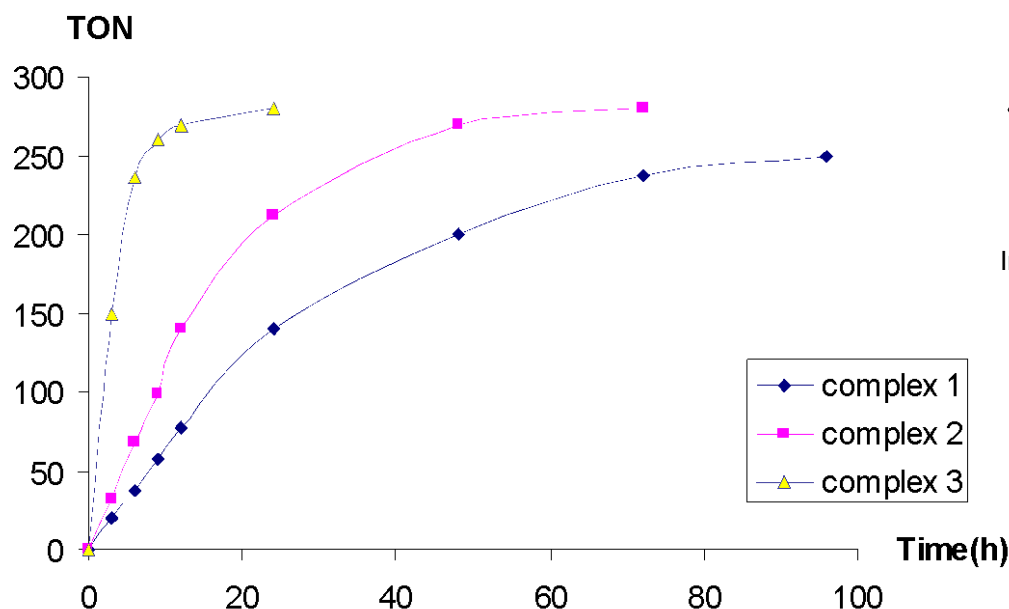
M. Gupta, W.C. Kaska, R. Cramer, C.M. Jensen; *J. Am. Chem. Soc.* **1997**, 119, 840.  
C.M. Jensen *Proceedings of the 1997 U.S. DOE Hydrogen Program Review* 307.  
C.M. Jensen US Patent 6,074,447 **2000**.

Introducing heteroatoms and/or functionalization into the ring system lowers  $\Delta H_{\text{dehy}}$

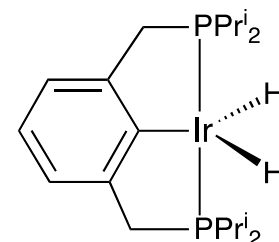


Combinations of LOHCs (i.e., N-ethylperhydrocarbazole) and heterogeneous catalysts (ie Rh on C or Pd on Al<sub>2</sub>O<sub>3</sub>) were previously investigated – G.P. Pez: A.R. Scott: A.C. Cooper: H. Cheng US Patent Appl. 2005/0002857

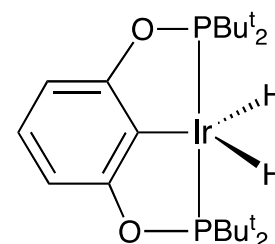
# Dehydrogenation of N-Ethylcarbazole Catalyzed by Ir PCP Pincer Complexes



$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{P}^t\text{Bu}_2)_2\}$  (1)



$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{P}^i\text{Pr}_2)_2\}$  (2)



$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(OP}^t\text{Bu}_2)_2\}$  (3)

Homogeneous pincer catalysts give higher rates of dehydrogenation at 2 orders of magnitude lower loadings than heterogeneous catalysts



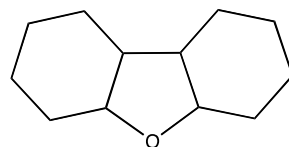


# LOC Selection

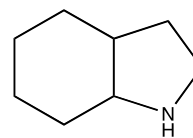
## Requisite Properties

- Sub-ambient melting point
- High boiling point
- Appropriate  $\Delta H_{\text{dehyd}}$
- Chemo-selectivity for dehydrogenation

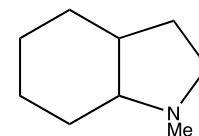
## Background LOC Screening



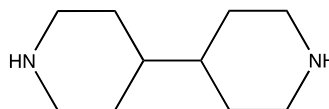
perhydrodibenzofuran, 4



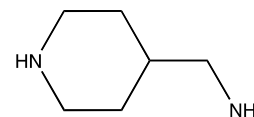
perhydroindole, 5



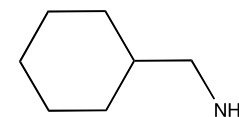
N-methyl perhydroindole, 6



4,4'-bipiperidine, 7



4-(aminomethyl)-piperidine, 8



aminomethylcyclohexane 9

### LOC

Perhydrodibenzofuran

4,4'-dipiperidine

Aminomethylcyclohexane

### Limitation

thermodynamics

polymerization

condensation products

Z. Wang, J. Belli, C. Jensen *Faraday Discuss*  
**2011**, 151, 297.



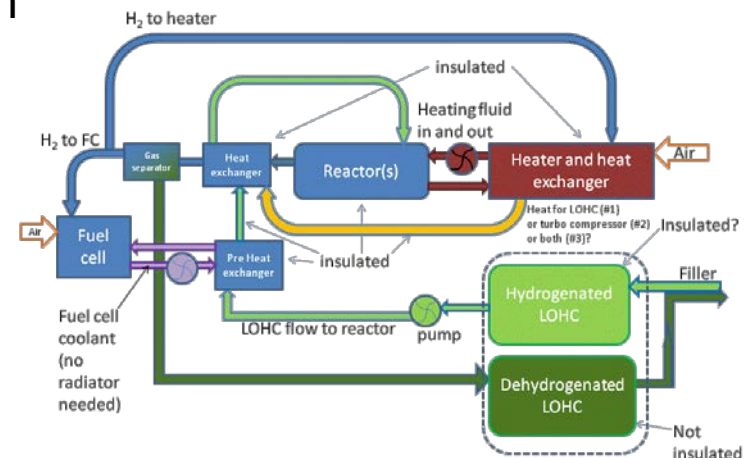
# Approach

**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
- **Systems design includes SINGLE “bladder” tank.**

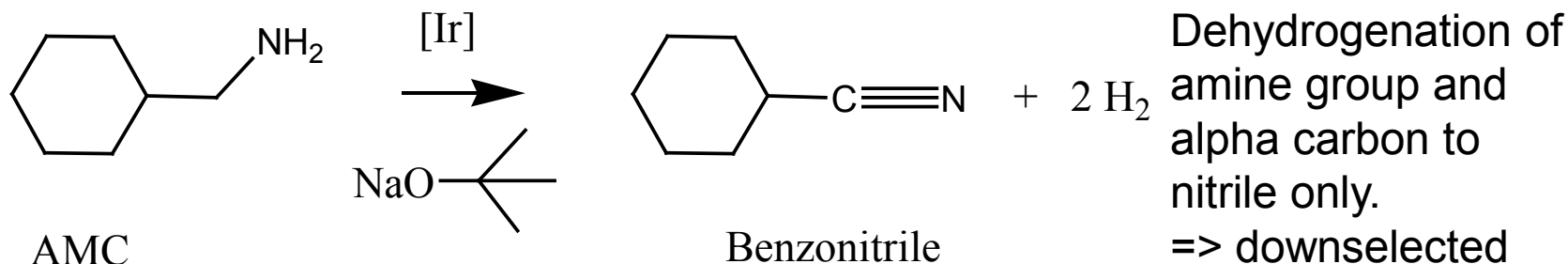




# Accomplishments

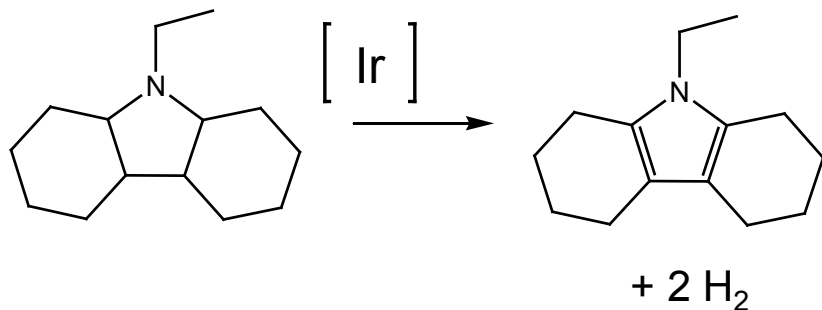
## Screening of Candidate LOCs

Previous year's results



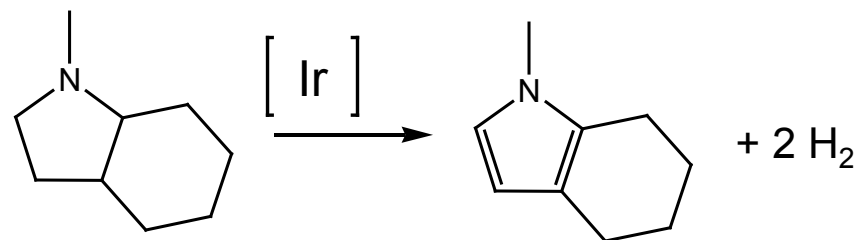
Only N-containing 5 Membered Rings Found Dehydrogenate at Practical Rates Below 200°C

Ethylperhydrocarbazole (EPHC)



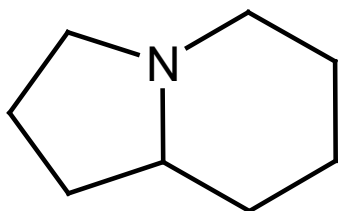
Practical rate at 180°C

Methylperhydroindole (MPHI)



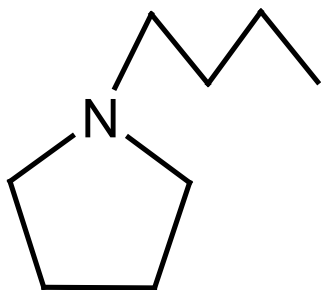
Practical rate at 160°C

## Screening of other LOCs with N-containing 5 Membered Rings



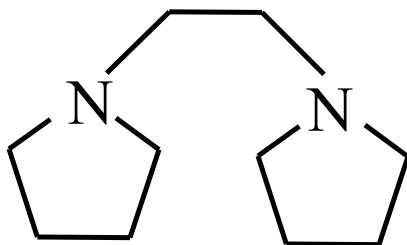
Perhydroindolizine (PHIZ)

- Only 8% conversion of 5 membered ring
- Impractical price, thermodynamics, and kinetics



Butyl Perhydropyrrolidine (BPHP)

- Pyrrolidine bp = 87°C, butylpyrrolidine 153°C
- Requires heating to only 140°C
- 100% dehydrogenation of ring in 18-20 hours
- ~2-5 faster than all other LOCs screened
- High sensitivity to impurities

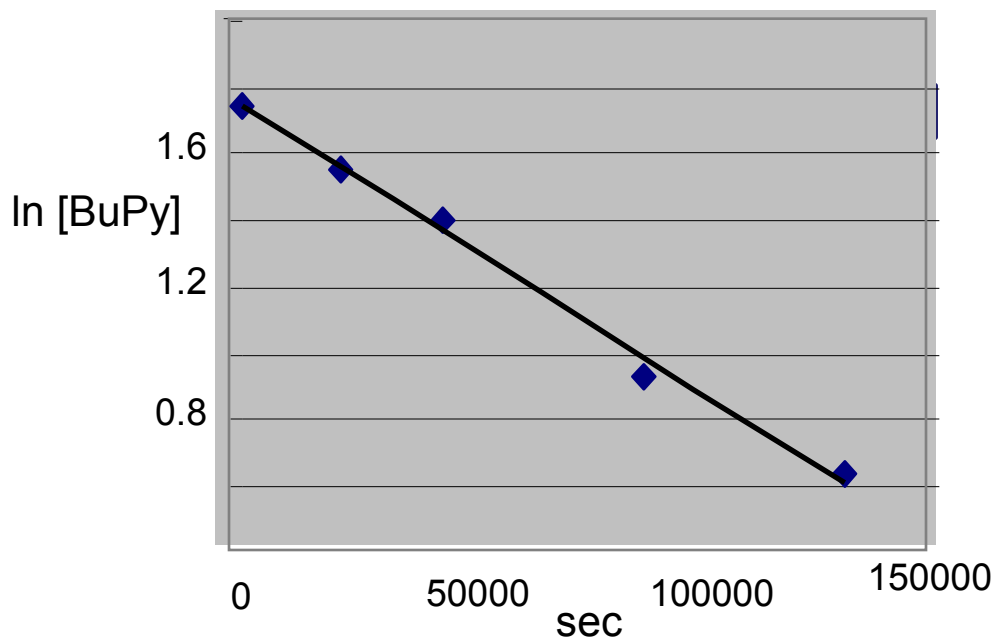


Bisperhydropyrrolidylethane (BPHPB)

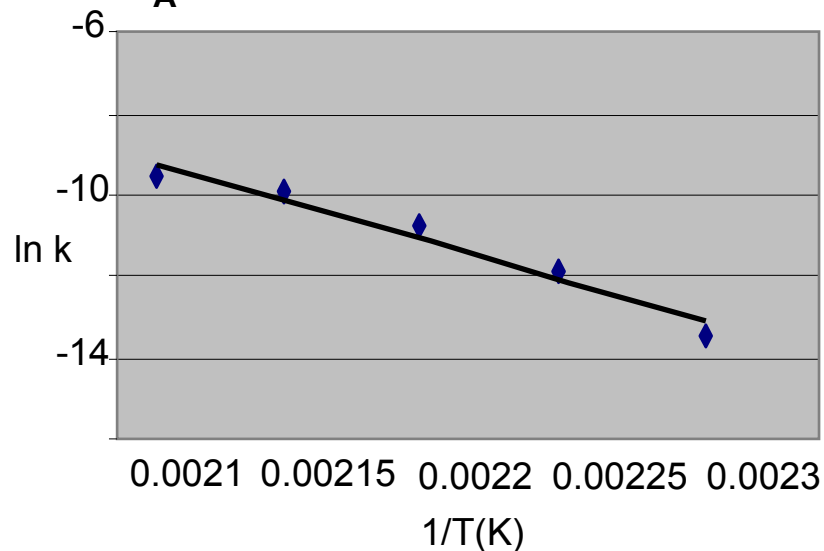
- no observed dehydrogenation

# Isothermal Kinetic Studies

First order kinetics observed



$E_A$  and  $A$  from Arrhenius Plots



	$E_a$ (kJ/mol)	$A$ ( $s^{-1}$ )
MPHI	132.2	$7.2314 \times 10^9$
EPHC	107.1	$4.531 \times 10^7$
BPHP	166.1	$2.170 \times 10^{14}$

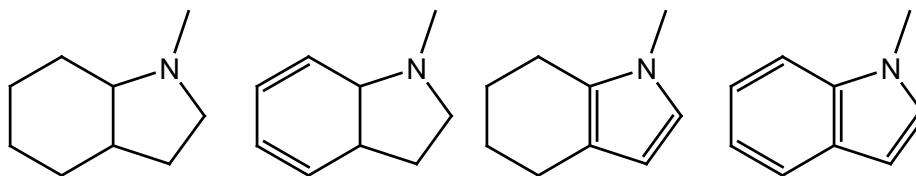
# Low Catalyst Concentrations are Required for Practical Viability

## Acceptable Rates at Very Low (100 ppm) Catalyst Concentrations

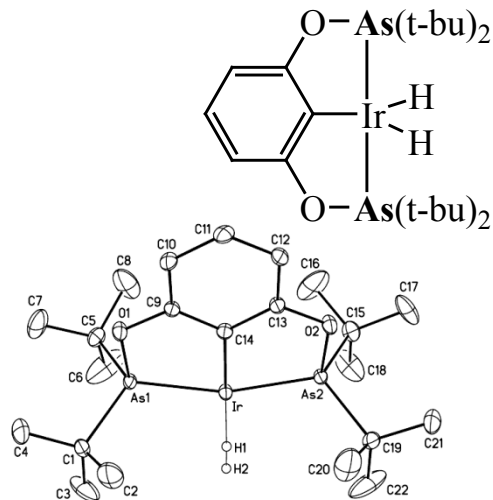
- High activity at low concentration allow Ir-based catalyst to be economically viable.
- Initial screenings of LOCs at 1 mol % concentration
- Detailed kinetic studies at 100 ppm concentration

## Hydrogenation with Pincer Catalyst

Temp	H <sub>2</sub> Pressure	Time	Yield %
70 °C	60 bar	48 hrs	0 : 3 : 0 : 97
145 °C	60 bar	72 hrs	0 : 83 : 0 : 17
100 °C	120 bar	36 hrs	0 : 89 : 1 : 10
180 °C	165 bar	4 days	0 : 89 : 1 : 10



# Screening of Alternative Arseno Pincer Dehydrogenation Catalyst



Catalyst	temp	Time	Substrate	Yield	TON*
P pincer	150 °C	24 hrs	COA/TBE	40%	~1,200
As pincer	125 °C	24 hrs	COA/TBE	10%	~300
As pincer	150 °C	24 hrs	COA/TBE	20%	~600
As pincer	200 °C	24 hrs	COA/TBE	1%	~30
P pincer	150 °C	24 hrs	BuPy	8%	~8
As pincer	150 °C	24 hrs	BuPy	3%	~3

\* TON = Turn over number

## Scale-up Cycling Studies

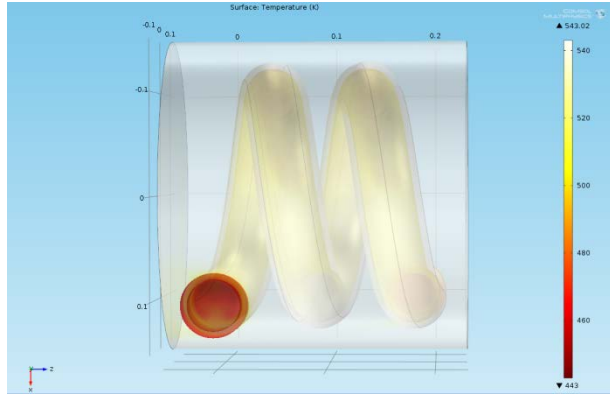
### MPHI Cycling Study

- 10x volume, 50 cycles of dehydrogenation/rehydrogenation
  - First 10 cycles show no detectable degradation of LOC or catalyst by either GC/MS or NMR analysis.
- ➔ TON is **at least** 100,000 (200,000 counting rehydrogenation)
- 50 cycles scheduled to be completed by AMR.



# Modeling Studies

## Previous results



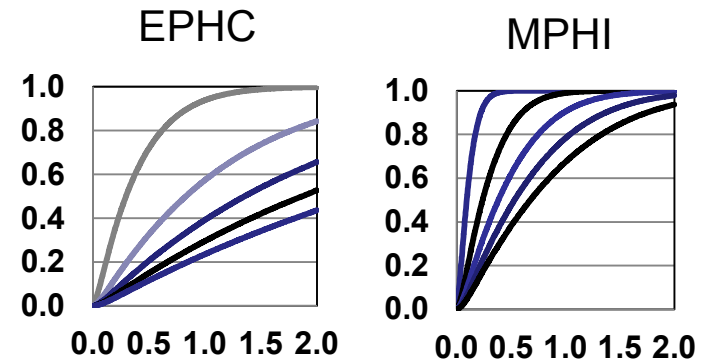
### Effective heat transfer in helical reactor allows improved packaging

- Reactor causes “shear” resulting in better heat transfer thus allowing a short, easy to package reactor.
- Smaller reactor reduces heat loss
- Matches findings of HSECoE studies of systems employing solid hydrides and liquid coolant which also show helical reactors to be most efficient.

**Rate of  $H_2$  production is also found to be improved in a helical reactor.**

Better dehydrogenation kinetics with MPHI

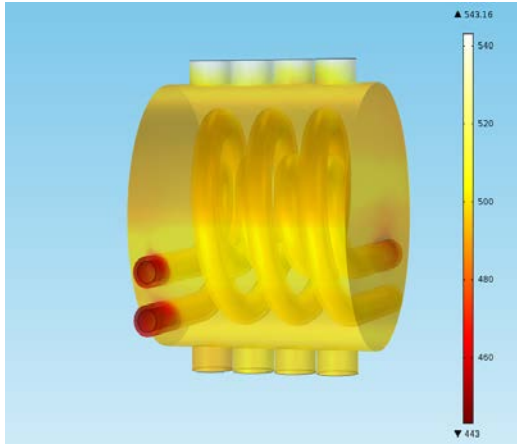
**→ Shorter tube is required to achieve 100% conversion.**



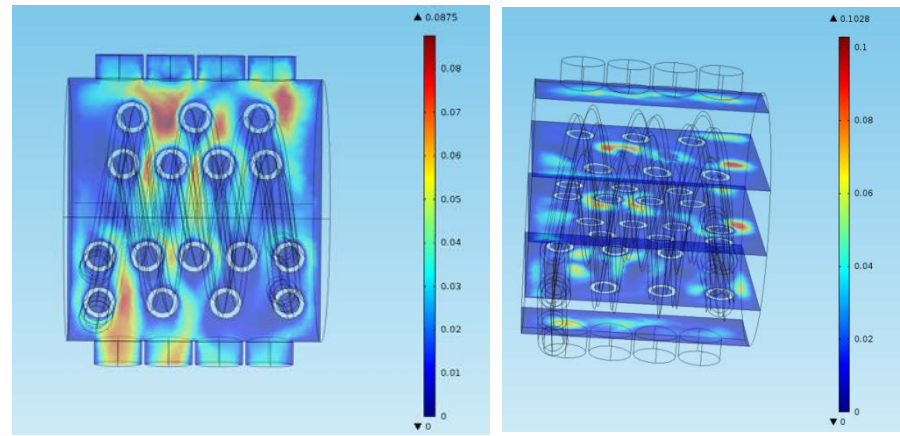


# Double Helical Reactor

Temperature Distribution



Velocity Distribution (t = 140 sec)



- Significant saving of space but not heating efficiency.
- Assemble prohibitively costly.

## Engineering activities were curtailed

- Per tech team advice and DOE guidance the engineering portion of the project were significantly .
- Much of the value of this portion of the project was already harvested from the general case analysis.
- Primary aspects have been to support PI for reviews, tune up analysis done already for higher fidelity, and documentation.

# Approach/Milestones



- M1 – Complete kinetics studies MPHI 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) ✓
- Go/No go decisions on MPHI, PHI, and AMC (month 12) ✓**
- M5 – Complete kinetics studies on alternative LOHCs (month 18) ✓
- M6 – Complete cycling studies (month 24)



- 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)

# 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**

- Finish cycling studies on methylperhydroindole

## **Reactor Design**

- Final modeling using “best” rate data
- Final Report to Prime (HHC) on design and modeling

# Summary

- PCPC pincer catalysts are effective (TON >100,000) for the dehydrogenation **and** rehydrogenation of methylperhydroindole at practically relevant temperatures and low (100 ppm) catalyst loadings.
- Modeling studies show that heat transfer is most effective in a helical reactor. Better heat transfer allows a short, easy to package reactor that reduces heat loss.

# Supplemental Slides

# Invited Presentations

1. “Development of Liquid, High Capacity Hydrogen Carriers”, C.M. Jensen, D. Brayton, S. Jorgensen, G. Severa, E. Rönnebro, M. Chong, T. Autrey, A. Karkamkar, and S. Orimo, Materials for Hydrogen Storage – Future Perspectives, Kirkenes, Norway, 06/20/12
2. “Development of Liquid, High Capacity Hydrogen Carriers”, C.M. Jensen, D. Brayton, S. Jorgensen, G. Severa, E. Rönnebro, M. Chong, T. Autrey, A. Karkamkar, and S. Orimo, International Symposium on Metal-Hydrogen Systems; Kyoto, Japan, 10/06/12.
3. “Development of Liquid, High Capacity Hydrogen Carriers”, C.M. Jensen, D. Brayton, S. Jorgensen, M. Chong, J. Wang and S. Orimo, 7<sup>th</sup> EMPA Hydrogen and Energy Symposium, Stoos, Switzerland 01/22/13.



# Approach/Plan

## **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.





# Approach/Plan

## **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.

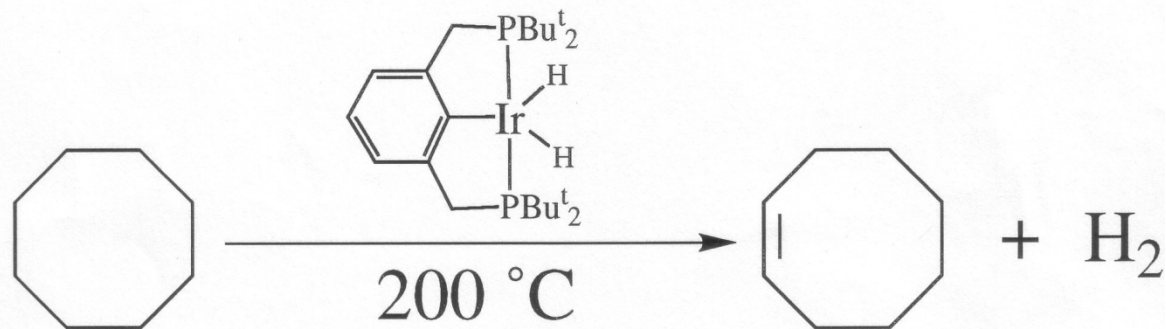
Subtask 2.2. Function evaluation at: 1) full flow condition; 2) idle 3) mid-speed/mid-load; and conditions.

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.

# Do Thermodynamics or Kinetics Limit the Dehydrogenation of LOCs?

Aliphatic dehydrogenations typically require the **enthalpically** unfavorable (exchange of 2 C-H bonds for 1 H-H bond and the pi bond of a C-C double bond). This must be overcome by sufficient temperature amplification of the **entropically** favorable generation of free hydrogen gas.

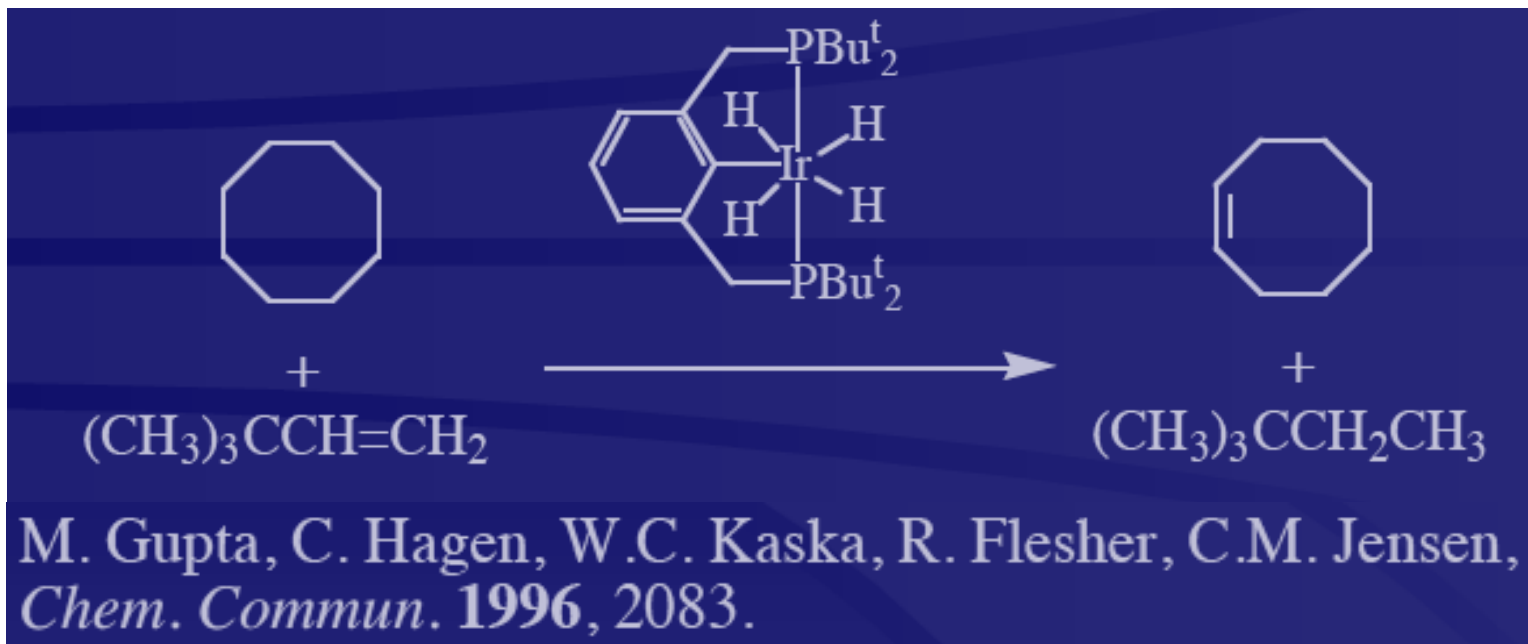


Xu, W.W.; Rosini, G.P.; Gupta, M.; Jensen, C.M.; Kaska, W.C.; Krough-Jespersen, K.; Goldman, A.S. *Chem. Commun.* **1997**, 2273.

# Transfer Dehydrogenation Reactions are Kinetically Limited

Transfer dehydrogenation - hydrogen is transferred from saturated C-H bonds to an unsaturated hydrogen acceptor molecule which forms stronger C-H than those in the starting saturated molecule.

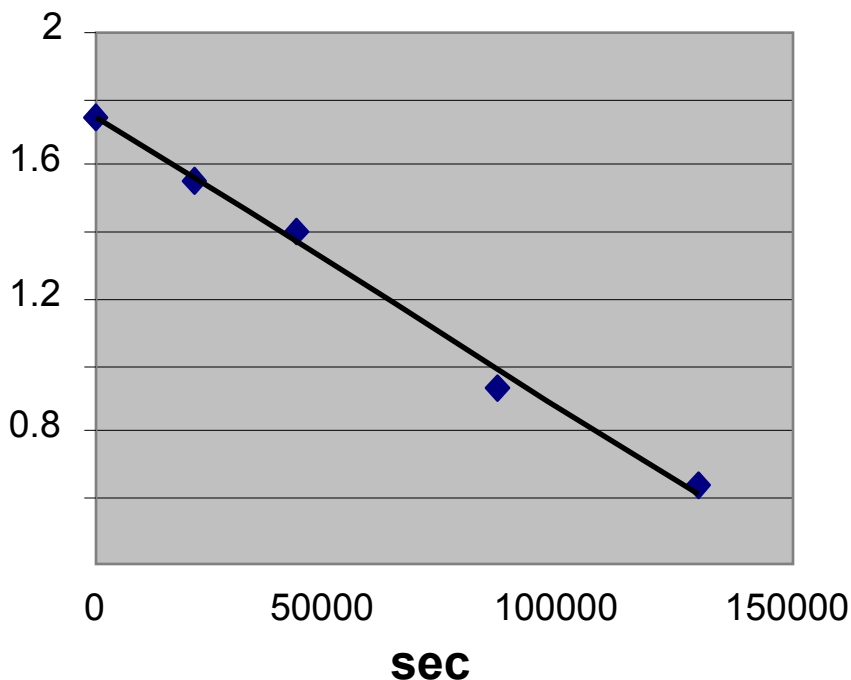
Transfer dehydrogenation is thermodynamically favorable at low temperatures and limited only by kinetic constraints.



# Isothermal kinetic studies

First order kinetics observed

**ln BuPy vs Time at 180 C**



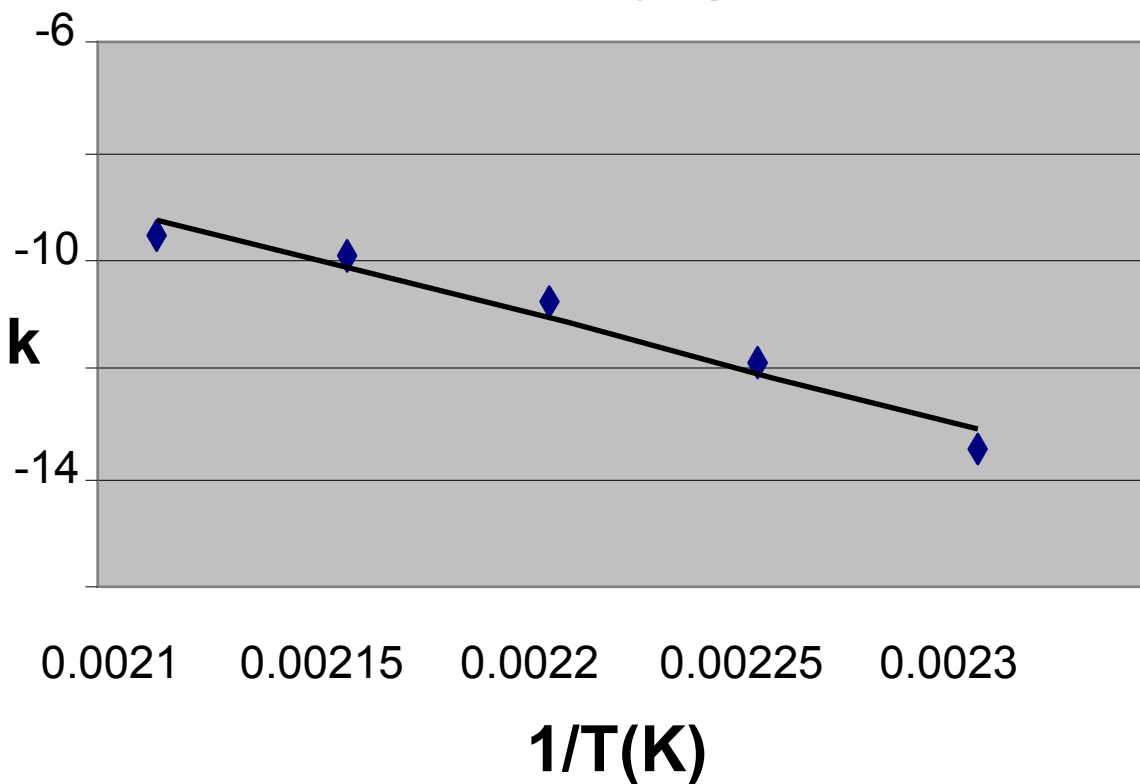
$$y = -0.0000088x + 1.7514213$$

$$R = 0.9928229$$

# Isothermal kinetic studies

## $E_A$ and A from Arrhenius Plots

**ln k vs 1/T**



$$y = -19975x + 33.011$$

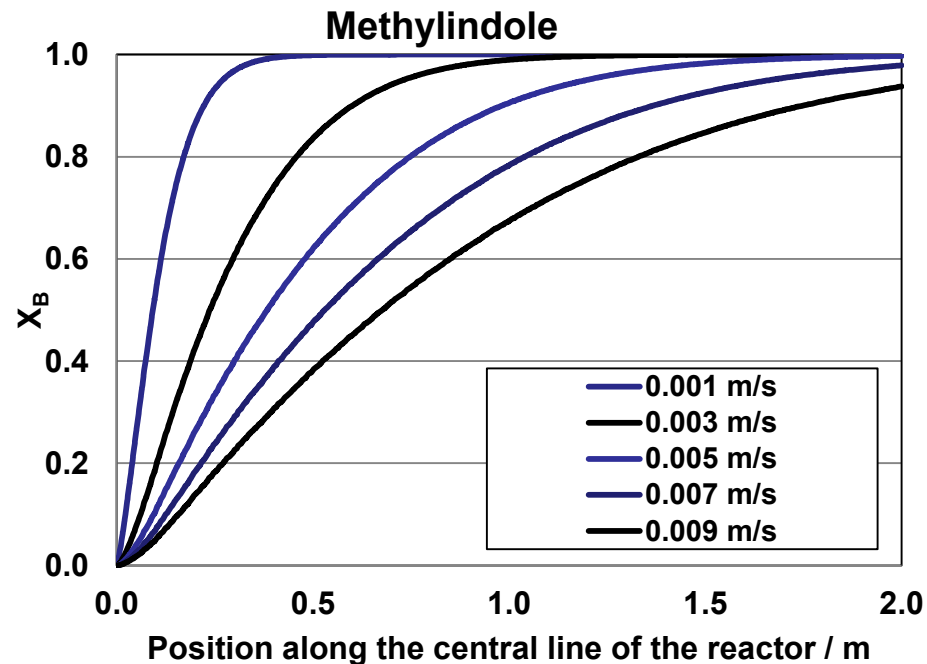
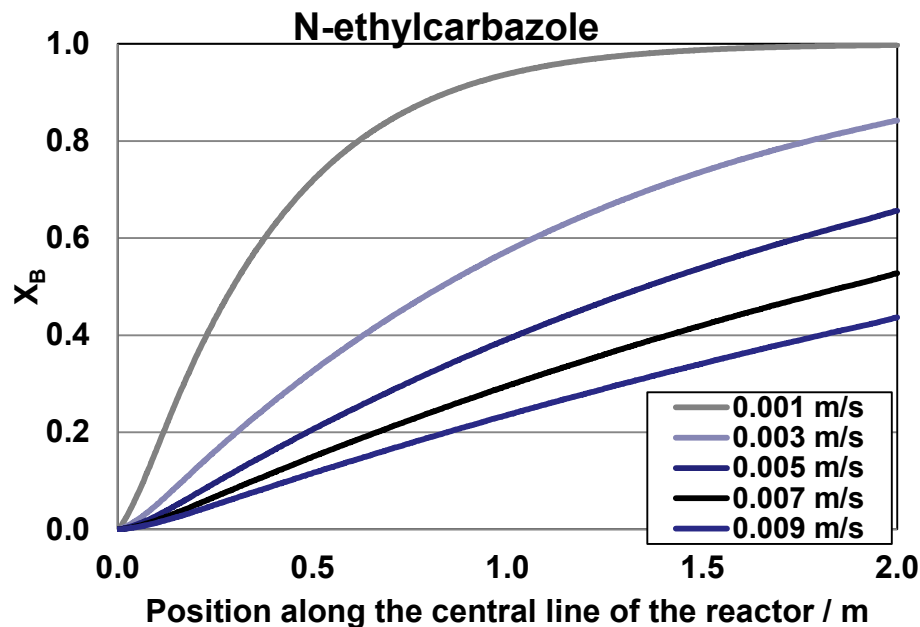
$$R = 0.9558$$

$$\ln k = -E_A/R (1/T) + \ln A$$

$$\text{Slope} \times R = E_A$$

$$33.011 = \ln A$$

$$e^{33.011} = A = 2.170 \times 10^{14}$$



- Fixed reactor geometry and conditions
- Require near 100% conversion
- 5x improvement in  $H_2$  production

MPHI gives  
higher throughput