III.9 Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen

Bernard Toseland (Primary Contact), Guido P. Pez

Air Products & Chemicals, Inc.
Corporate Science and Technology Center
7201 Hamilton Street
Allentown, PA 18195
Phone: (610) 481-8907; Fax: (610) 481-7719
E-mail: toselaba@airproducts.com

DOE Technology Development Manager: Monterey R. Gardiner

Phone: (202) 586-1758; Fax: (202) 586-9811
E-mail: Monterey.Gardiner@ee.doe.gov

DOE Project Officer: Jesse Adams

Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

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- United Technologies Research Corporation (UTRC), East Hartford, CT
- Pacific Northwest National Laboratory (PNNL), Richland, WA
- BMW Hybrid Technology Corporation, MI

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Objectives

- Develop a conceptual design and fabricate an initial 0.1 to 1 kW prototype of a dehydrogenation reactor/heat exchange system to deliver H_2.
- Perform an economic evaluation of the delivery and storage system for the liquid carrier H_2 delivery concept.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section (3.2.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Lack of Hydrogen/Carrier and Infrastructure Options Analysis

(E) Low Cost, High Capacity Solid and Liquid Hydrogen Carrier Systems

(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs

Technical Targets

This project is directed at providing the dehydrogenation reactor technology and economic analysis for a liquid phase carrier that will enable an integrated delivery and storage of hydrogen, thereby meeting the DOE 2010 targets for hydrogen storage density and refueling time.

Accomplishments

- Completed analysis of monolith catalyst support behavior.
  - While monolith catalyst supports can provide efficient use of the metal, flow instabilities can limit the reactor efficiency.
  - The geometry of monolith cells is an important factor in maintaining high catalyst efficiency.
- CFD (computational fluid dynamics) modeling of two-phase flow in a narrow channel with gas generation at the walls revealed several potential novel design issues, which will be addressed in future work.
- Demonstrated the feasibility of dehydrogenation using microchannel (inside diameter <2 mm) reactors, while maintaining the high selectivity.
- Incorporated the H2A delivery cost model into the economic models for the liquid carrier hydrogen delivery system. The projected delivery cost was \$2.6-4.3/kg of H_2 at 350 bar. Dehydrogenation onboard the vehicle could reduce this cost by >\$1/kg due to the elimination of compression and gas storage costs.

Introduction

The scheme for the integrated production, storage and delivery of hydrogen using reversible liquid carriers is illustrated in Figure 1. A liquid carrier LQ* is catalytically hydrogenated and transported in its LQ*H_2 hydrogenated form to a distribution center. Hydrogen is liberated from the carrier either at the delivery station or onboard the vehicle. The "spent" (dehydrogenated) liquid carrier LQ* is then returned to the hydrogen source for re-hydrogenation. This scheme would allow

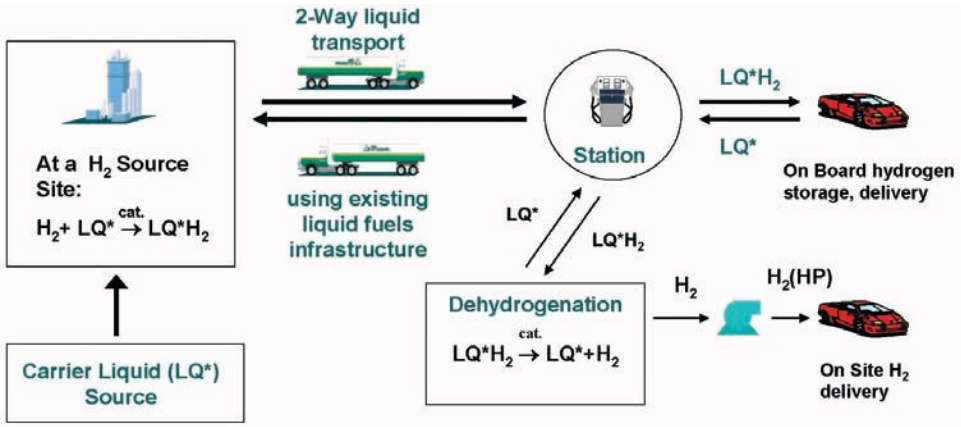

FIGURE 1. Schematic of Liquid Carrier Concept

the use of the existing infrastructure for fuel delivery and potentially reduce the need for high-pressure storage of H_2 onboard a vehicle.

The liquid carrier and dehydrogenation catalyst discovery and development work has been performed in a complementary DOE project entitled "Design and Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen."

Approach

This delivery scheme requires the development of a catalytic dehydrogenation reactor, which is the principal objective of this project. The design principles necessary for the dehydrogenation reactor to function for both onboard vehicle (i.e., mobile) and stationary applications will be developed. Design work will concentrate on features needed for a mobile reactor, the more constraining problem. The major deliverable of the project will be a stationary reactor at a 0.1 to 1 kW equivalent that embodies the design principles of an onboard unit. A study to determine the viability of the liquid carrier as a credible hydrogen storage option within a hydrogen economy will also be performed.

Integration of the reactor with the fuel cell and with the automobile engine will involve considerations such as the requirements of high gas flow rate, significant heat transfer load and the changing gas-to-liquid ratio, as needed to meet DOE targets. Partners with expertise in these areas will provide guidance for reactor design. PNNL will provide expertise in microchannel reactor design, UTRC will model fuel cell systems, and BMW will model vehicle integration.

Results

We had shown previously that thin-film catalysts improved catalyst efficiency and that their use in monolith catalyst structures produced high-quality hydrogen at reasonable rates. However, the monoliths were unexpectedly sensitive to gas flow rates. Thus, we investigated the flow patterns in the monolith reactor by augmenting the instrumentation in the existing reactor and by modeling studies using CFD.

Flow studies using the new instrumentation showed temperature fluctuations in the flow upstream of the monolith, indicating an unstable fluid flow field. Our analysis of causes of this unstable flow led to the surprising finding that there was a small amount flow out of the entrance of the monolith against the overall pressure gradient. Recent literature references show that several types of oscillations are possible when bubbles grow during flow in microchannels, and for high rates of bubble generation, alternating flow patterns both upstream and downstream, are predicted [1,2]. This alternating flow field complicates reactor design, since it affects the residence time of the fluid in the reactor. We conclude that while microchannel reactors such as monoliths can give high conversion and selectivity, feed distribution will be important for the final design.

Since the structure of the flow field strongly affects reactor performance, an investigation of the fluid mechanics of single- and two-phase flow in a microreactor using CFD was undertaken. We simulated the gas flow due to reaction by using a distributed injection of hydrogen at the wall of the reactor so that we did not have to include the complexity of simultaneous flow and chemical reaction. The simulation showed that the triangular shape of the individual channels in the monolith causes areas of low flow at the vertices of the triangle, which potentially allows for gas buildup at the wall. We also found that circular tubes have only thin layers of low flow and would be less susceptible to such buildup. The combination of high gas flow rate relative to liquid flow rate and the generation of gas at the wall results in a flow pattern in which the gas flow is along the inside of the tube wall instead of the centerline of the tube,

as would be expected for the usual case of mixed gas-liquid flow entering the tube. This flow pattern seems to promote early transition to spray flow. The spray flow regime means that the concentration of liquid on the reactor walls is low. This would reduce reactor efficiency, since the liquid must be in contact with the catalyst for reaction to occur. Thus, the study shows that generation of gas at the walls of the reactor leads to novel design issues. Tube shape, catalyst distribution and gas flow pattern must all be part of the final reactor design consideration.

The techniques used to make thin-film catalysts for the monolith were adapted to the construction of single-tube microchannel reactors, with catalyst deposited as a thin film on the inside wall of the tube. Reactor inside diameters ranged from 1 to 2 mm. The continuous-flow reactor apparatus was modified to accept the single-tube reactors. We demonstrated the feasibility of dehydrogenating liquid carrier in these single-tube microchannel reactors.

Typical results using these microchannel reactors are shown in Figure 2. Data are well behaved and look typical for a plug flow reactor. Conversions as high as 90% were reached, albeit for low flow rates. Typical results from another set of experiments are shown in Table 1. An annular reactor (1 mm diameter) with an axial multipoint thermocouple in the center of the reactor was used to demonstrate that the reactor was isothermal. When this thermocouple was removed to give a single open channel, the yield remained constant. This result indicates that the reactor is not unduly sensitive to flow changes (as long as the walls remain wetted with fluid), since removing the thermocouple changes the flow pattern while not altering the amount of catalyst. Finally, the conversion upon restarting after a 14-day period was essentially unchanged from the initial result. Thus, we conclude that microchannel reactors can be a viable reactor type for a dehydrogenation reactor, and further work should be continued.

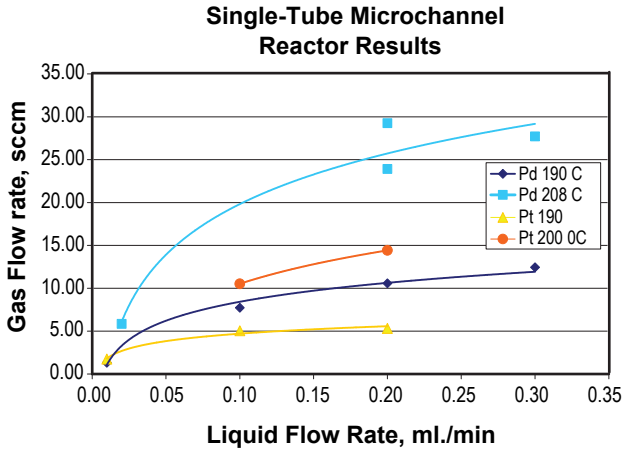

FIGURE 2. Single Tube Microchannel Reactor Results

TABLE 1. Microchannel Reactor Results Demonstrating Stability of Reactor for a Single Experimental Condition

Microchannel Reactor Results. Reactor Temperature 250°C

	Feed Rate (ml/min)	H_2 Flow (sccm)	Conversion (%)
Annular Flow	0.10	11.35	18.85
Channel Flow	0.10	10.59	17.61
Restart after 14 days	0.10	9.67	16.07

Product Quality

Hydrogen quality remains high at elevated temperatures with our simple phase separator. Previous results showed that high-purity hydrogen was produced with Pd catalyst at 200°C. Studies have now shown that hydrogen purity remains high (>99.99%) for temperatures as high as 250°C for all reactor types. No known poisons were found after extensive analytical probing. Furthermore, we have shown, using newly-developed analytical techniques, that no higher molecular weight compounds are formed in the liquid phase. Thus, we conclude that a single-stage separator should be suitable to produce high-quality hydrogen for use in a fuel cell.

Toxicology testing revealed that neither N-ethylcarbazole nor perhydrogenated N-ethyl carbazole are mutagenic, as judged by the negative Ames test. However, perhydrogenated N-ethyl carbazole was found to be corrosive and acutely toxic using other standard tests. Thus, while perhydrogenated N-ethyl carbazole remains a suitable model compound for reactor research, it could present concerns for commercial use.

Economics

The preliminary economic study reported last year was extended to include the cost of dehydrogenation in the forecourt. In addition, the results were recalculated using the assumptions of the H2A model; these are summarized in Figure 3. While N-ethyl carbazole was used as the representative liquid carrier (LC) molecule, the analysis is general enough to be applicable to a range of other H_2-regenerable liquid carriers. The cost of hydrogen delivery is defined as the cost of the LC catalytic hydrogenation process combined with the expense of a two-way transport to and from the fueling station and the cost of dehydrogenation and compression at the filling station. This analysis shows that the costs of the dehydrogenation at the forecourt are significant. Onboard dehydrogenation would eliminate compression and most of the storage costs. Thus, a successful demonstration of a prototype reactor, coupled

Air Products' Liquid Carrier Economics Summary

- Hydrogenation 0.86-2.5 $/kg
- Distribution 0.14 $/kg
- On-site Dehydrogenation 1.63 $/kg
  - Compression 0.86 $/kg
  - Storage 0.52 $/kg
  - Dispenser 0.04 $/kg
  - Balance of Station 0.21 $/kg
- Projected Delivery Cost - $2.6-$4.3/kg

FIGURE 3. Liquid Carrier Economics Summary

with a low-cost carrier molecule, would greatly enhance the economic viability of the LC concept.

Future Directions

- Start work at PNNL on microchannel reactors. Test several prototypes embodying separate design principles. Make decision on design of final reactor.
- Begin system analysis at UTRC and BMW and integrate the results into the reactor design work.
- Build reactor test system at BMW.
- Issue report on economics analysis.

References

1. Xu, J., Feng, Y., and Cen, J. International Journal of Heat and Mass Transfer, 50 (2007) 857-871.

2. Wang, G., et al., International Journal of Heat and Mass Transfer, 50 (2007) 4297-4310.