III.14 Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen

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- Pacific Northwest National Laboratory (PNNL), Richland, WA (A. Karim, W. TeGrotenhuis, Y. Wang)
- BMW Technology Corporation, Woodcliff Lake, NJ (J. von Wild, T. Friedrich, W. Bittl)

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Project End Date: March 31, 2011

Objectives

The primary objective of this project is to design and fabricate optimized dehydrogenation reactor/heat exchange systems to deliver hydrogen using liquid organic hydrogen carriers. Specifically, the project comprises the following tasks:

- Liquid organic hydrogen carrier sourcing and processing (Task 1).
- Dehydrogenation reactor development. Iterative design and fabrication of 0.1 to 1 kW prototypes of dehydrogenation reactor/heat exchange systems to deliver H_2 (Task 2).
- Conduct an economic evaluation of the delivery and storage system for the liquid carrier H_2 delivery concept (Task 3).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section (3.2.4) of the Fuel Cell 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
(G) Storage Tank Materials and Costs

Technical Targets

TABLE 1. Delivery Hydrogen Carriers

Category	2005 status	FY 2012	FY 2017
Carrier H_2 Content (% by weight)	6.2%	6.6%	13.2%
Carrier H_2 Content (kg H_2/liter)	0.054	>0.013	>0.027
Carrier System Energy Efficiency (from the point of H_2 production through dispensing at the forecourt, %)		70%	85%
Total System Cost Contribution (from the point of H_2 Production through dispensing at the forecourt, \$/kg of H_2)		\$1.70	<\$1.00

FY – Fiscal Year

Discovery of hydrogen carriers that maximize the carrier H_2 content was the subject of a separate project for H_2 storage (“Design and Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen”, DE-FC36-04GO14006) that was completed in FY 2009. The objectives of the current project address the carrier system energy efficiency (through activities in Tasks 1 and 2) and total system cost contribution evaluation (Task 3).

Accomplishments

- A microchannel dehydrogenation reactor prototype developed by PNNL has successfully achieved a 7X improvement over packed-bed reactor performance; the reactor demonstrated 1.5 g H_2/g Pt/minute catalyst productivity in initial proof-of-principle testing.
- BMW has successfully performed dehydrogenation tests at conversion rates above 90% with packed-bed and annular tube reactors, provided by Air Products.
- BMW has established a direct in situ gas analysis of the produced hydrogen during dehydrogenation.
- BMW completed the construction of a (re) hydrogenation unit (5 liter inner volume, 100 bar and 250°C max working pressure and temperature)

specially designed to handle the exothermic hydrogenation reaction. Testing the newly built facility demonstrated complete hydrogenation (up to >99% conversion).

- BMW performed a comparative theoretical parameter study for the two different catalysts, palladium and platinum, during system evaluation.

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Introduction

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.

This project is directed at providing the reactor technology, integration of reactor designs with vehicle and stationary power sources, and economic analysis for a liquid phase carrier that will enable an integrated delivery and storage of hydrogen, while meeting the DOE targets for hydrogen storage density and delivery efficiency. Due to decreased FY 2010 funding (vs. FY 2009) and delays in receiving obligated funds, work towards FY 2010 objectives was delayed until the third quarter of FY 2010. The decreased funding level has resulted in the performance of no experimental work by Air Products or UTRC. Therefore, the reported results represent less than one year of effort.

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 one 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" reactors are under development at PNNL. After initial testing at PNNL, the reactors will be used for integration studies at BMW. BMW's objective is to evaluate the integration of liquid carrier storage systems with hydrogen internal combustion engines. This will define certain configurations of integrated systems, determine the preliminary requirements to guide reactor development and allow modeling of more complex scenarios to show overall system performance needs. Additional reactor testing will occur at BMW. 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. This will define certain configurations of integrated systems, determine the preliminary requirements to guide reactor development and allow modeling of more complex scenarios including transient operation. Air Products is supplying the necessary liquid carrier and conducting an economic evaluation of the use of liquid carriers for hydrogen distribution.

Results

Task 1. Liquid Phase Hydrogen Carrier Raw Materials Sourcing and Processing

Air Products is responsible for providing perhydro-N-ethylcarbazole and perhydrofluorene for reactor testing at PNNL and BMW. A suitable inventory of the two hydrogenated liquid carriers exists to supply all of the carrier needs for reactor testing anticipated during FY 2010. The successful completion and testing of a hydrogenation reactor at BMW adds additional flexibility for sourcing liquid carrier under this task.

Task 2. Dehydrogenation Reactor Development and Systems Integration Modeling

PNNL: The microchannel reactor concept originally pursued in FY 2009 focused on segregating the liquid carrier from the H_2 being produced to prevent the catalyst from drying out as the 2-phase flow transitioned from exclusively liquid to up to 98% H_2 gas by volume. Catalyst was coated onto thin porous substrates that wetted the liquid carrier and behaved as wicks. When placed in a microchannel with a vapor plenum adjacent to the wick, the H_2 was separated from the liquid as it was generated to keep the catalyst from drying out. Proper balancing of the liquid and vapor pressures keeps the liquid in the wick by capillarity and causes the liquid to flow through the wick. Experimental results from microwick reactors showed significantly lower catalyst productivity in comparison to a packed bed of 210-420 micron particles. The two principal causes were volatilization of the liquid carrier and diffusion limitations.

N-ethylcarbazole has a small but significant vapor pressure at the operating temperatures of 200-230°C that allowed the liquid carrier to volatilize into the vapor plenum and bypass the catalyst, which limited conversion and suppressed catalyst productivity. In addition, an analysis of diffusion limitations in the packed-bed revealed that the reaction kinetics are an order of magnitude faster than the H_2 diffusion rate within the pores of the liquid-filled catalyst particles and is of the same order of magnitude as the H_2 diffusion rate through the liquid boundary layer surrounding the particles. Furthermore, the wick reactor concept exacerbates the mass transfer resistance by slowing the liquid space velocity and increasing the mass transfer boundary layer thickness. The project team concluded that although the wick reactor effectively accomplished its intended purpose of segregating gas and liquid and keeping the catalyst wetted, mass transfer limitations is the more important technical issue to address.

The effort shifted toward brainstorming ideas that would enhance mass transfer. A reactor concept emerged that enabled using smaller catalyst particles to enhance internal and external mass transfer without introducing untenable pressure drop through the reactor. Proof-of-concept results from this new 'suspended slurry' concept are shown in Figure 1 for three different versions. The data showing conversion as a function of catalyst loading divided by liquid feed rate are compared to results from a packed bed of 210-420 micron catalyst particles. Quantitative comparison is facilitated by fitting to first-order reaction rate kinetics. The best results obtained show a 7X increase from packed bed productivity of 0.2 g H_2/g Pt/minute to 1.5 g H_2/g Pt/minute at 90% conversion for the suspended slurry reactor.

At the outset of the project, a catalyst productivity target was set at 2 g H_2/g Pt/min to enable microchannel reactor technology that could be installed on a vehicle to support H_2 production for primary power. The project has now achieved 75% of this initial target at 90% conversion with significant gains remaining as this novel technology matures.

BMW: The planned upgrade of the dehydrogenation reactor testing apparatus with additional test equipment (e.g. flow meter, temperature controller and pressure gauges) was successfully completed. With the new equipment, a quantified validation of prototype reactors developed during the project during FY 2010 will be possible. To establish the reactor test protocols, dehydrogenation measurements with a packed-bed reactor using a 5% Pd on alumina catalyst were completed. Following this, the reactor testing progressed to a microchannel annular tube reactor with a platinum catalyst (Figure 2), originally constructed by Air Products. For all experiments, an excellent repeatability of the test results could be demonstrated.

The dehydrogenation reactor testing apparatus capability has been extended by an in situ direct gas analysis of the produced hydrogen. The extension of the test rig is shown on the right hand side ("H_2 quality testing") of Figure 3. Routine analysis of the hydrogen produced from the dehydrogenation reactor confirmed the high purity of the hydrogen product.

In support of system design activities in Task 2, the necessary reactor residence time for 95% conversion of the fully hydrogenated N-ethylcarbazole have been calculated for reactors containing platinum (Figure 4). Similar modeling clearly shows much faster reaction kinetics of platinum in comparison to palladium at a given temperature. The comparison of platinum-catalyzed dehydrogenation at different temperatures shows an increase of reaction speed by a factor of approximately 10, if temperature is increased by 100 K. Very short residence times can be achieved at temperatures suitable for heat integration with hydrogen internal combustion engines.

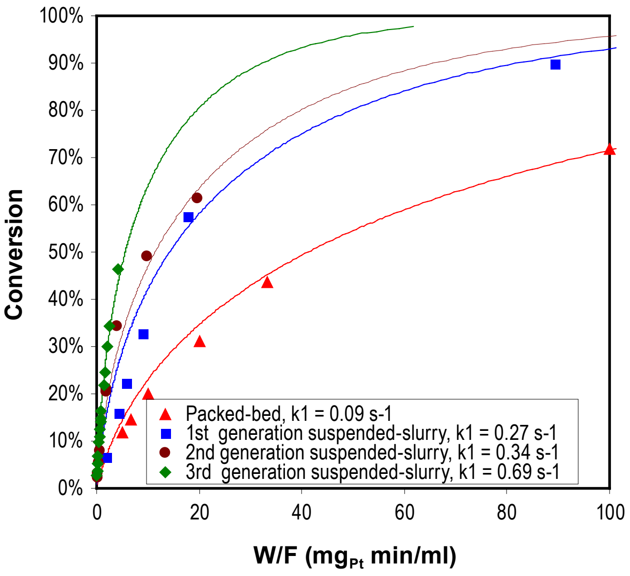

FIGURE 1. Comparison of Catalyst Productivity between Three Versions of the 'Suspended-Slurry' Concept to a Packed-Bed of 210-420 Micron Particles

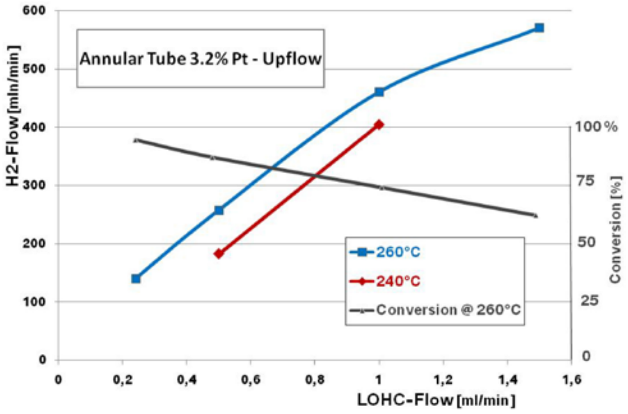

FIGURE 2. Dehydrogenation Testing Results using an Annular Tube Reactor with 3.2 wt% Loading of Platinum

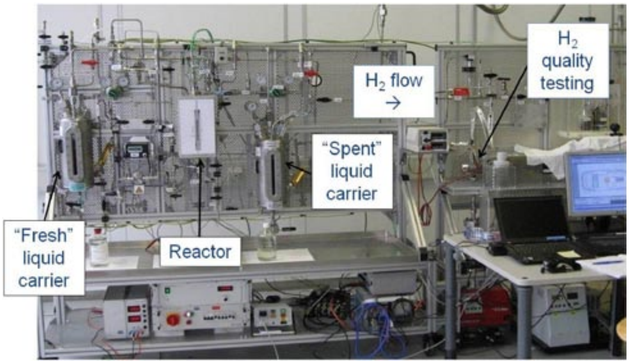

FIGURE 3. Overview of the Current Dehydrogenation Reactor Testing Apparatus at BMW (Note the newly added gas analysis equipment on the right side of the picture.)

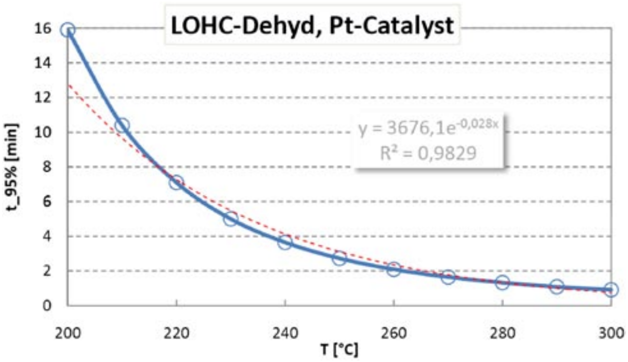

FIGURE 4. Temperature Dependence of the Reaction Time (In Minutes) for Releasing 95% of the Theoretical Hydrogen Capacity from Perhydro-N-ethylcarbazole using a Supported Platinum Catalyst (t_95%)

For the (re)hydrogenation of liquid organic hydrogen carrier, an apparatus has been constructed at BMW. The apparatus can process several liters of liquid organic hydrogen carrier during the exothermic hydrogenation reaction. It consists of a commercially available autoclave from Swiss company Buechi (5 liter inner volume, 100 bar and 250°C max working pressure and temperature) with a magnetically coupled turbo stirrer. The autoclave is oil heated by using a Julabo Forte HT60-C.U. system with a max working temperature of 400°C, in combination with a water cooling system (max cooling power 15 kW). Based on designs of similar autoclaves in use for liquid organic hydrogen carrier hydrogenation at Air Products, process diagrams have been drawn and a worst case overtemperature/overpressure scenario analysis has been performed. Based on the derived results, during the risk assessment, we decided to operate the autoclave unit in a separate, remote controlled autoclave room.

The autoclave was tested by performing several test hydrogenations and it was possible to easily handle the exothermic reaction and to finally achieve reaction conversions of up to 99%.

Task 3. Hydrogen Delivery Economics

A detailed economic analysis was completed in FY 2009 and is in preparation as a report to DOE. Based upon our analysis, we consider the H_2 liquid carrier economics to be favorable, in the range of \$0.85–\$4.50\$/kg H_2 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.

Conclusions and Future Directions

- A viable microchannel dehydrogenation reactor concept has been invented that is capable of achieving catalyst productivity to support H_2 delivery on board vehicles. Further development of this new, novel technology promises additional improvements. Proof-of-concept reactors that are heated with hot gas and scalable to larger reactors will be first demonstrated at 0.1 g H_2/min (nominally equivalent to 100 W_e proton exchange membrane fuel cell output) and subsequently scaled to 1 g H_2/min.
- A fully tested and capable dehydrogenation reactor testing apparatus is ready for the testing of the third-generation dehydrogenation reactor prototype (scheduled for the fourth quarter of FY 2010) and the final proof-of-concept reactor (FY 2011, pending funding).
- Extension and modification of existing dehydrogenation testing apparatus from electric heating to gas heating of the reactor.

FY 2010 Publications/Presentations

1. "Liquid Organic Hydrogen Carriers (LOHC) - An auspicious alternative to conventional hydrogen storage technologies" (Oral Presentation), J. von Wild, T. Friedrich, A. Cooper, B. Toseland, G. Muraro, W. TeGrotenhuis, Y. Wang, P. Humble, A. Karim, WHEC2010, Essen/Germany, May 20th, 2010.

2. "Liquid Organic Hydrogen Carriers (LOHC) - An auspicious alternative to conventional hydrogen storage technologies" (Extended Abstract Publication), J. von Wild, T. Friedrich, A. Cooper, B. Toseland, G. Muraro, W. TeGrotenhuis, Y. Wang, P. Humble, A. Karim, WHEC2010, Essen/Germany.

3. "Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen" (Poster Presentation), Alan Cooper, U.S. DOE Hydrogen and Vehicle Technologies Annual Merit Review, June 2010.