Reversible Liquid Carriers for an integrated Production, Storage and Delivery of Hydrogen

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Overview

Timeline

- Start: Date 8/2005
- Team Kickoff 10/2008
- Project end March 2011
- 49% Complete

Budget

- Total project $4,131,138
  - DOE share (75%)
  - Contractor share (25%)
- Funding received in FY08: $1,971,670
- Funding for FY09

Barriers

- Barriers addressed

E. Solid and Liquid Carrier Transport

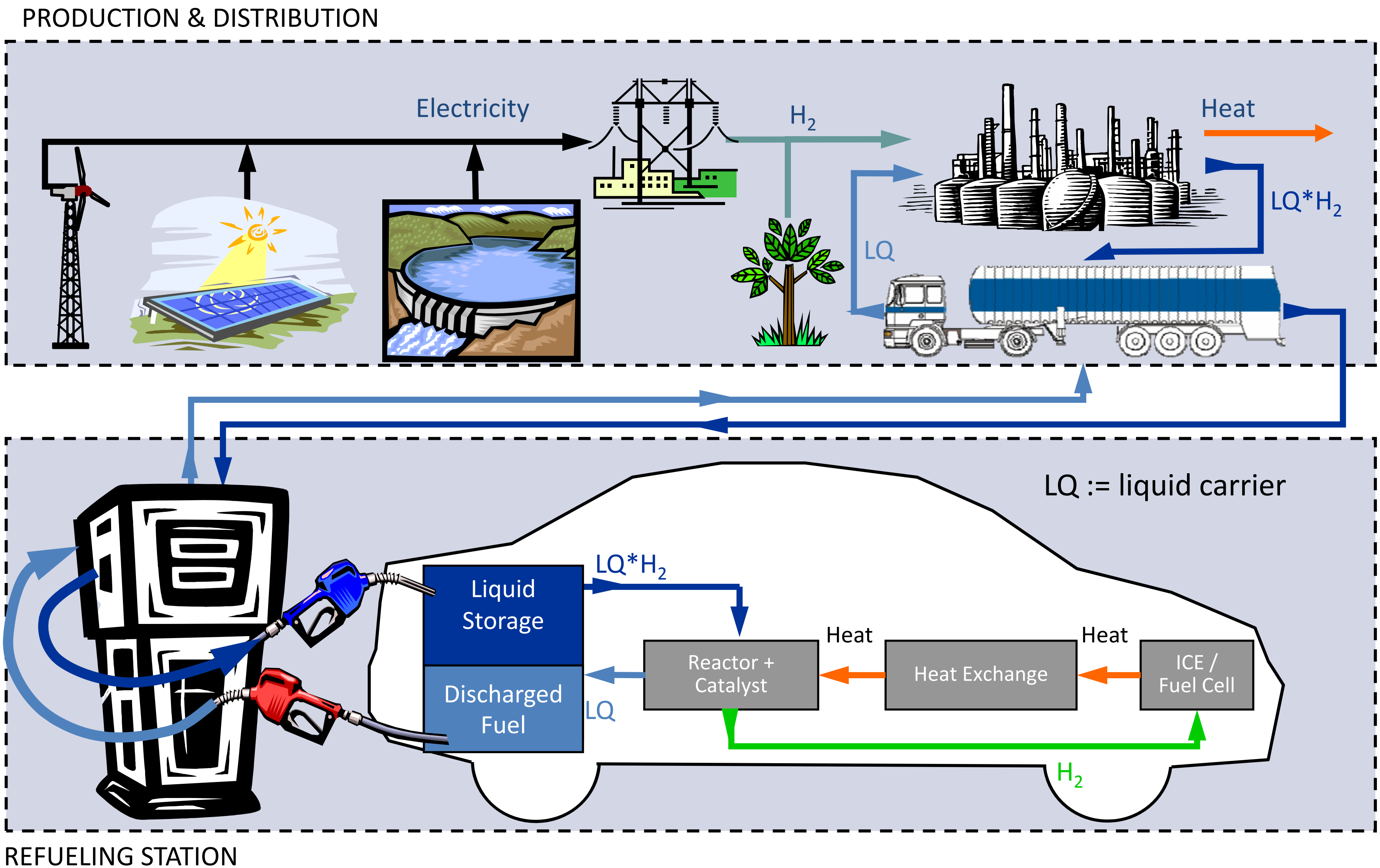
A. Hydrogen/Carrier and Infrastructure Options Analysis

F. Hydrogen Delivery Infrastructure Cost

Partners

- Pacific Northwest National Laboratory/Battelle
- United Technologies Research Center (UTRC)
- BMW Group

Approach



PRODUCTION & DISTRIBUTION
Electricity
H_2
Heat
LQ*H_2
LQ
LQ := liquid carrier
Liquid Storage
Discharged Fuel
LQ*H_2
LQ
Reactor + Catalyst
Heat
Heat Exchange
Heat
ICE / Fuel Cell
H_2
REFUELING STATION

Specific Project Approach

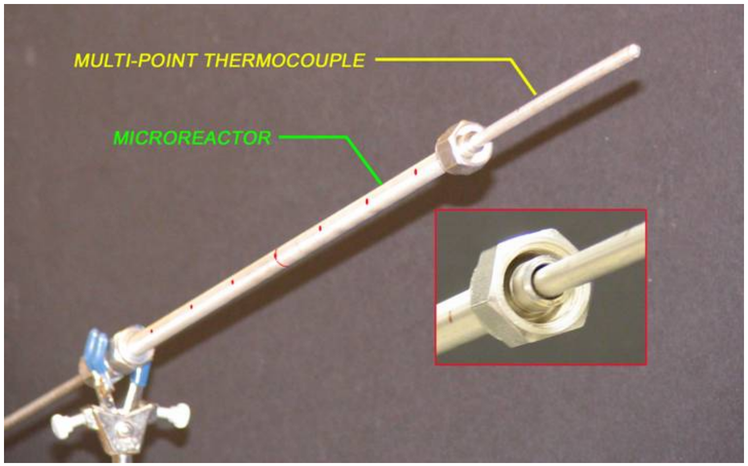
- Mobile Reactor initial focus
  - Rationale: This is the most constrained challenge. Data gathered will be applicable to all delivery modes, FC, ICE and forecourt, since reaction heat will be supplied by high temperature fluid stream for all reactor types.
- N-Ethyl Carbazole, while not suitable for commercial use is suitable as a test fluid.
  - Model compound allows reactor characterization, and economic studies but is not final material.
  - Evaluate economic potential using N-ethylcarbazole as a model compound
- Modeling will be used to simulate, optimize and evaluate each mode of hydrogen delivery

Collaboration

- BMW
  - Model integration of ICE and automobile
  - Testing prototypes
    - Evaluate performance
    - Provide operational parameters
- UTRC
  - Model integration of FC and reactor.
    - Forecourt
    - Automobile
- PNNL
  - Design of microreactors
  - Fabrication of prototype(s)

- AP
  - Testing of single microchannel reactors and packing for forecourt reactors
  - Providing materials
  - Testing prototypes (ICE)
  - Project Coordination

Microchannel Reactor Results



Typical Results 250^{0}C

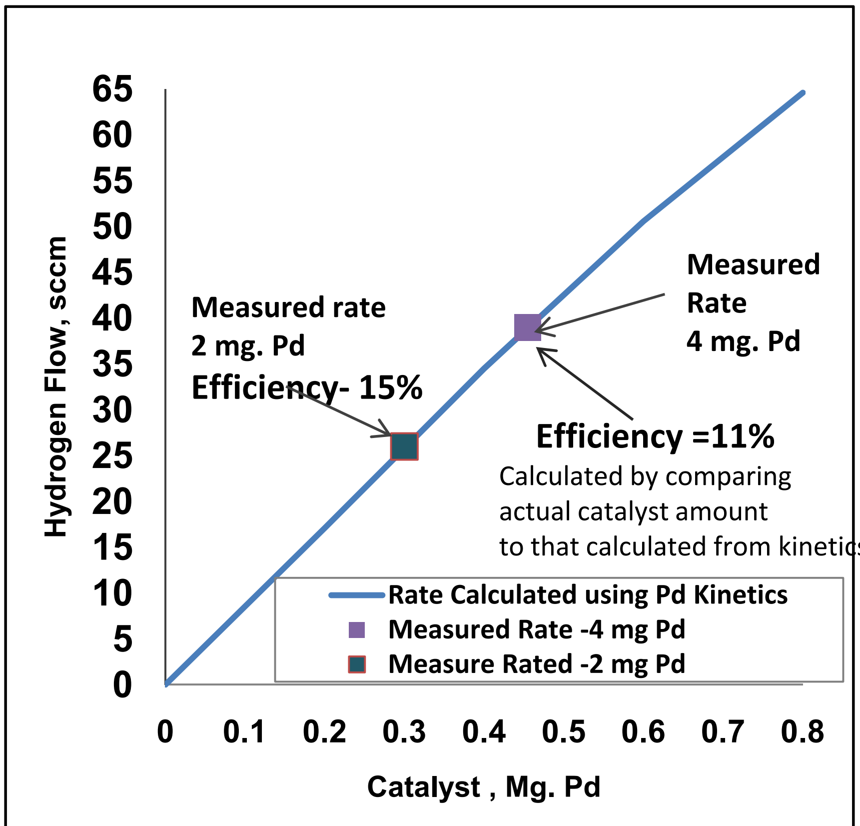
Catalyst	Feed Rate (ml/min.)	H_2 Flow (sccm)	Conversion (% available H_2)
Pt	0.1	52	80
	0.4	193	74
	1	421	65
Pd	0.1	23	35
	0.4	50	20
	1	75	12
Pd (particles)	0.1	59	91
	1	458	71

Single-tube microchannel reactors performed well

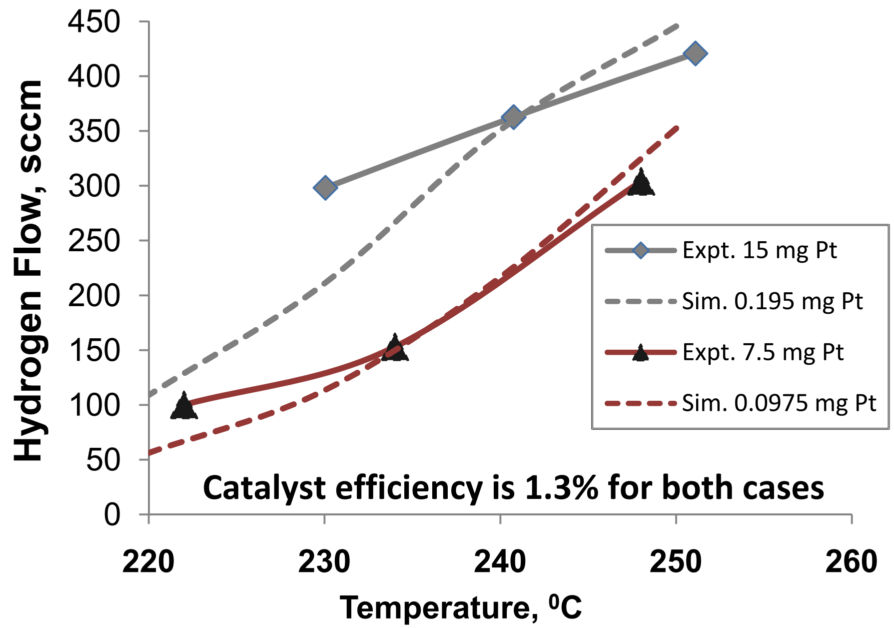
- Stable catalyst coating method was established.
- Reactor diameters from 2.55-0.5mm were demonstrated. (5 mm for particles)
- Single-pass conversions as high as 90% achieved.
- Temperatures from 190-250^{0}C were achieved.

Efficiencies of Microchannel Reactors

Pd Catalyst microchannel Reactor shows low catalyst efficiency and little effect of reactor length.



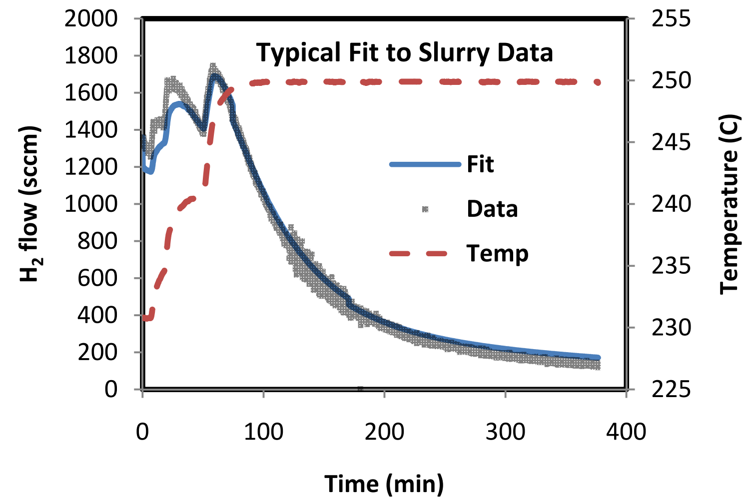
Pt Catalyst microchannel Reactor shows low catalyst efficiency and little effect of reactor length.



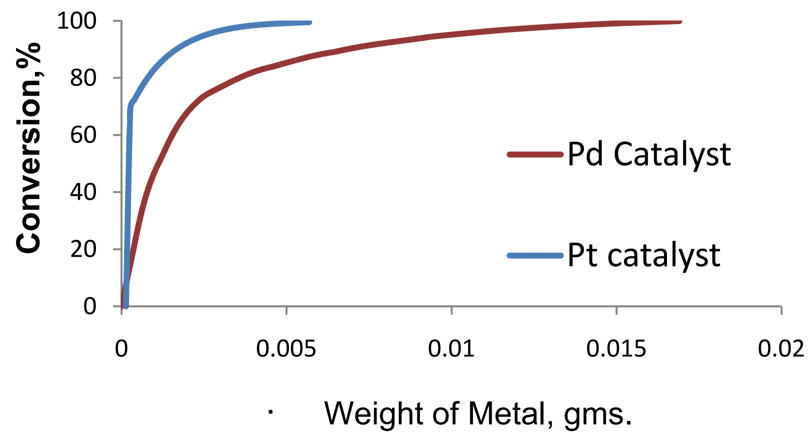
What is Primary cause of low efficiency?

Kinetics Modeling

- Dehydrogenation modeled adequately as three reactions in series.
- Batch experiments using slurry catalyst (small particles to eliminate mass transfer resistances) used for primary data.
- Activity of other catalyst forms done on the basis of the weight of the metal. (We expect some reduced efficiency when used in a thin film (typically 50% reduction based on APCI monolith experience))
- Kinetic expressions used in process models and to evaluate reactor performance or strategy. E.g., for Pd takes 40% more metal to go from 90 to 95 % conversion.



Pd vs. Pt
250^{0}C and 0.25 ml/min.

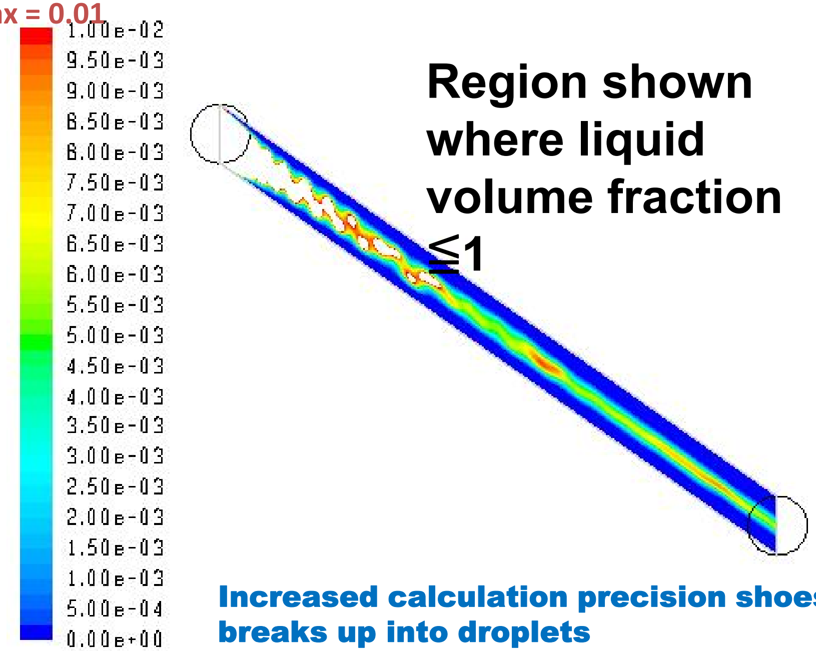


Technical Accomplishment

CFD analysis of microchannel reactor flow

Re-analysis of tubular flow pattern in microchannel

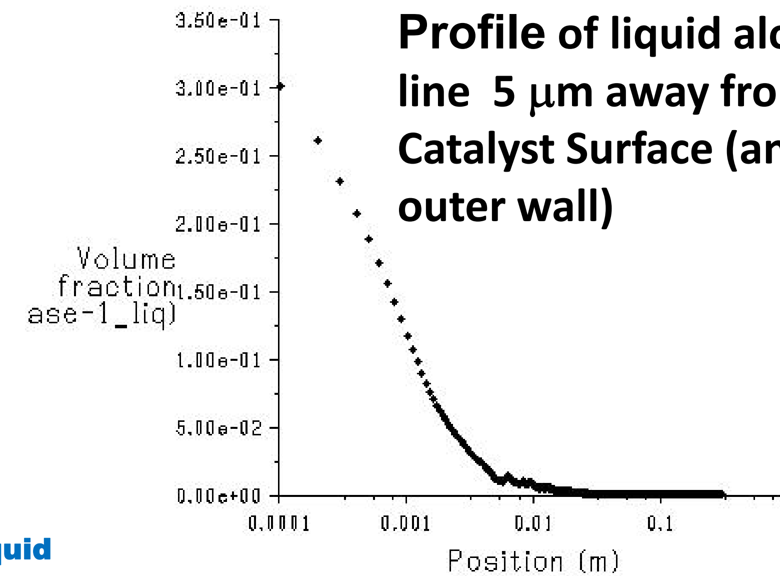
N-ethylcarbazole conc.
max = 0.01



Increased calculation precision shoes liquid breaks up into droplets

N-ethylcarbazole conc.
min= 0.0

CFD Analysis of Liquid Distribution in Annular Microchannel Reactor



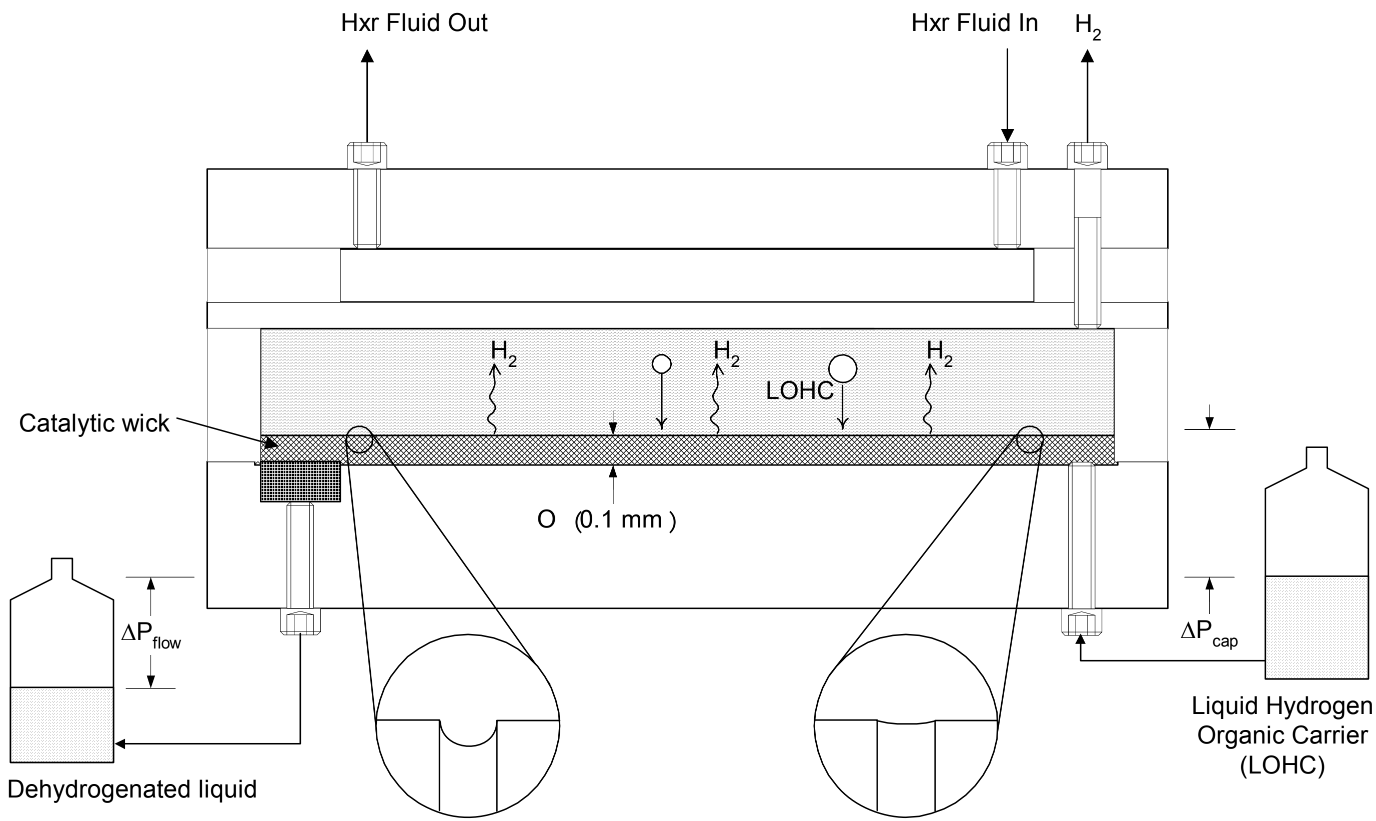
Profile of liquid along a line 5 μm away from the Catalyst Surface (annular outer wall)

Liquid Volume Fraction at catalyst surface decrease dramatically along Tube Length

Conclusion: Extremely low amount of liquid at Catalyst Surface limits catalyst efficiency

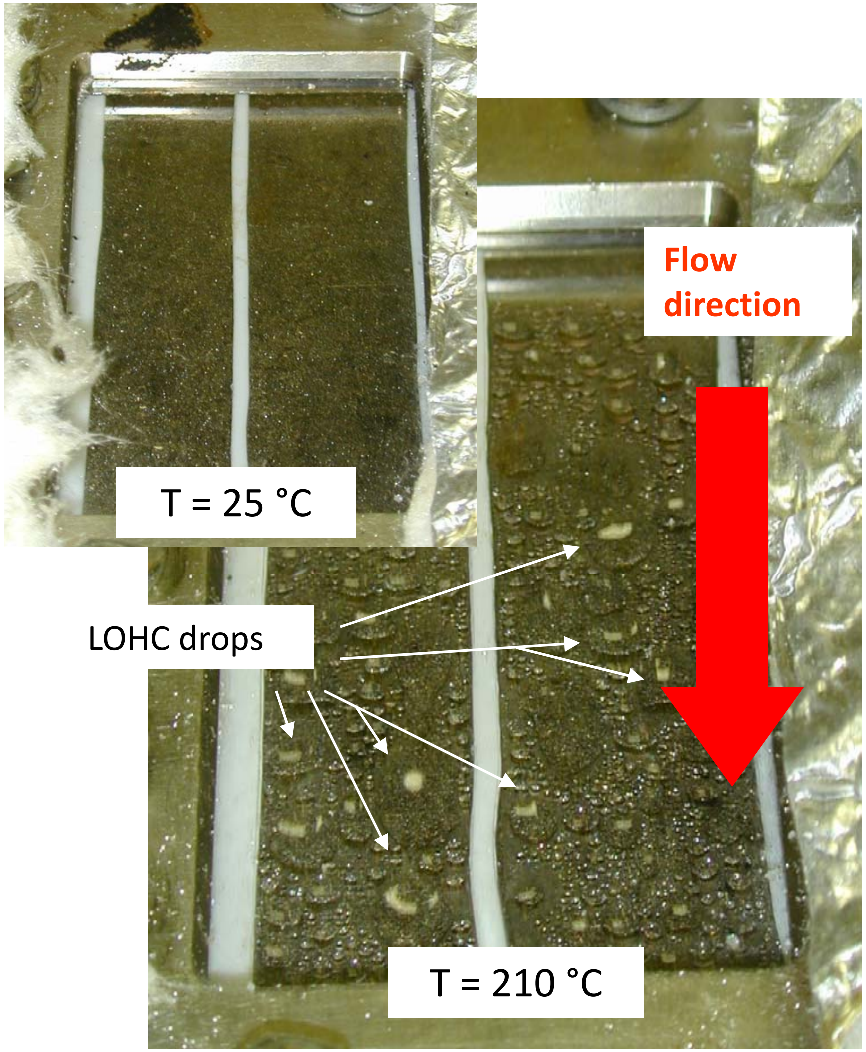
Microchannel Dehydrogenation Reactor
Technical Approach

- Address the issue of low liquid volume at catalyst surface by :
  - Segregating gas from liquid within the reactor
  - Keeping the catalyst wet and increasing liquid residence time
- Improve heat transfer to support endothermic reaction
  - Using laminate architecture
- Scale-up by numbering up channels



Microchannel Dehydrogenation Reactor
Technical Progress and Path Forward

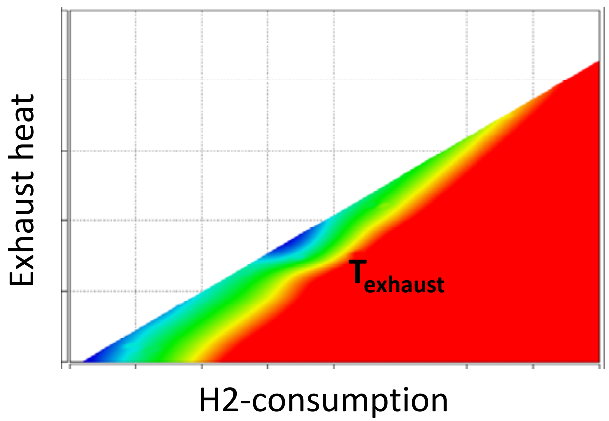
- Single Channel Microwick Reactor
  - Approx. 5 cm x 6 cm footprint
  - 1-3 mm deep
  - Sapphire window to observe phase segregation
  - Heated with microchannels from below
  - Targets
    - 1 mg Pt/cm2
    - ~60 W_e equivalent power (0.06 g H_2/min)
- Initial results
  - Excellent gas-liquid separation at room temperature
  - Discovered unexpected phenomena at > 100ºC
    - 'Free liquid' forms stable liquid droplets
    - Liquid droplets become entrained in gas flow
    - Reduces wicking flow capacity
  - 17% target catalyst loading
  - 2% H_2 productivity



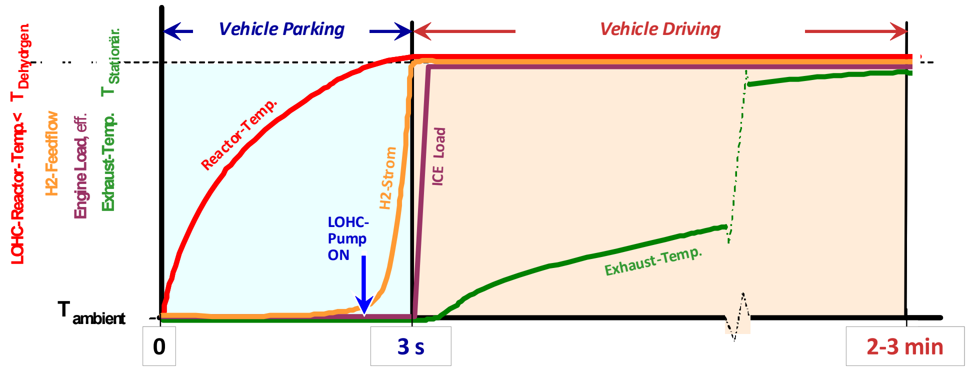
Single channel catalytic wick

Technical Accomplishments
Integration ICE and Liquid Carriers

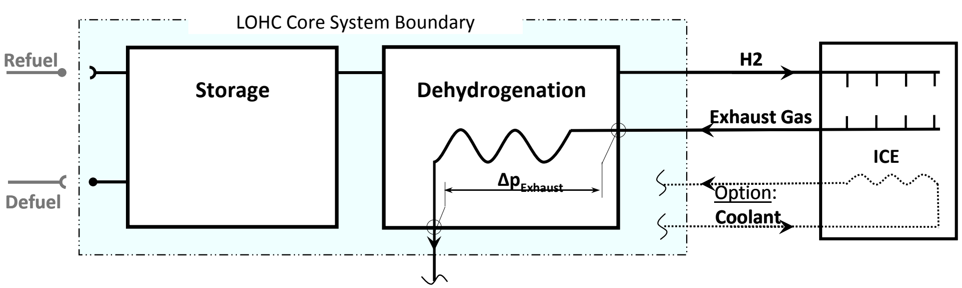
Combining operating characteristics of ICE
e.g. Exhaust gas conditions



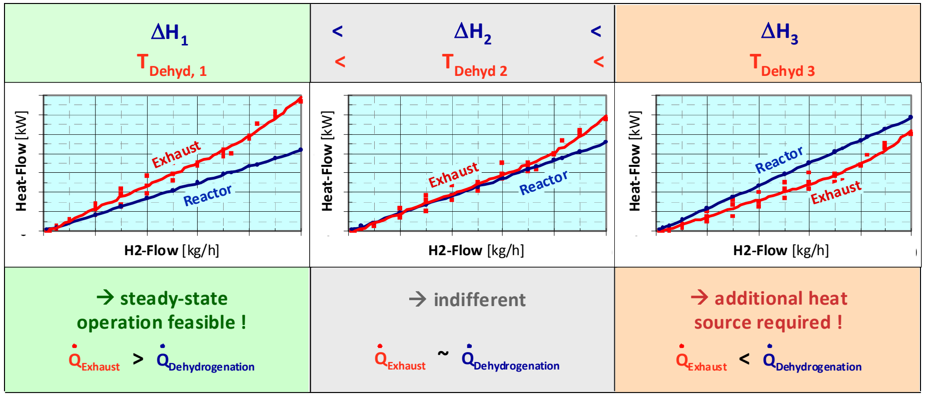
Performance Requirements
e.g. Transient Run-up of Reactor



LOHC-System
System Objectives



Steady-State Operation of Reactor
$T_{Dehydrogenation}$ vs. ΔH



Initial modeling has defined feasible operating points depending upon characteristic of liquid carriers

Tech Accomplishments/Relevance

Estimation of full-size core reactor:

- Target: 10 kg H_2/h , 60 kW thermal
- Heat transfer limiting reactor size
  - Current reaction rate (no mass transfer issues) support this
  - Case 1: Demonstrated in commercial-ready devices
  - Case 2: Laboratory demonstrated

Heat transfer limit	$\frac{\text{Heat Exchange Area}}{\text{Reactor Volume}}$	Demonstrated		Laboratory	
		500	[m^2 / m^3]	**1000**	[m^2 / m^3]
		60	[kW]	60	[kW]
Gas heated	**Reactor Volume**	**2,8**	[l]	**1,4**	[l]
	Heat Exchange Area	**1,4**	[m^2]	**1,4**	[m^2]
	Reactor Mass	**11**	[kg]	**6**	[kg]
Oil heated	**Reactor Volume**	**0,5**	[l]	**0,2**	[l]
	Heat Exchange Area	**0,24**	[m^2]	**0,24**	[m^2]
	Reactor Mass	**2**	[kg]	**1**	[kg]

Conclusion:
Reactor size estimations should be suitable for use in automobile

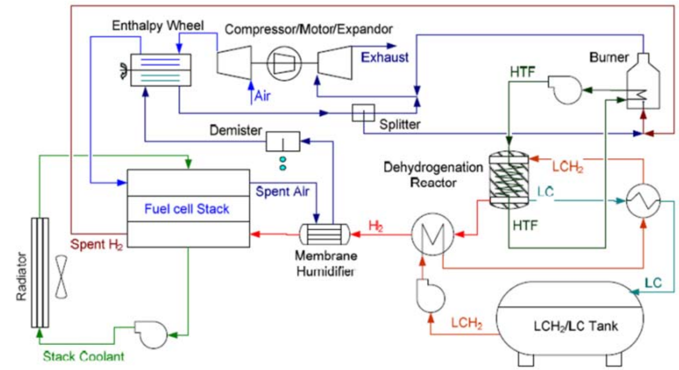
Fuel Cell / Forecourt Integration Modeling

United Technologies Research Center

Leveraging UTRC Fuel Cell modeling (gPROMS), system models are being constructed to evaluate on-board performance and apply waste heat sources to drive the dehydrogenation process at the forecourt.

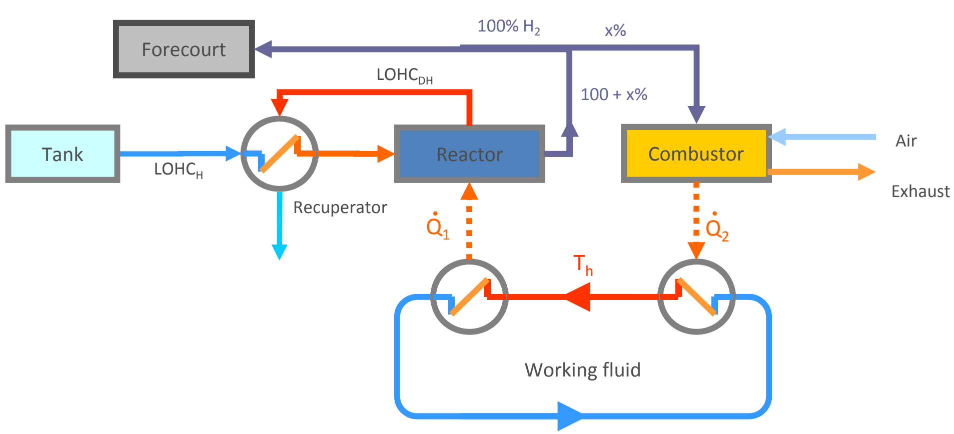
gPROMS

- On-board
  - Extend Argonne National Lab on-board analysis: modify configuration, incorporate PNNL reactor performance, conduct trade-off studies (weight, volume, kinetics, efficiency).



"System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE H_2 Program Review, May 2007.

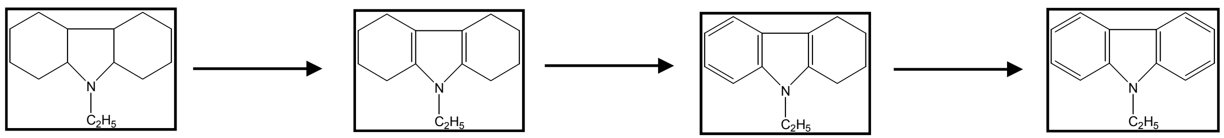
- Forecourt baseline configuration
  - Burn H_2 for dehydrogenation process



Forecourt/FC Modeling

United Technologies Research Center

- Reactor kinetics
  - Air Products model incorporated into UTRC gPROMS models

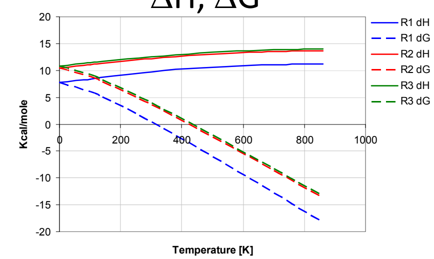


$$\mathrm{R1}: A \rightarrow B + 2H_2$$
$$\mathrm{R2}: B \rightarrow C + 2H_2$$
$$\mathrm{R3}: C \rightarrow D + 2H_2$$

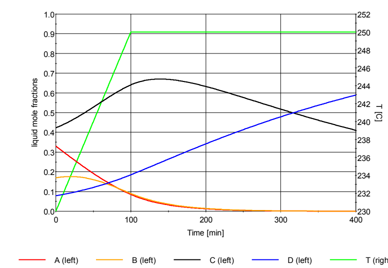
$$k_i = k_{i,o} \exp\left(\frac{E_{a,i}}{RT_{ref}}\left(1 - \frac{T_{ref}}{T}\right)\right)$$

T_{ref} = 400 K

ΔH, ΔG



Implementation validated



- Forecourt modeling: Several system configurations for hydrogen generation using the liquid carrier are being modeled leveraging existing models to improve heat utilization efficiency for the overall plant.

Summary

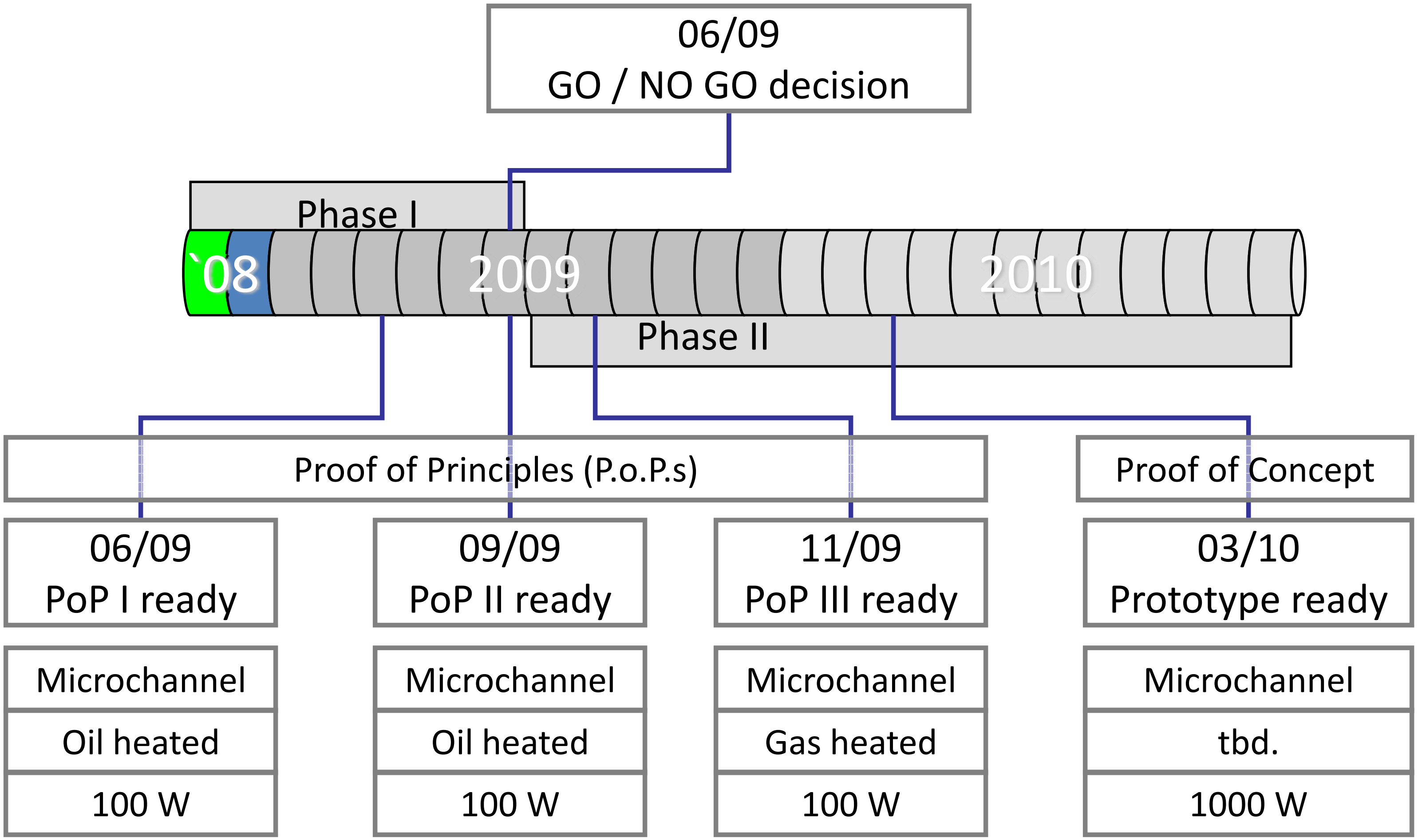
- Microchannel reactors
  - Dehydrogenation successful over a variety of conditions
  - Low catalyst efficiency was traced tothe high gas flow rate.
  - Experimental work to separate gas flow and increase liquid contact is underway.
- Modeling
  - Forecourt/FC: We have begun building system models
    - to evaluate on-board performance and
    - the dehydrogenation process at the forecourt.
  - Initial modeling of ICE
    - determined that the reactor size should be feasible for an automobile
    - defined stable operating point depending upon the characteristics of the carrier fluid

Future Work

Project Overview

- Reactor Testing
  - Test novel catalyst forms (foams) for forecourt reactor
  - Improve the gas-liquid separation in a Microwick Reactor
- Modeling
  - Incorporate reactor models into Fuel Cell/ Forecourt Modeling and perform trade-off analysis
  - Continue high-level system evaluation for ICE by adding necessary components with the goal of evaluating dynamic system characteristics
- Supply
  - Provide hydrogenated feed for all partners
  - Scale up hydrogenation process

Future Work –
Microchannel Reactor Development Milestones



JvW, Oct 29 2008