

III.C.1 Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen

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- United Technologies Research Corporation, East Hartford, CT
- Pennsylvania State University, State College, PA
- Battelle, Richland, WA

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Objectives

- Develop liquid phase hydrogen carrier raw materials.
- Develop a conceptual design and fabricate an initial 0.1 to 1 kW prototype of a dehydrogenation reactor/heat exchange system to deliver H₂.
- Perform an economic evaluation of the delivery and storage system for the liquid carrier H₂ 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, economic analysis and raw materials sourcing data for a liquid carrier that will enable meeting the Hydrogen Delivery 2012 Target of \$1.70/gge.



Approach

Our approach to an integrated production, storage and delivery of hydrogen using reversible liquid carriers is illustrated schematically in Figure 1. At any H₂ source, a liquid carrier LQ* is catalytically hydrogenated, and then transported in its LQ*H₂ hydrogenated form to a distribution center for vehicle fueling or stationary H₂ delivery. The latter requires the development of an appropriate catalytic dehydrogenation reactor, which is the principal objective of this project. The “spent” dehydrogenated liquid carrier LQ* is then returned to the hydrogen source for re-hydrogenation. The liquid carrier and dehydrogenation catalyst discovery and development work is being performed in a complementary DOE project entitled “Design and Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen.” The dehydrogenation step could occur at the refueling site or on-board the vehicle.

Accomplishments

Dehydrogenation Reactor Development - We concentrated on two reactor types, continuous flow reactors – both packed beds with pelleted catalysts and monolith structured packings – and batch reactors, for determining kinetics. Reactor systems capable of gathering engineering data that had been designed and built with Air Products funds were used for the work.

Our test compound, perhydro N-ethyl carbazole, was dehydrogenated over a variety of 3 mm diameter pelleted catalysts: Pd on alumina, Pt/Re on alumina and Pt/Ir on alumina, in the packed bed. In all cases, the dehydrogenation proceeded normally, and reactor behavior was typical of a trickle bed. Furthermore, the hydrogen purity was >99.9%, even though only a simple tangential flow separator was used to isolate the gaseous product. In our proposal, we anticipated that packed

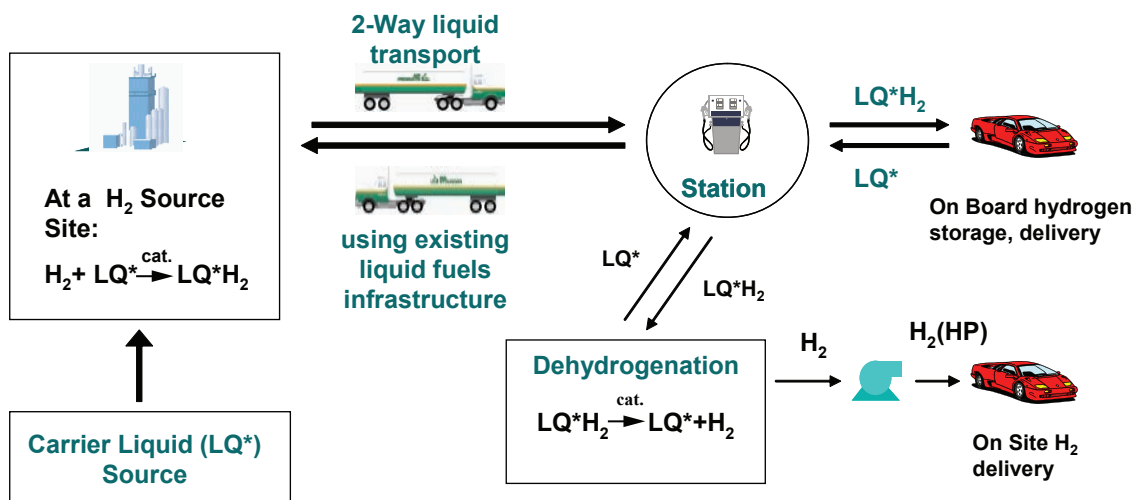


FIGURE 1. An Integrated Production, Storage and Delivery of Hydrogen — Using Reversible Liquid Carriers (LQ*H₂)

beds would suffer from inefficiencies due to high gas flow rate and catalyst size. An understanding of the flow limitations was obtained by feeding hydrogen to the inlet of the reactor to simulate high gas flow rates that would be found in a full-scale reactor. Typical results are summarized in Figure 2. The addition of hydrogen caused a “drying out” of the catalyst surface. The dry catalyst surface is not effective for reaction, and the flow of product hydrogen decreased. Hydrodynamics clearly limits catalyst efficiency at high gas flow rates.

We anticipated a second limitation on reaction rate from a slow diffusion of large molecules like N-ethyl carbazole through catalyst pores, i.e., intraparticle diffusion. The effectiveness factor, defined as the ratio of measured reaction rate for the catalyst particle to the rate for the catalyst with no diffusion effects, captures this effect. Our developed model for the kinetics of the reaction conducted in the stirred batch reactor on micron-size particles was used to predict the reaction rate with no diffusion effects. An effectiveness factor of about 0.08 was estimated, i.e., the rate of reaction for the pellet is only 8% of that for very small particles. Said another way, if all the catalyst were available for reaction, only 8% of the metal would have been needed. These measured effectiveness factors are close to the values predicted by standard correlations and similar to those seen in industrial practice for like molecules, e.g., hydrodesulfurization of fuels in trickle-bed reactors.

One way to reduce the diffusion effect and to increase the efficiency of the catalyst is to decrease the diameter of the particle. This was done by using a monolith, coated in its interior surfaces with a thin layer of catalyst as a continuous flow reactor. Corrugated, 0.05 mm “fecralloy: (iron-chromium alloy) foils were coated with a tightly-adhering gamma alumina washcoat. The coated foils were then assembled to form

a 400 cpsi (cells per square inch) honeycomb monolith. The desired catalytic metal was then introduced as a washcoat onto the monolith surface.

The catalyst on the first monolith made had only a low dispersion. Even so, metal usage was better than that for pellets, presumably because the thin layer of catalyst reduces the diffusion path and thereby raises the effectiveness factor. The second monolith had a higher metal dispersion. Metal usage was now excellent, with effective factors >0.5 compared to 0.08 for the pellets. Subsequently, five different monoliths were prepared. All had good performance: metal efficiency was high, conversions as high as 50% at 230°C were achieved, and flow rates were commensurate with the metal loading. Thus, the goals of increasing metal usage efficiency were realized by using thin channel reactors.

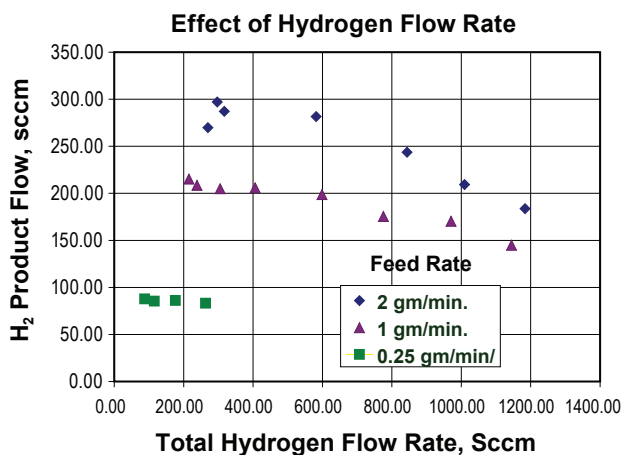


FIGURE 2. Effect of Adding H₂ to the Reactor Feed to Simulate High Gas Flow Rates

Initial studies show that reaction rates using monoliths are diminished by high gas flow rate. Two-phase flow proceeds through four regimes as gas flow rate increases: bubbly, Taylor flow (slug flow), annular flow, and gas-continuous with liquid mist [1]. Thus, flow effects are likely complicated, and additional data is needed to develop rational scaleup guidelines.

The ability to measure the reaction rate of monoliths free of flow rate effects is important, both to understand monoliths and to prepare for microchannel reactor work. We have adapted the CatRak [2] apparatus, previously developed by Air Products. This reactor provides a well-defined flow field for measuring reduction kinetics, free of mass-transfer effects, with monoliths.

This developed thin-film catalyst technology, developed for the monolith, should also be useful for coating the channels of microchannel reactors. Thus, this work not only helps define packed-bed performance and limitations but should also be useful for microchannel technology.

Catalyst Life and Reaction Kinetics - The hydrogenation/dehydrogenation of N-ethyl carbazole showed remarkable stability using Pd on alumina as the catalyst. No decomposition products were found in the liquid product, and the hydrogenation rate remained constant for the last six runs. In addition to continuous runs, feed and catalyst were held for 140 hours in a batch at reaction conditions. Only a small amount of methane and ethane was generated. No byproducts were detected in the liquid by gas chromatography. Thus, the material appears stable, even for inordinately long exposure to reaction conditions. Other catalysts did cause some byproduct make; e.g., Pt on alumina showed as high as 1% impurities. However, it is important to note that stable catalyst life and product quality have been routinely achieved with commercially available catalysts.

Analysis of the partially dehydrogenated liquid showed that the reaction of perhydrogenated N-ethylcarbazole proceeds stepwise. Two hydrogen molecules are produced in each step until there is complete aromatization to N-ethylcarbazole. A method for quantitating the kinetics of the semi-batch catalyst test runs was developed using Air Products proprietary software. Good fits were obtained using a first-order consecutive reaction mechanism. The semi-batch catalyst screening runs are non-isothermal, allowing both reaction parameters and activation energies to be fitted to a kinetics model. These kinetic expressions are vital for reactor design. They were used, for example, in determining the effectiveness factor for pelleted catalyst.

Hydrogen Liquid Carrier Economics – We conducted an analysis of the integrated production storage and delivery of the hydrogen concept (Figure 1) using N-ethyl carbazole as a representative liquid carrier (LC) molecule. However, the analysis is general enough to be applicable to a range of other H₂-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. At this stage of the analysis, LC dehydrogenation costs at the forecourt or on-board are not included.

Calculations were done at three levels of scale: at a 1,000 MMSCFD (million standard and cubic ft/day) full operative scale, at 100 MMSCFD – the size of a large steam methane reformer (SMR), and at 20 MMSCFD for forecourt H₂ generation. For each scale, the hydrogen delivery cost was calculated (in 2005 dollars) on the basis of a number of operational factors; of those factors, percentage carrier loss, cost of carrier and catalyst efficiency were found to have the greatest impact. A sensitivity analysis was performed for each of these variables. The resulting calculated distribution of cost for hydrogen delivery at the 1,000 MMSCFD scale is shown in Figure 3. This cost (per kg of bound H₂ in liquid carrier) ranges from \$0.86 to \$4.50, with a mean at \$1.86, and a 90% percentile value of \$2.62. The sensitivity of the mean value to several variables

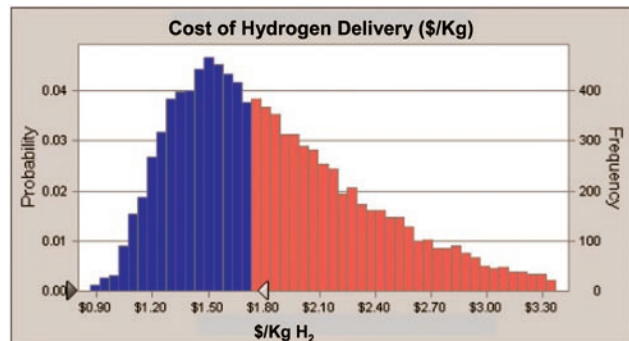


FIGURE 3. Probability Distribution for Cost of Hydrogen Delivery (\$/kg of bound H₂)

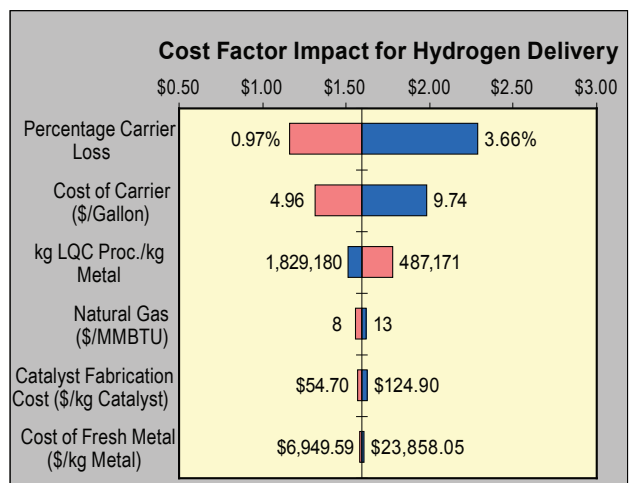


FIGURE 4. Cost Factor Impacts for Hydrogen Delivery (\$/kg of bound H₂) as a Function of Major Operational Costs

is graphically shown in Figure 4, in which the relative effect on cost for the above-cited variables is evident.

Our expectation is that it should be possible to meet H₂ delivery targets with a carrier cost under \$10 a gallon, a catalyst productivity >10⁶ kg/kg active metal, and a carrier loss rate of less than 2% per year.

Future Directions

- Start work at Battelle on microchannel reactor. Expertise and reaction data acquired with batch reactor monoliths will be used as a basis for designing a 0.1 kW prototype microchannel dehydrogenation reactor.
- Begin system analysis work at United Technologies Research Corporation.
- Update and complete economics analysis.

Special Recognitions & Awards/Patents Issued

1. B. Toseland, G. Pez and P. Puri, U.S. 20060143981 A1, Dehydrogenation of Liquid Fuel in a Microchannel Catalytic Reactor.

References

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2. Machado, R.M., Koniski, J. E., and Kohler, S., U.S. Patent, 7074962 B2, (2/2002).