

# **Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen**

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PD046

# Overview

## Timeline

- Start date: 8/2005
- Team kickoff: 10/2008
- Project end: 09/2011
- 60% Complete

## Budget

- Total project \$4,131,118
  - DOE share 75%
  - Contractor share 25%
- Funding received in FY09:
  - \$0
- Funding for FY10:
  - \$358,575

## Barriers

- Barriers addressed:
  - E. Solid and Liquid Carrier Transport
  - A. Hydrogen/Carrier and Infrastructure Options Analysis
  - F. Hydrogen Delivery Infrastructure Cost

## Partners

- Pacific Northwest National Laboratory (PNNL)
- BMW Group
- United Technologies Research Corporation (UTRC)

# Relevance

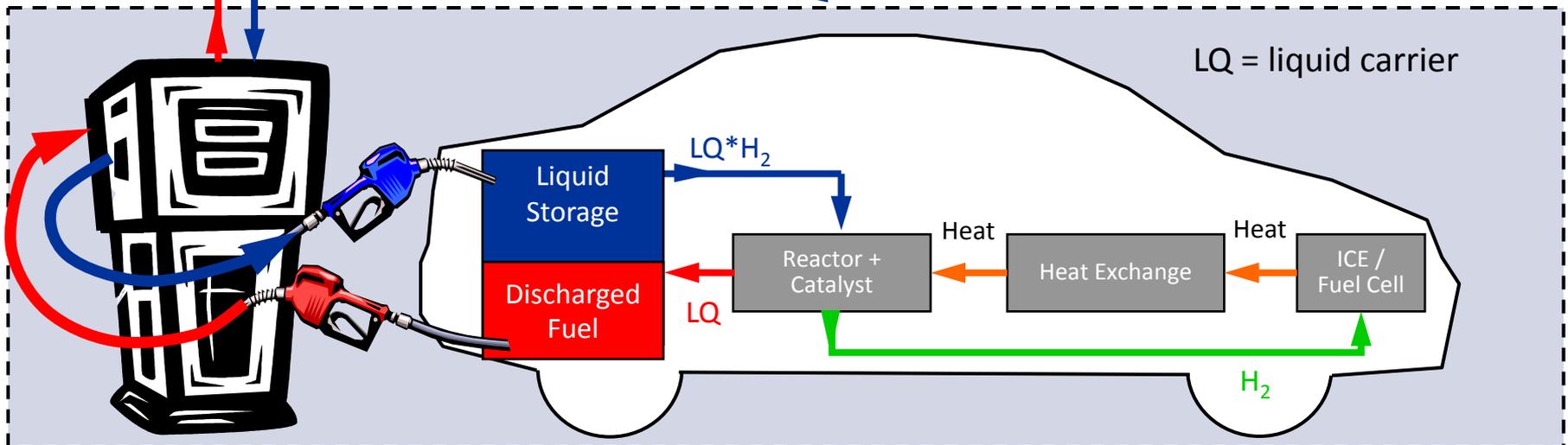
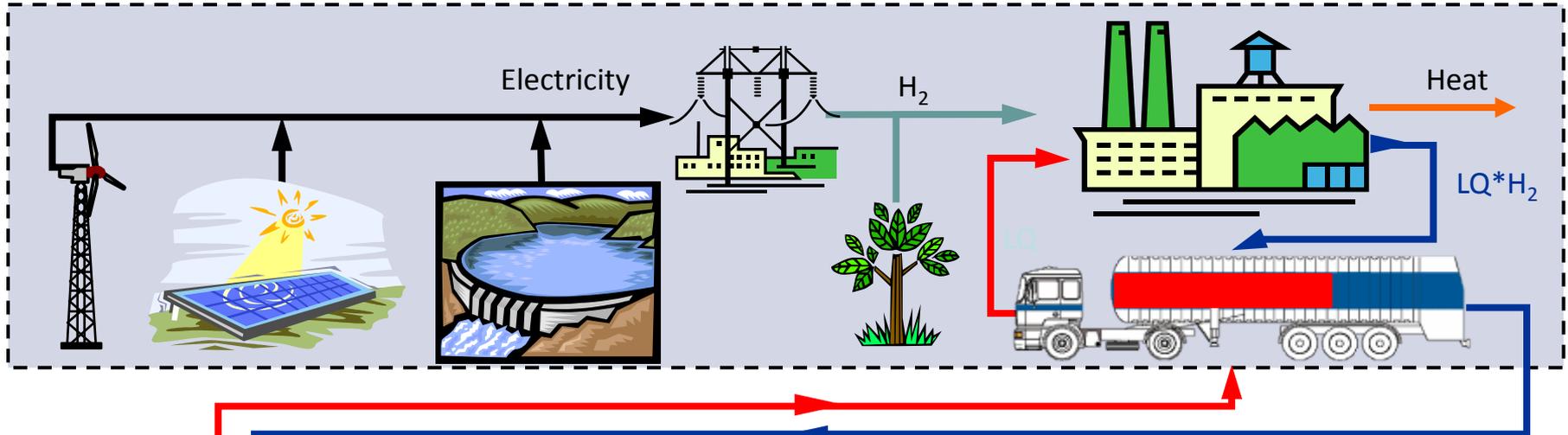
- The overall objective of this project is to develop a conceptual design and fabricate an initial 0.1 to 1 kW prototype of a dehydrogenation reactor/heat exchange system to deliver hydrogen via liquid carrier materials. The project is divided into 3 tasks:
  - Liquid phase hydrogen carrier raw materials sourcing and processing (Task 1)
  - Dehydrogenation reactor development. Develop a conceptual design and fabricate an initial 0.1 to 1 kW prototype of a dehydrogenation reactor/heat exchange system to deliver H<sub>2</sub> (Task 2)
  - Hydrogen delivery economics. Conduct an economic evaluation of the delivery and storage system for the liquid carrier H<sub>2</sub> delivery concept (Task 3). A detailed economic analysis was completed in Q3FY09 and is in preparation as a report to DOE. Based upon our analysis, we consider the H<sub>2</sub> liquid carrier economics to be favorable, in the range of 0.85 – 4.50 \$/kg H<sub>2</sub> delivery cost with respect to current DOE targets, provided that certain performance and cost targets can be achieved for the liquid carrier, hydrogenation catalyst productivity, liquid carrier loss rate and dehydrogenation efficiency.

<b><i>H2 Delivery using Hydrogen Carriers (DOE Targets)</i></b>			
<b>Category</b>	<b>2005 status</b>	<b>FY2012</b>	<b>FY2017</b>
Carrier H2 Content (% by weight)	6.2%	6.6%	13.2%
Carrier H2 Content (kg H2/liter)	0.054	>0.013	>0.027
Carrier System Energy Efficiency (from the point of H2 production through dispensing at the forecourt) (%)		70%	85%
Total System Cost Contribution (from the point of H2 Production through dispensing at the forecourt) (\$/kg of H2)		\$1.70	<\$1.00

# Approach

An alternative approach for the large-scale delivery of hydrogen from large central production facilities to forecourt users (e.g. customers at fueling stations) is the use of reversible carrier media that liberate hydrogen at the point of use. The hydrogen can be obtained from the carriers at the fueling station for subsequent dispensing to vehicles. Ideally, the carrier can be used for hydrogen storage onboard the vehicle and hydrogen can be released on demand for vehicle propulsion. Primary advantages of carrier-based distribution of hydrogen potentially include lower capital and operating costs, higher efficiency, and enhanced safety.

## PRODUCTION & DISTRIBUTION



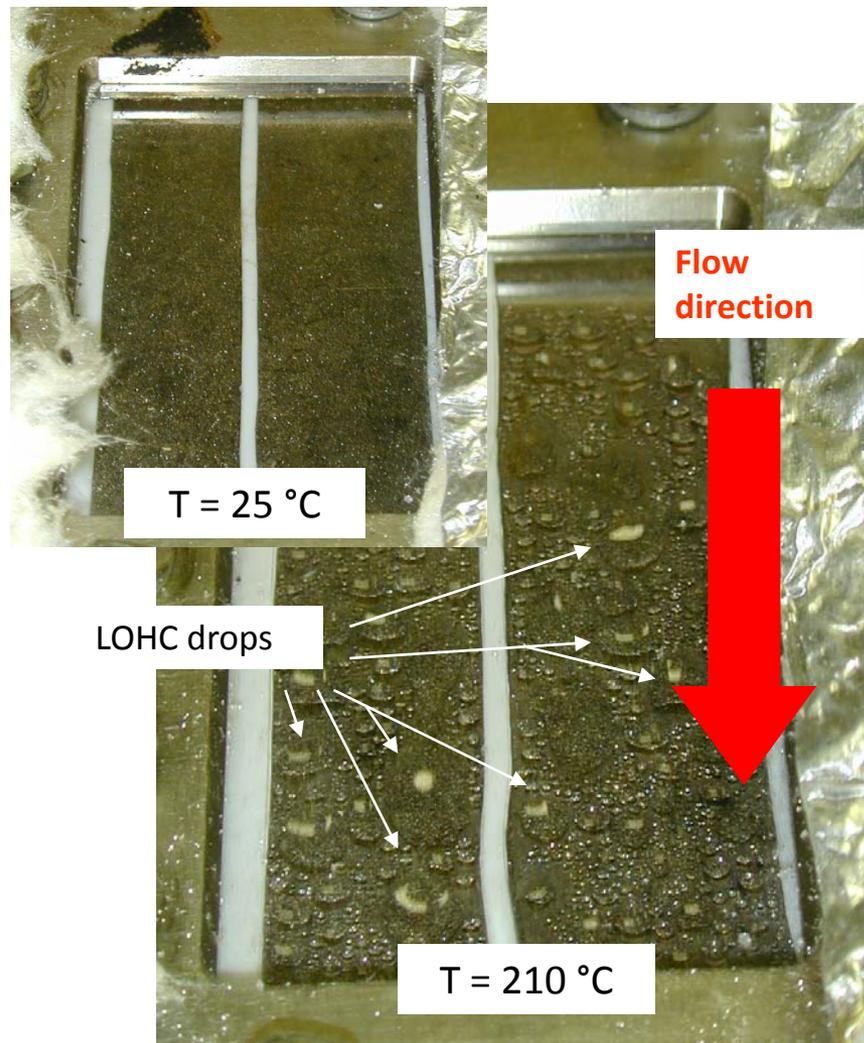
## REFUELING STATION

# Approach

- Efficient dehydrogenation of the liquid carrier is integral to the viability of this concept for hydrogen storage and delivery.
  - Microchannel reactor technology was identified at an early stage as a promising reactor architecture for carrier dehydrogenation. The technical approach is to develop catalyst substrates that are able to effectively segregate liquid from gas and release the hydrogen as it is generated from the catalyst structure.
  - PNNL is a leader in the development of microchannel reactors and in collaboration with Air Products and BMW, several generations of “proof-of-principle” (PoP) reactors have been developed at PNNL. After initial testing at PNNL, the reactors will be used for integration studies at BMW.
    - Milestone: Demonstration of Generation 1 PoP reactor (Q3FY09) – Completed
    - Milestone: Demonstration of Generation 2 PoP reactor (Q1FY10) – Completed
    - Milestone: Demonstration of Generation 3 PoP reactor (Q3FY10) – On-track pending FY10 funding
- Data from the reactor testing will be used by UTRC for the modeling of stationary and mobile fuel cells. UTRC’s objective is to evaluate the integration of liquid carrier storage systems with fuel cell systems.
- Conduct detailed economic analysis of the delivery and storage system for the liquid carrier H<sub>2</sub> delivery concept.
  - Milestone: Submission of final economic analysis report to DOE (Q3FY10) – On-track pending FY10 funding

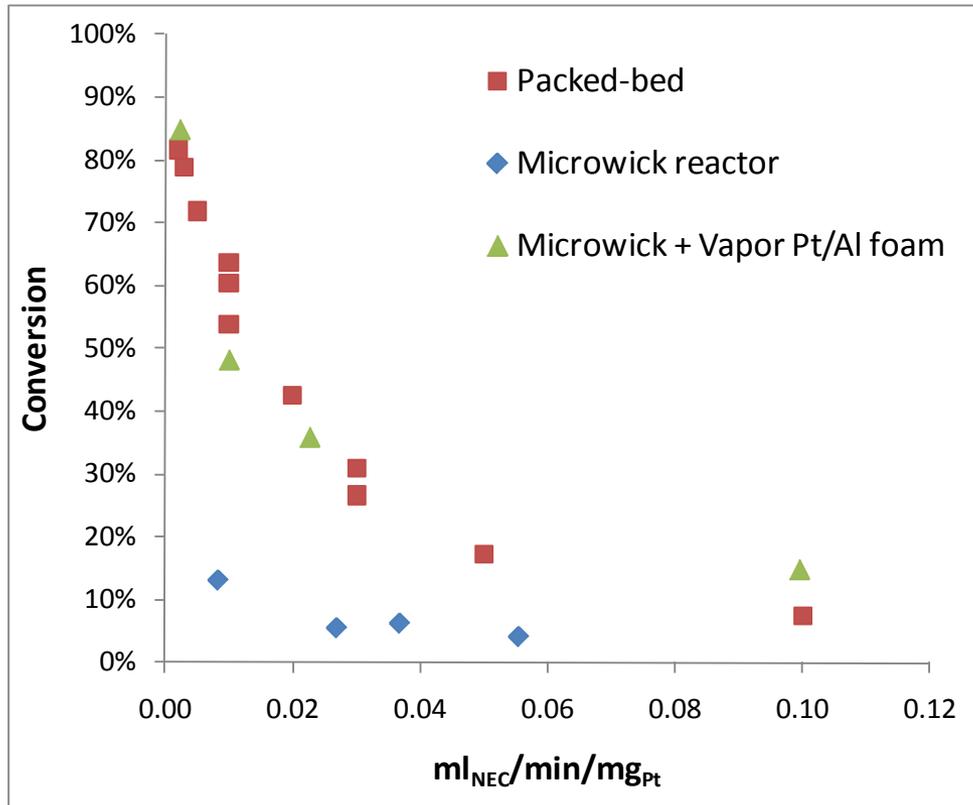
# Previous Technical Accomplishments: Microchannel Dehydrogenation Reactor Testing

- Single Channel Microwick Reactor
  - Approx. 5 cm x 6 cm footprint
  - 1-3 mm deep
  - Sapphire window to observe phase segregation
  - Heated with microchannels from below
  - Targets
    - 1 mg Pt/cm<sup>2</sup>
    - ~60 W<sub>e</sub> equivalent power (0.06 g H<sub>2</sub>/min)
- Unexpected phenomenon
  - Excellent gas-liquid separation at room temperature
  - As reactor heated to > 100°C
    - 'Free liquid' forms stable liquid droplets
    - Liquid droplets become entrained in gas flow
    - Caused by Marangoni effect due to heating from below and colder window above
    - Mitigated by heating window
- Microwick Reactor Results
  - 17% target catalyst loading
  - 2% H<sub>2</sub> productivity
  - Maximum conversion < 20%



Single channel catalytic wick

# Technical Accomplishments: Increased Conversion by Adding Catalyst in the Gas Channel



Perhydro-N-ethylcarbazole conversion as a function of space velocity (reaction temperature 230°C, packed-bed i.d. 5.2 mm, catalyst particle size 210-420 μm).

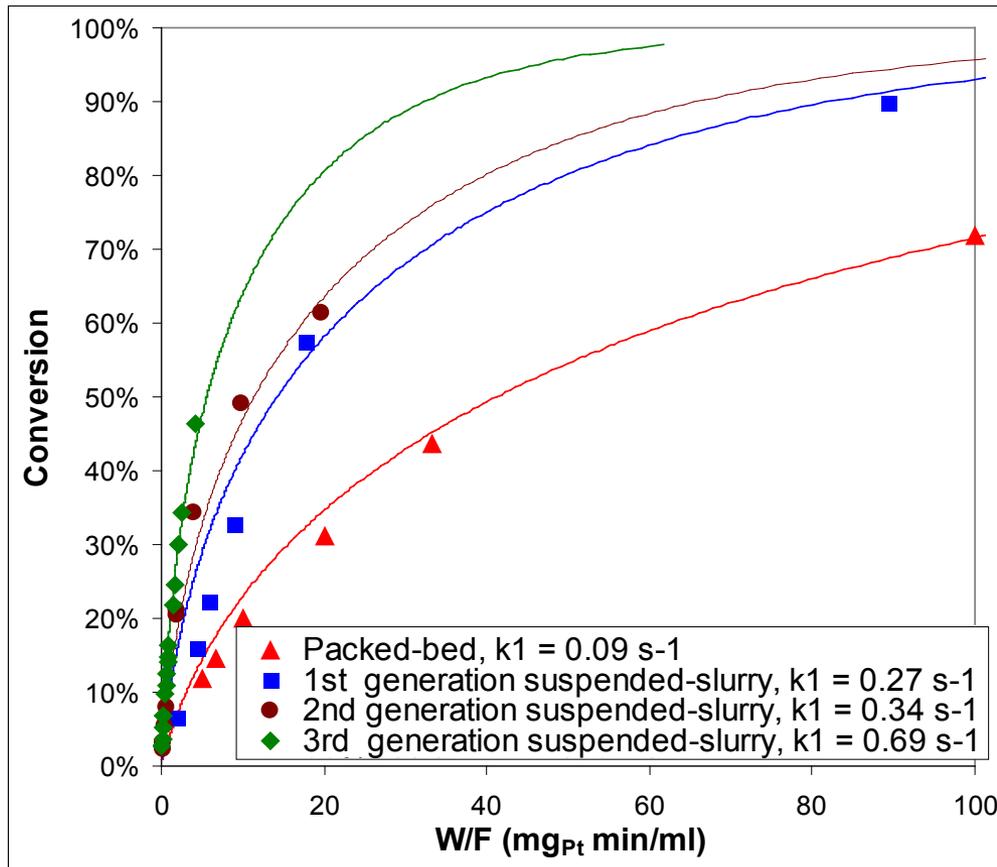
- Hypothesized that low conversion in the wick reactor was caused by losses to vapor phase despite low volatility of perhydro-N-ethylcarbazole at 230°C. Confirmed by adding foam loaded with catalyst to vapor channel.
- The results suggest that the performance of the wick reactor, even with catalyst in the gas channel, is similar to that of a packed bed.
- Led to analysis of transport limitations (focusing on diffusion) for the wick and packed-bed reactors.

# Technical Accomplishments

## Diffusion Limitation Analysis

- Packed bed analysis:
  - 210-420  $\mu\text{m}$  particles
  - The reaction rate is an order of magnitude faster than the  $\text{H}_2$  diffusion rate within the pores of the catalyst particles filled with liquid carrier
  - The reaction rate is of the same order of magnitude as the  $\text{H}_2$  diffusion rate through the liquid carrier boundary layer surrounding the particles
- Wick reactor analysis:
  - Liquid space velocity is reduced in wick reactor
  - Resulting in thicker diffusion boundary layer that increases mass transfer resistance
- Conclusions:
  - Diffusion limitation in the bulk should be minimized by increasing the mass transfer coefficient (higher Reynold's number) and/or decreasing the boundary layer.
  - On the other hand, internal diffusion can only be enhanced by decreasing the diffusion length inside the particles (i.e., particle diameter and tortuosity).
  - **A new reactor type that decreases the diffusive resistance is needed**

# Technical Accomplishments: Demonstration of a Reactor with Enhanced Productivity

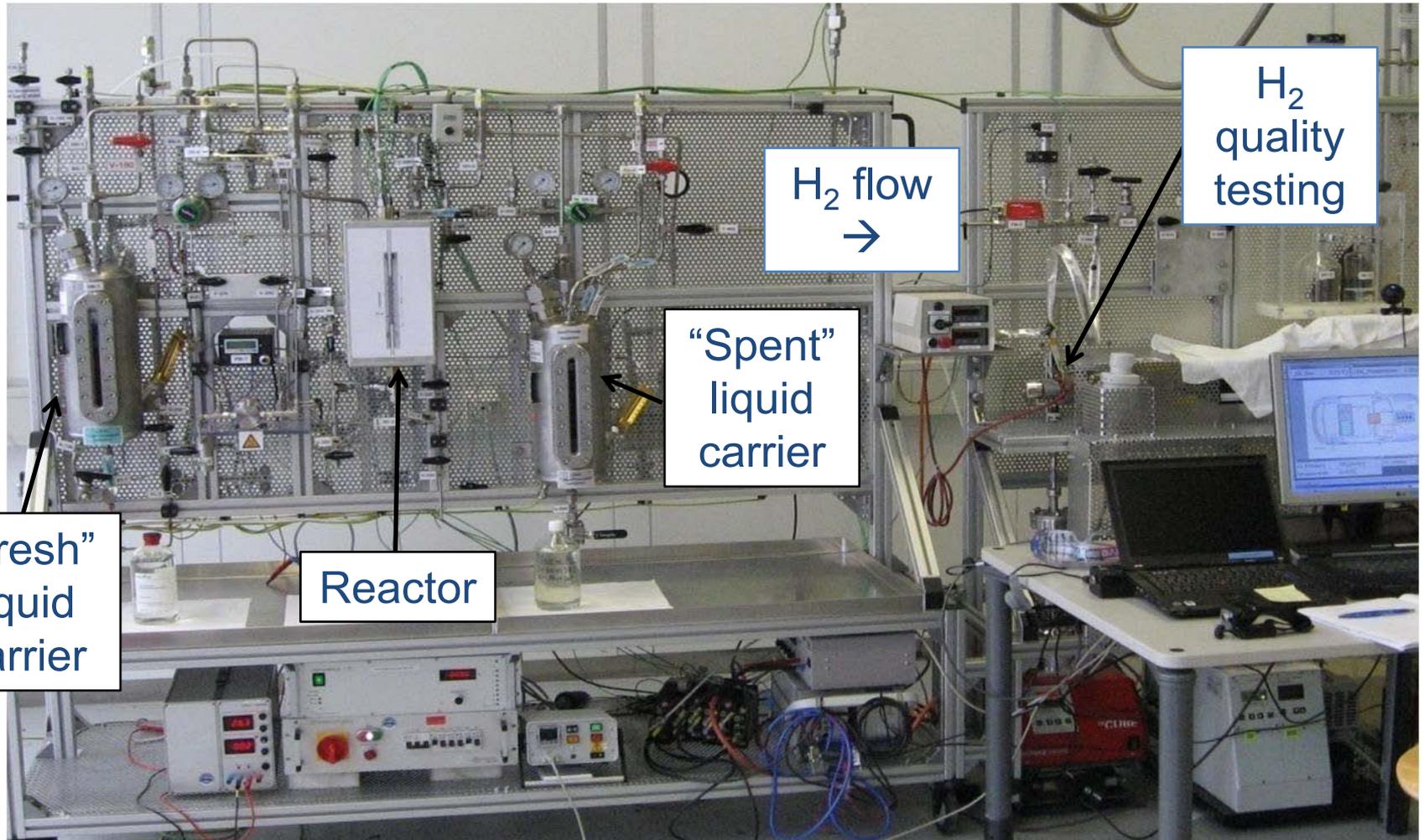


Comparison between packed-bed and suspended-slurry reactors for the dehydrogenation of perhydro-N-ethylcarbazole at 230 C, P = 1 atm. (packed-bed i.d. = 5.2 mm; catalyst particle size = 210-420  $\mu\text{m}$ ). The solid lines are first-order reaction rate kinetics fit of the experimental data.

Reactor	H <sub>2</sub> productivity at 90% conversion (g <sub>H2</sub> /g <sub>Pt</sub> /min.)
Packed-bed	0.2
Suspended-slurry	1.5
Target	2

A significant increase in conversion (7X) relative to the 1<sup>st</sup> generation reactor (along with very low pressure drop)

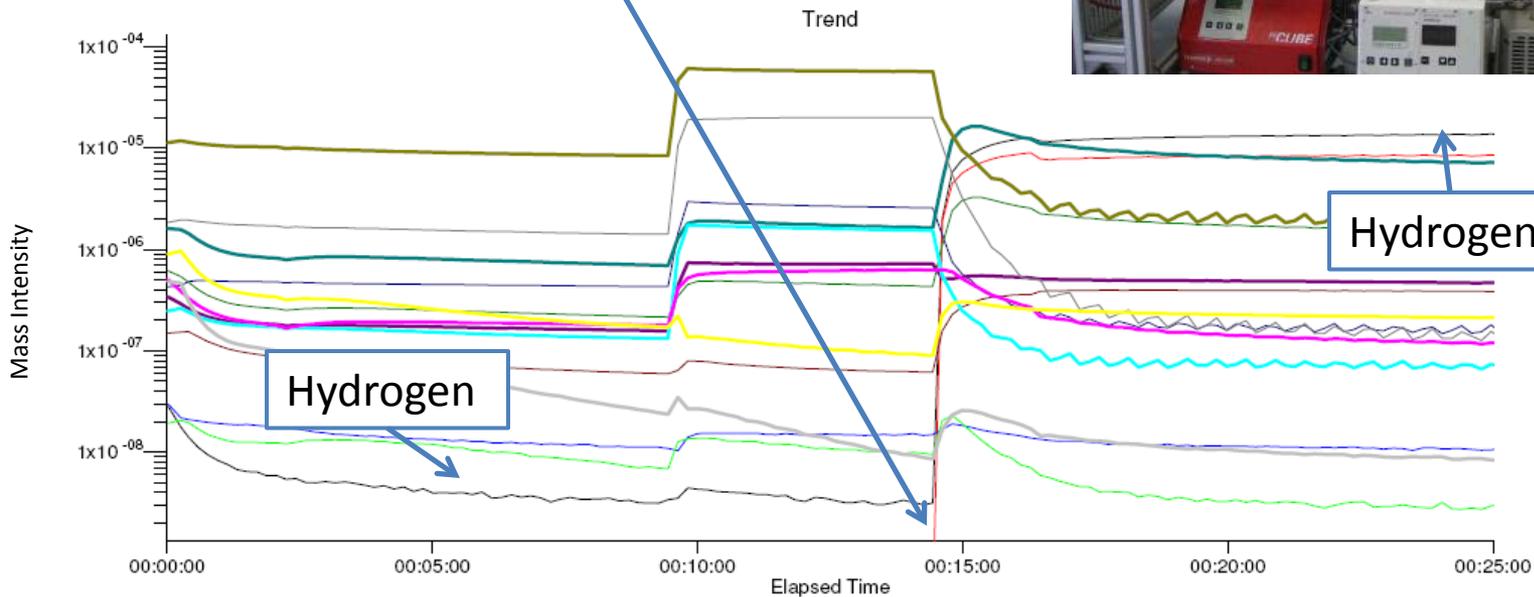
# Technical Accomplishments: Completion of Dehydrogenation Reactor Test Stand



# Technical Accomplishments: Demonstration of High Hydrogen Quality from the Liquid Carrier



Beginning of analysis of hydrogen from  
dehydrogenation reactor

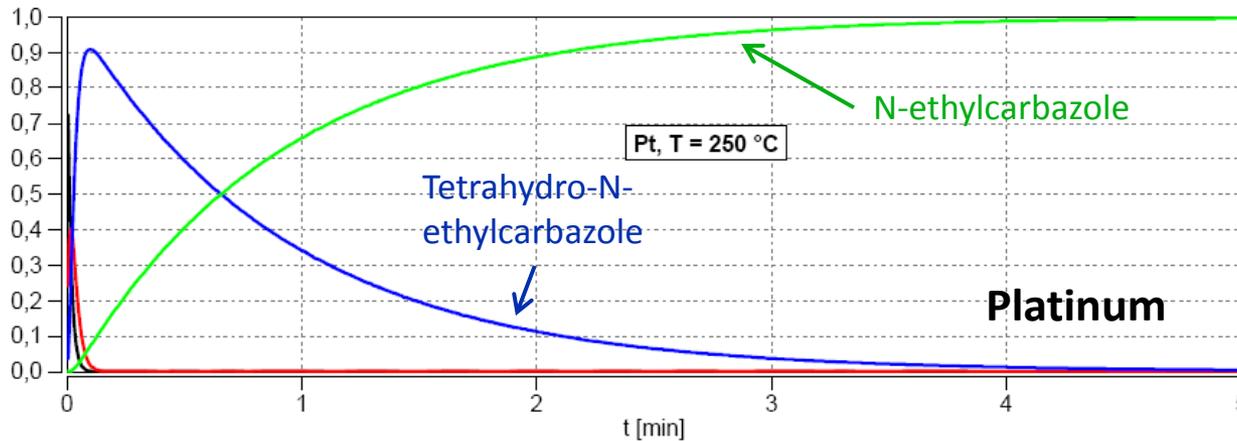


Hydrogen

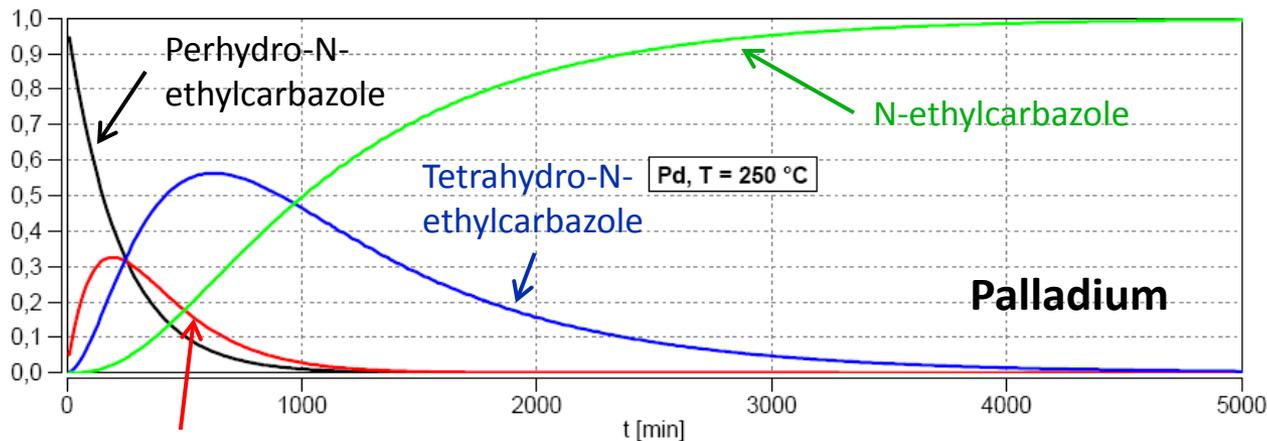
Hydrogen

- |  |  |
|--|--|
| — Hydrogen : From 2.84e-008 To 1.38e-005       | — Nitrogen : From 1.13e-005 To 2.04e-006       |
| — Helium : From -1.27e-010 To 8.59e-006        | — Oxygen : From 1.85e-006 To 1.56e-007         |
| — Carbon 12 : From 2.98e-008 To 1.05e-008      | — Argon 36 : From 1.94e-008 To 2.96e-009       |
| — Nitrogen 14 : From 4.28e-007 To 1.81e-007    | — Argon : From 2.48e-007 To 7.38e-008          |
| — Hydrocarbon 15 : From 1.49e-007 To 3.84e-007 | — Carbon dioxide : From 5.04e-007 To 1.20e-007 |
| — Oxygen 16 : From 3.40e-007 To 4.70e-007      | — LOHC-Fragment : From 9.02e-007 To 2.13e-007  |
| — OH group : From 6.15e-007 To 1.54e-006       | — Fluorocarbon : From 4.81e-007 To 8.38e-009   |
| — Water : From 1.61e-006 To 7.26e-006          |  |

# Technical Accomplishments: Modeling of Dehydrogenation Kinetics for Platinum and Palladium Catalysts



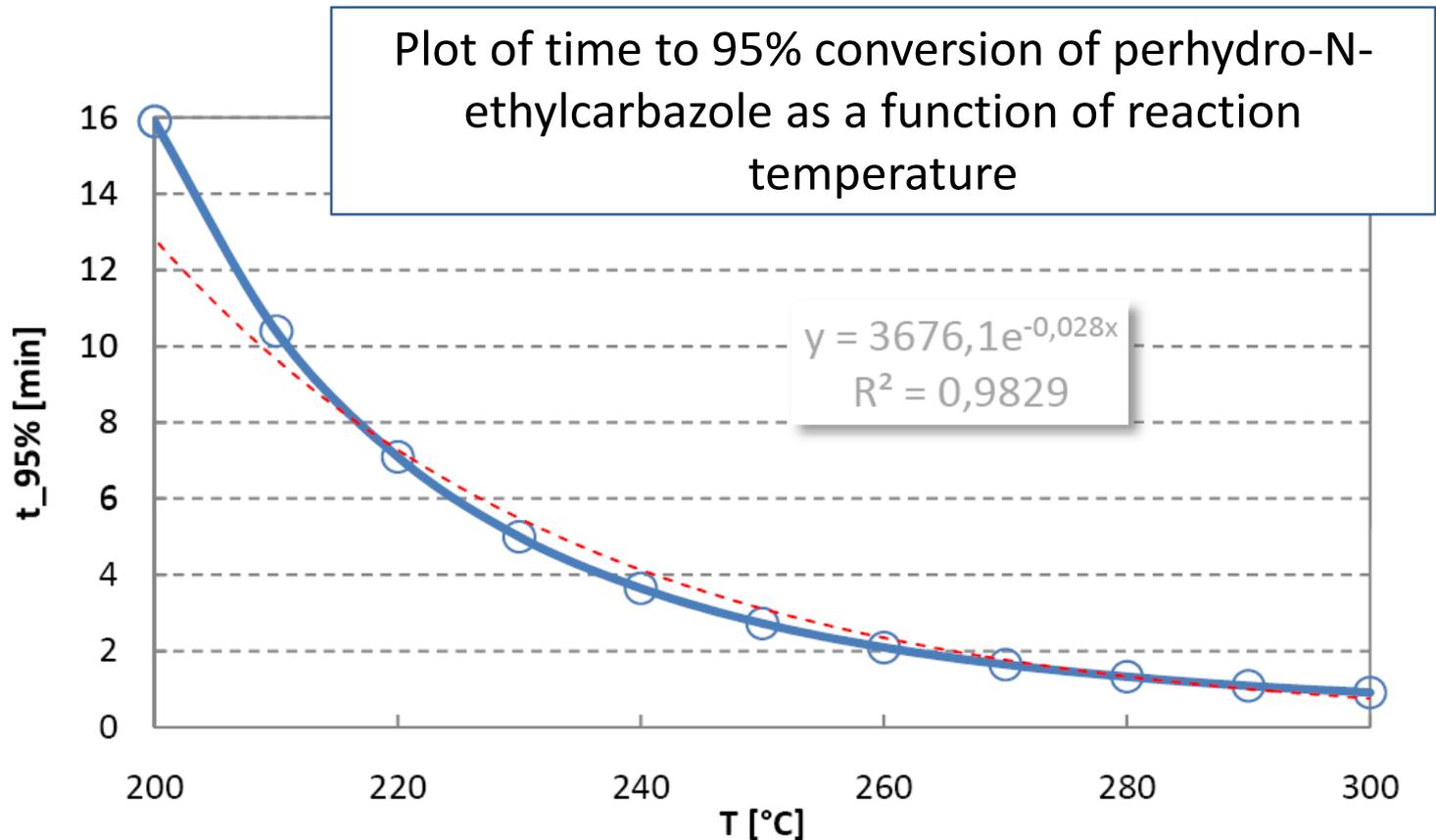
Platinum has a significantly higher rate for the dehydrogenation of perhydro-N-ethylcarbazole



Octahydro-N-ethylcarbazole

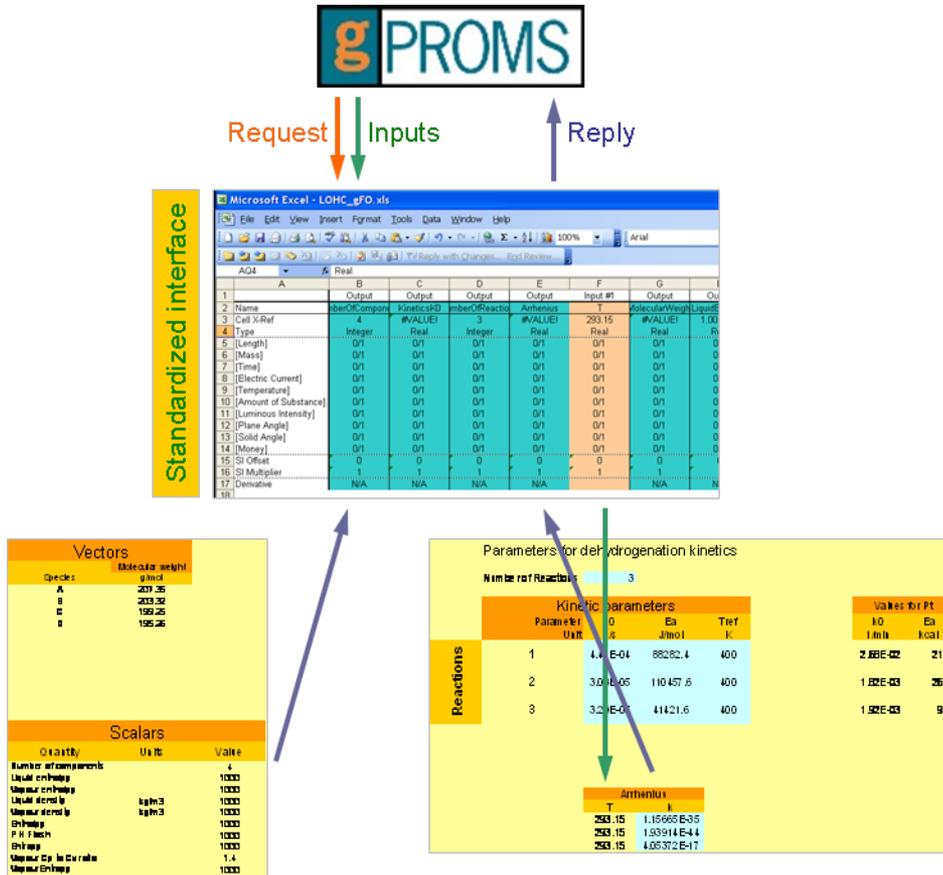
Note the very different time scales for Pd and Pt catalysts

# Technical Accomplishments: Modeling of Dehydrogenation Kinetics for Platinum Catalysts



Very short residence times can be achieved at temperatures suitable for heat integration with hydrogen internal combustion engines

# Technical Accomplishments: System-level Modeling of Dehydrogenation Reactor with Fuel Cell Systems



- Developed system model components in gPROMS software for smooth interfacing of a liquid carrier and the dehydrogenation reactor with the currently existing library.
- This introduces the specific properties of the liquid carriers into the currently existing and validated gPROMS components that UTRC has used in the past for system modeling.

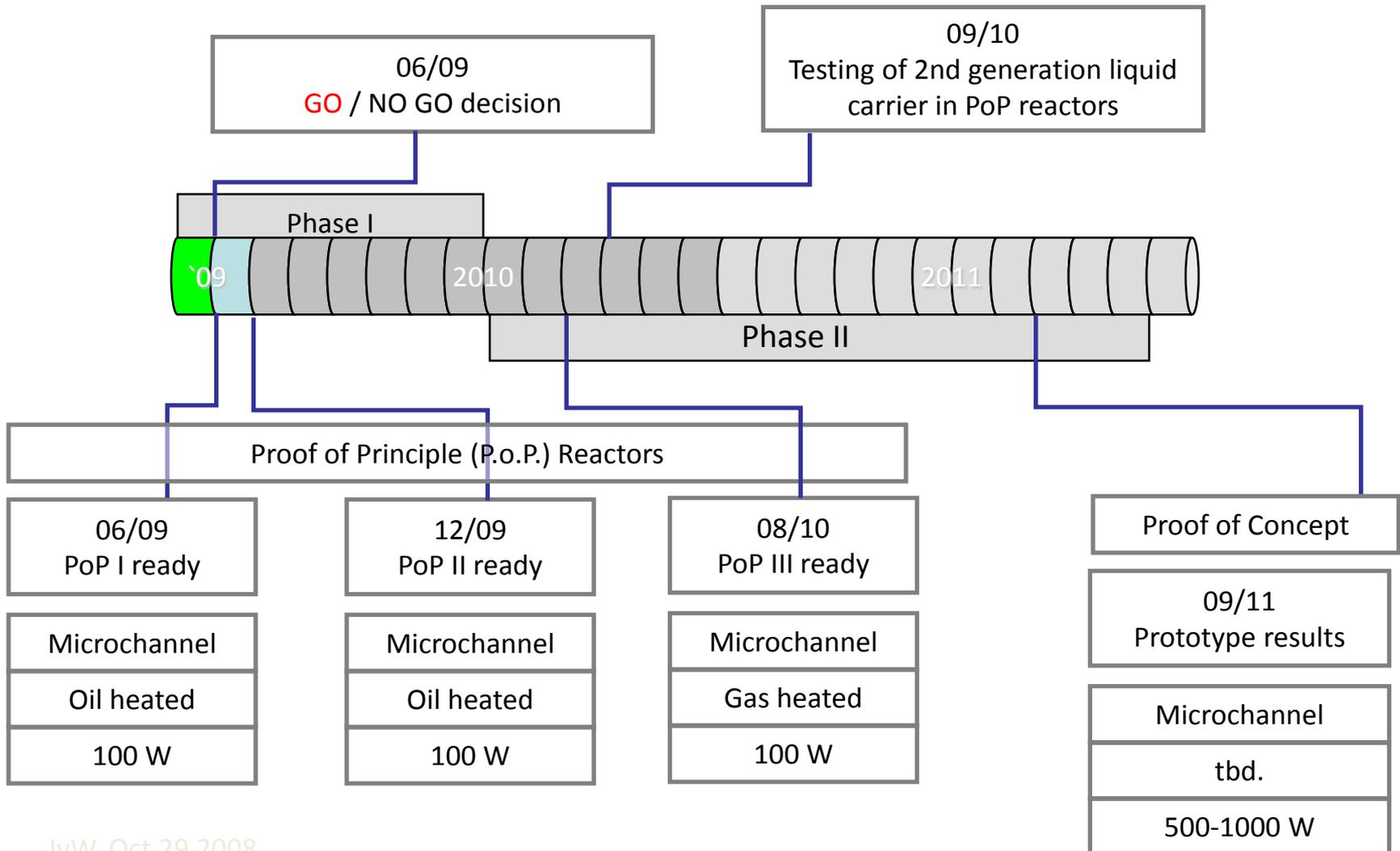
Excel interface to gPROMS for supplying liquid carrier properties.

# Collaborations

- Subcontractors:
  - Pacific Northwest National Laboratory (PNNL)
  - BMW Technology Corporation
  - United Technologies Research Corporation (UTRC)
- Others:
  - Penn State University
  - U.S. Dept. of Energy



# Proposed Future Work



# Summary

- Dehydrogenation reactor prototypes have demonstrated greatly enhanced productivity
  - Lower precious metal loadings → lower reactor cost
- The economic analysis of using liquid carriers for hydrogen delivery suggests a “delivery cost” of \$0.85 – 4.50/kg of H<sub>2</sub>

<i>H<sub>2</sub> Delivery using Hydrogen Carriers (DOE Targets)</i>				
<b>Category</b>	<b>2005 status</b>	<b>2009 status</b>	<b>FY2012 goal</b>	<b>FY2017 goal</b>
Carrier H <sub>2</sub> Content (% by weight)	5.7%	6.7 wt. % (1)	6.6%	13.2%
Carrier H <sub>2</sub> Content (kg H <sub>2</sub> /liter)	0.054	0.062	>0.013	>0.027
Carrier System Energy Efficiency (from the point of H <sub>2</sub> production through dispensing at the forecourt) (%)		TBD	70%	85%
Total System Cost Contribution (from the point of H <sub>2</sub> Production through dispensing at the forecourt) (\$/kg of H <sub>2</sub> )		\$0.85 – 4.50 (2)	\$1.70	<\$1.00

(1) Using 2<sup>nd</sup> generation carrier (perhydrofluorene)

(2) Determined using assumptions detailed in pending economic analysis