

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

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This presentation does not contain any proprietary or confidential information



Overview

Timeline

- 1 April 2005
- Sept. 2008
- “New Start”

Budget

- Total project \$4,131,138
 - DOE share (75%)
 - Contractor share (25%)

Partners

- United Technologies Research Corporation (UTRC)
- Penn State University
- Battelle/PNNL

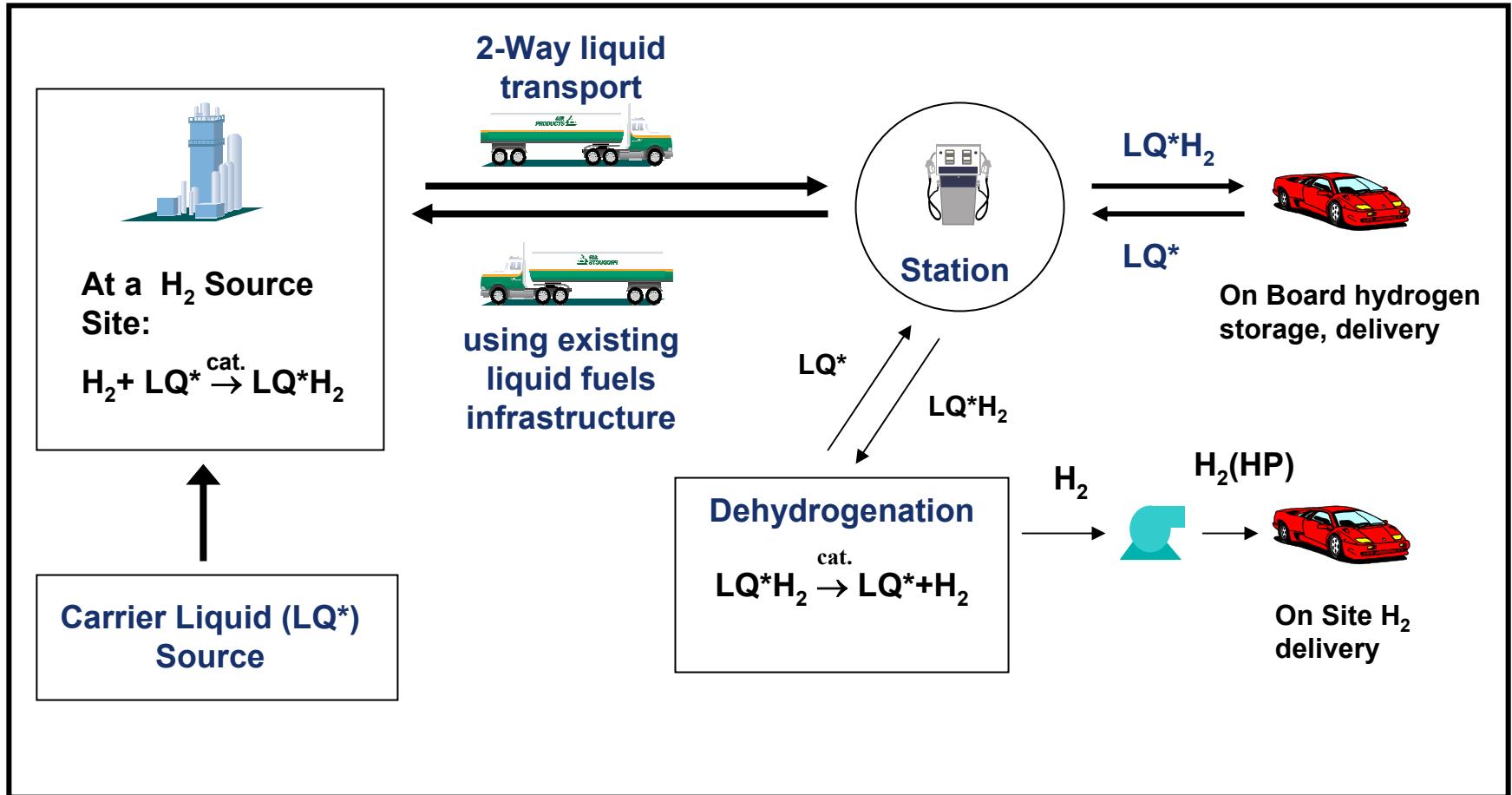
Barriers

E. Solid and Liquid Hydrogen Carrier Transport

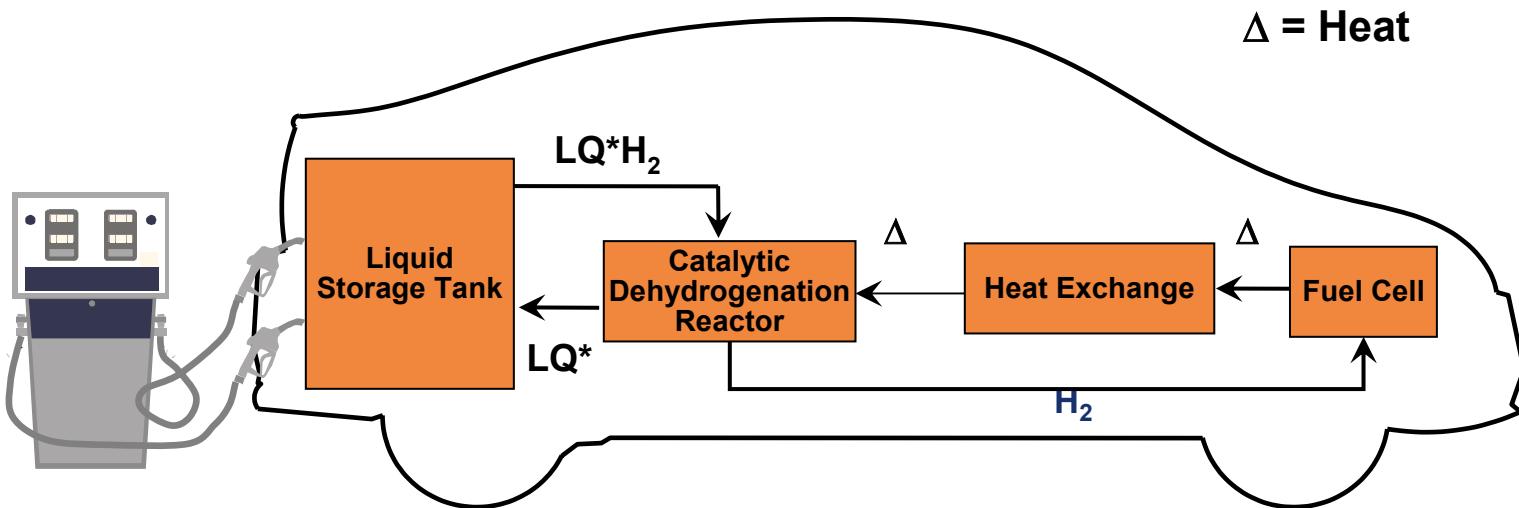
A. Hydrogen/Carrier and Infrastructure Options Analysis

F. Hydrogen Delivery Infrastructure Cost

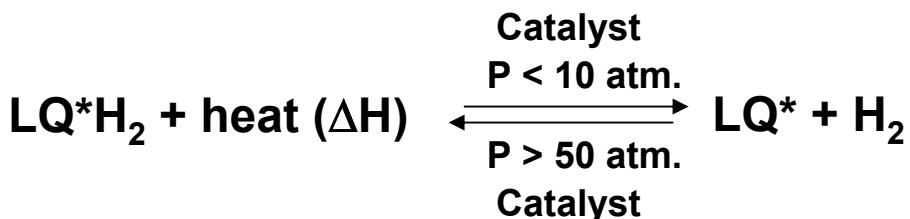
An Integrated Production, Storage and Delivery of Hydrogen – Using Reversible Liquid Carriers (LQ^*H_2)



Vehicular hydrogen storage and delivery using off-board regenerable liquid carrier (LQ*)



- Conformable shape liquid tank with design to separate liquids;
22.5 gallons of LQ^*H_2 for 5 kg hydrogen at 6 wt. % and unit density
- Use of waste heat from FC to drive dehydrogenation reaction. Radiator size credit



Maximum overall energy efficiency; by
(a) Recovering heat from the hydrogenation exotherm ($-\Delta H$) and (b) utilizing the FC's waste heat to drive the endothermic (ΔH) dehydrogenation.

Needs for Liquid Carrier Hydrogen Storage and Delivery Concept

1. Optimal liquid carrier (LQ*) compositions, their discovery, chemical synthesis and scale up
2. Effective catalysts for carrier hydrogenation and dehydrogenation steps (evaluation in batch mode)
3. Dehydrogenation reactor/heat exchange system for delivering a controllable continuous flow of hydrogen on board a vehicle or at a stationary site.
4. Low cost raw material sources for carrier
5. Hydrogen delivery, overall system economics

Addressed in concurrent
“Design and Development
of New Carbon-based Sorbents
for an Effective Containment
of Hydrogen” project (ST-14)

Objectives of
this “H₂ Delivery”
project

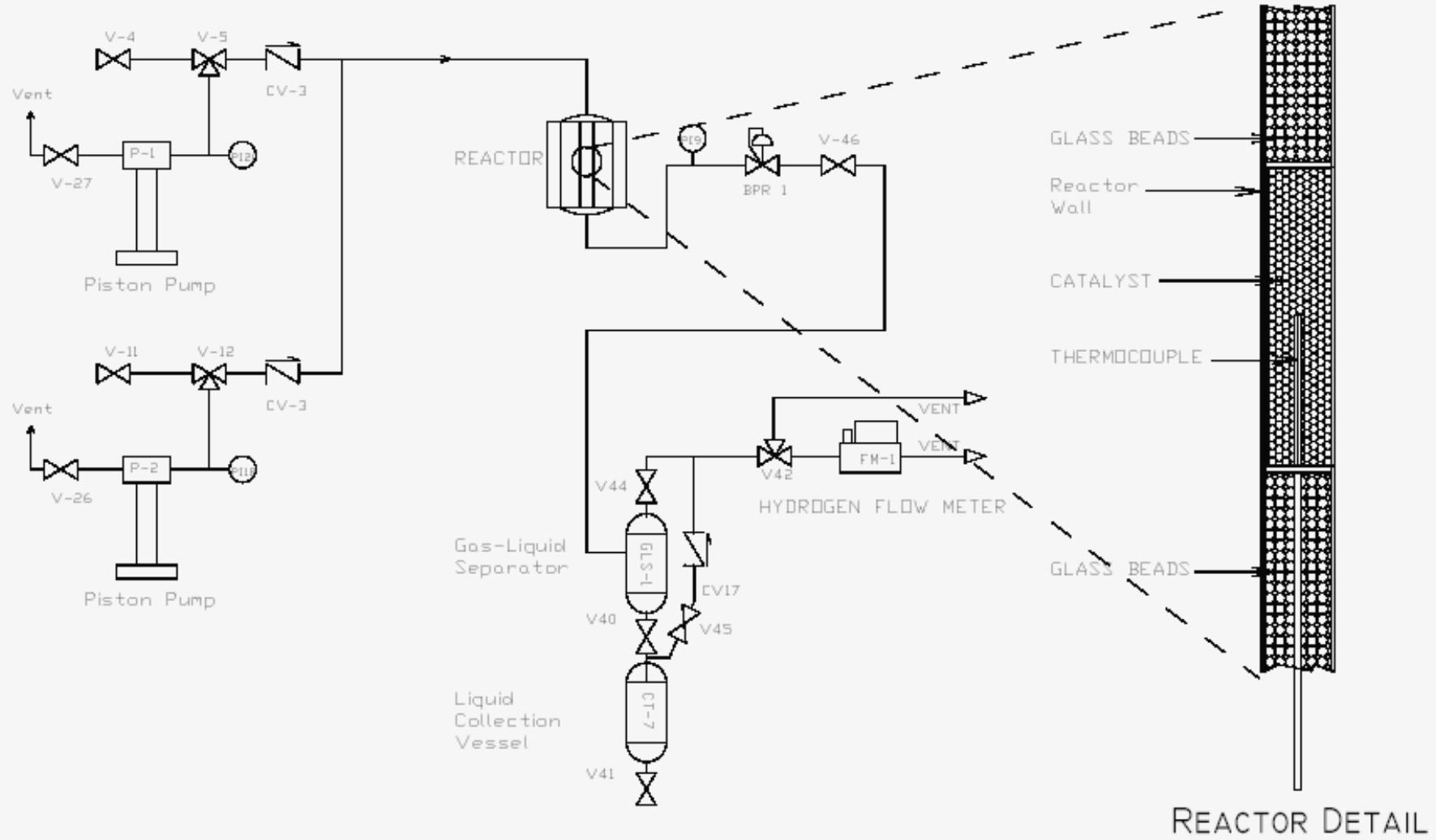
Dehydrogenation Reactor Design and Development: Project Deliverables (FY 08):

- Prototype reactor capable of delivering enough hydrogen (~1g H₂/min.) to power a 1 kW engine
 - Reactor capable of sustained operation
 - All features compatible with a mobile fuel cell
- Conceptual design for reactor that functions with balance of power plant of a vehicle

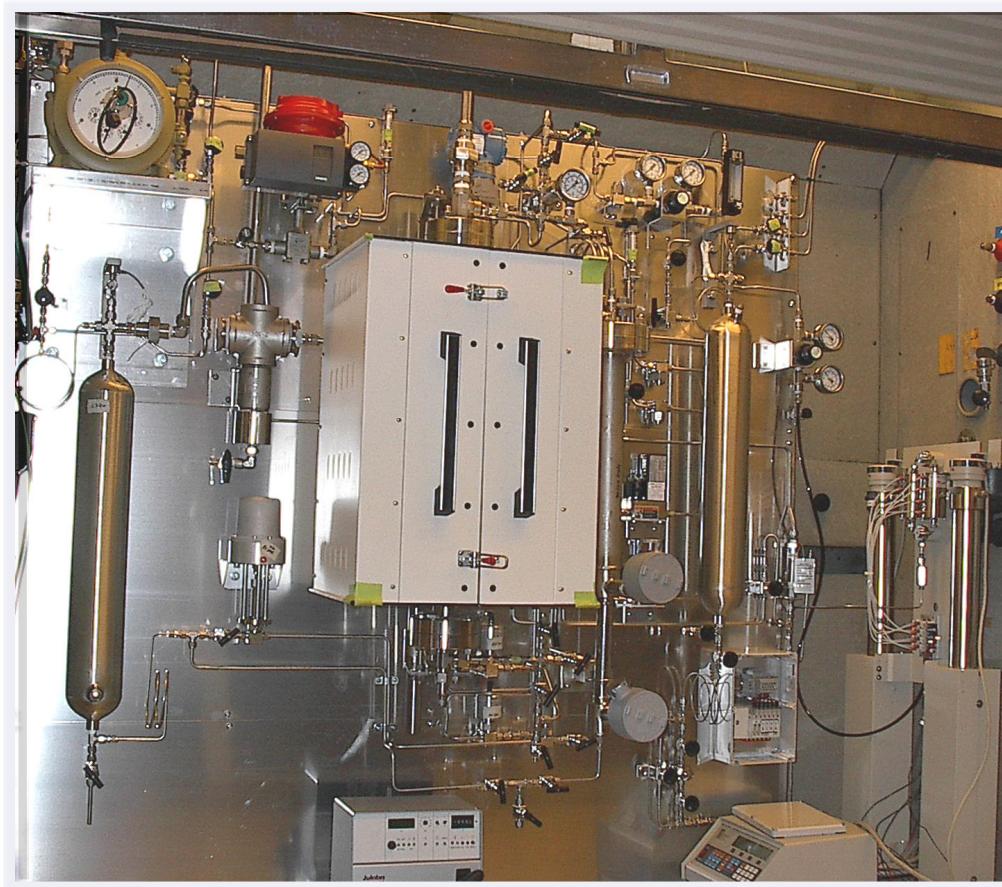
Dehydrogenation Reactor Design and Development Work Plan

- Initial demonstration in packed-bed reactor (FY 05)
 - On-going.
- Advanced reactor designs: (FY 06, 08)
 - Structured packings, monoliths, membrane reactors
 - Microchannel reactors (Battelle) (FY 06-08)
- Considering reactor requirements for its functioning in an on-board system (UTRC): (FY 06, 07)
 - System level modelling
 - Options for temperature upgrading of FC waste heat

CONTINUOUS PACKED BED REACTOR (DOWNFLOW OPTION)



Dehydrogenation Reactor Test System

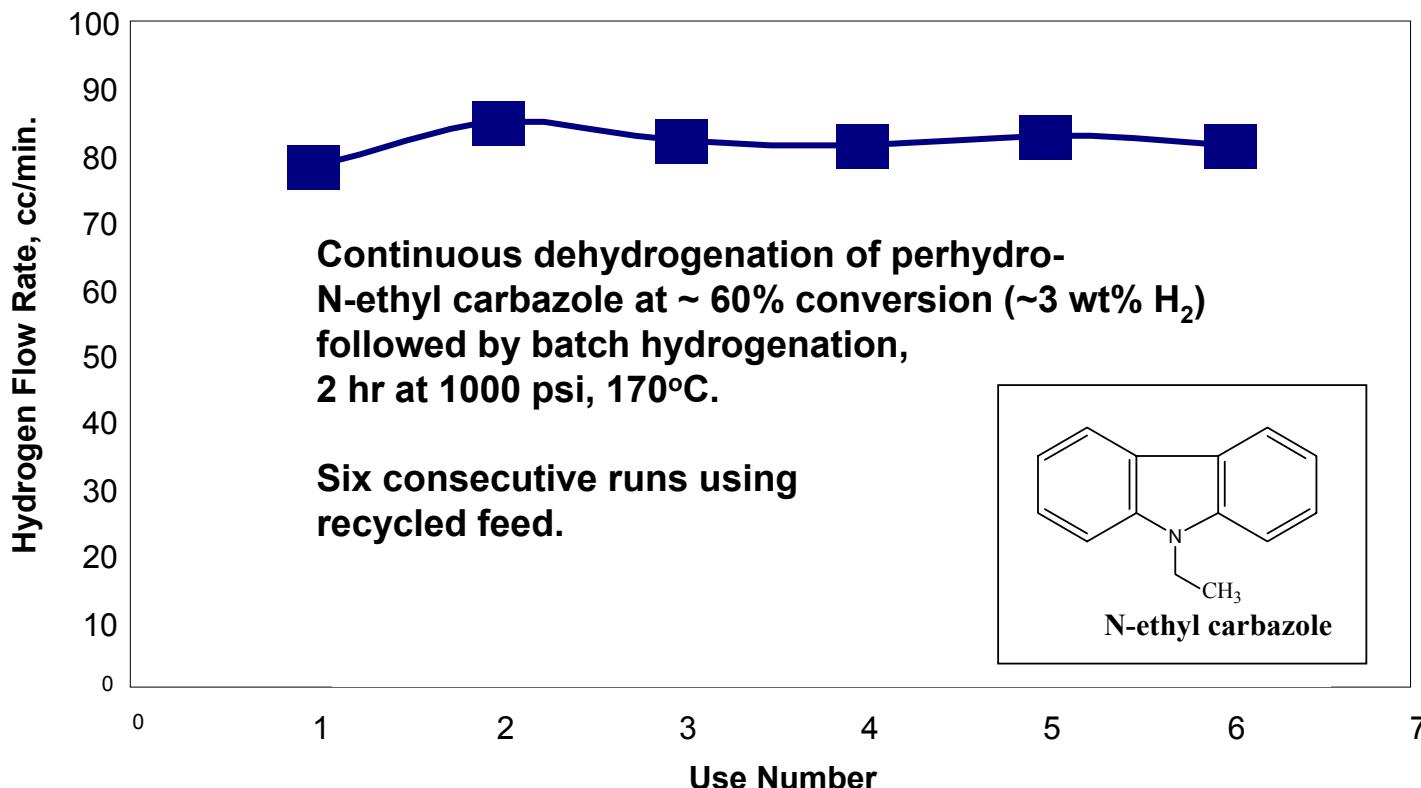


2" Packed Bed Reactor



Packed Bed Reactor Dehydrogenation/Hydrogenation Cycling Demonstration

190°C; 0.25 ml./min/ Liquid Flow



Typical Quality of Hydrogen from continuous flow reactor experiments

- Gas chromatography/Mass spectroscopy analysis

Component	Mole %
Hydrogen	99.9+
Methane	0.0013%
Ethane	0.0083%
Carbon Monoxide	ND*
C3's	ND
C4's	ND
C5's	ND
C6's	ND

***ND – Not Detected**

Typical Reactor Results for Dehydrogenation of Perhydro N-Ethyl Carbazole

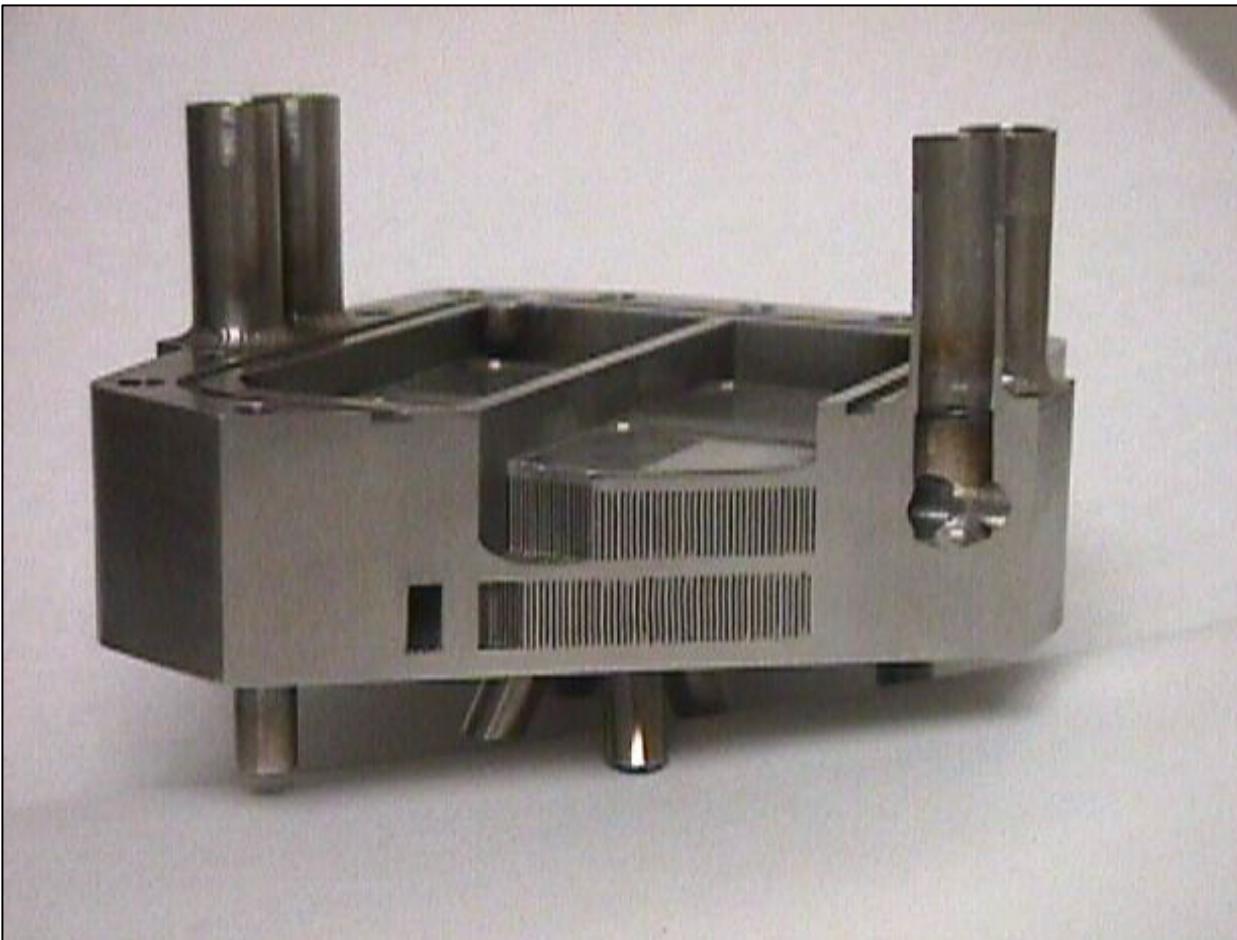
Feed Rate (ml/min)	Temp C	Hydrogen Flow (sccm)	Conversion %
0.1	190	44	78
1	190	326	54
2	190	508	42

Effect of Temperature

2	215	815	68
1	222	463	78
0.1	222	60	100

Note the high flow rate (508 sccm or 0.045 g H₂/min.), and full conversion but at the higher temperature.

Illustration of a Microchannel Reactor



Battelle 50 kW microchannel integrated combustor-gasoline vaporizer. Full size unit, ~ 13 cm at longest dimension.

Carrier Raw Materials Sourcing and Processing

Goals: Identification of low cost raw materials for synthesis of carrier (eg. N-heterocyclic molecules from fossil fuel sources)

Review of raw material recovery and purification options

Study by Profs. S. Eser, C. Song of Penn State Energy Institute (Report FY 06)

Hydrogen Delivery Economics for Liquid Carrier Concept

Economics on basis of performance, cost and benefit

- Production of carrier liquid
- Re-hydrogenation of spent liquid
- Two way transport to a fueling station site
- Equipment for dehydrogenation of carrier

Potential benefits from recovery of hydrogenation exotherm (~ 20% of H₂'s LHV) and use of waste heat from FC to reduce vehicle's radiator size

First pass economics, mid FY 07, final report in FY 08.

Summary, Future Work

Liquid carrier concept for an integrated storage and delivery of hydrogen. Entails:

- Carrier discovery, synthesis, hydrogenation/dehydrogenation catalysis - in batch mode. (Complementary DOE hydrogen storage project, ST-14)
- Dehydrogenation reactor design and development

Deliverable: A 1 kW equivalent H₂ source (~1g H₂/min) reactor designed for a mobile application.

Approach: From packed bed to advanced (eg. microchannel) reactors (with Battelle, UTRC)

Accomplished: Construction of dehydrogenation reactor test equipment
Demonstration of continuous H₂ production from carrier using a packed bed reactor and recycled feed.

- Hydrogen delivery economics
- Low cost raw material sources for carrier synthesis (Penn State)

Publications and Presentations

- New Start

Hydrogen Safety

- The most significant hydrogen hazard associated with this project is: hydrogenation of liquid carriers
 - overpressure and over-temperature scenarios
- Liquid carriers are hydrogenated in our laboratories at scales ranging from 4 – 5000 cc/batch
 - Hydrogen pressure typically 700-1200 psia
 - Heat of hydrogenation (exothermic) must be removed from hydrogenation to prevent overheating – most relevant at large scale

Hydrogen Safety

Our approaches to deal with this hazard are:

- Detailed Design Hazard Review (DHR) for all hydrogenation operations – with signoff from EH&S personnel
- Engineering controls
 - Overpressure relief devices (i.e. rupture discs)
 - Hydrogen monitors for leak detection
 - Linked to reactor control for automatic shutdown in the event of a hydrogen leak from the reactor
 - Over-temperature shutdown
 - Linked to reactor control for automatic shutdown in the event of a temperature excursion
 - Use a second, independent thermocouple from temperature controller