

III.13 Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen

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Objectives

The overall objective of this project is to develop a conceptual design and fabricate an initial 0.1 to 1 kW prototype of a dehydrogenation reactor/heat exchange system to deliver hydrogen. Air Products is partnering in this project with PNNL, BMW and UTRC. Specifically, the project comprises the following tasks:

- Liquid phase hydrogen carrier raw materials sourcing and processing (Task 1).
- Dehydrogenation reactor development. Develop a conceptual design and fabricate an initial 0.1 to 1 kW prototype of a dehydrogenation reactor/heat exchange system to deliver H₂ (Task 2).
- Hydrogen delivery economics: conduct an economic evaluation of the delivery and storage system for the liquid carrier H₂ delivery concept (Task 3).

Technical Barriers

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

Technical Targets

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

Discovery of hydrogen carriers that maximize the carrier H₂ content was the subject of a separate project in H₂ storage (“Design and Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen”, DE-FC36-04GO14006) that was completed in Fiscal Year 2009. The objectives of the current project addresses the carrier system energy efficiency (through activities in Tasks 1 and 2) and total system cost contribution evaluation (Task 3).

Accomplishments

- Air Products has found a suitable commercial version of the test compound, N-ethylcarbazole. This material exhibited a higher rate of hydrogenation than the previously used material, which had been obtained from a laboratory materials supplier.
- PNNL performed a series of experiments with a single-channel proof-of-principle reactor operated at 210-225°C. Volatilization of the liquid is a plausible

explanation for the low productivity and low conversion, and steps are being taken to suppress volatilization.

- BMW completed initial setup of a microchannel reactor test apparatus in the second quarter of FY 2009. All pretests with an Air Products' packed-bed reactor have been successfully finished.
- UTRC modified a pre-existing system model of a coal gas-fueled solid oxide fuel cell (SOFC) plant with heat reutilization to run on hydrogen as fuel. In the modified model the anode recycle ratio replaces the steam-to-carbon constraint, allowing hydrogen operation using a relatively cool fuel inlet (<150°C).
- Continuing work at Air Products has demonstrated that stable catalyst supports can be made on microchannel reactors. Dehydrogenation is possible in these reactors at reasonable rates; however, the reactor is mass transfer limited due to the high gas flow rates at relatively high conversions. This limit is due to the flow of hydrogen at the walls, causing poor contact between the liquid and catalyst. Computational fluid dynamics (CFD) modeling of two-phase flow in a narrow channel with gas generation at the walls revealed a previously unknown circulation flow.
- BMW has supplied operating characteristics of a hydrogen-operated engine, and the team has reached agreement on a set of specifications for the laboratory reactor.
- An economic assessment of the liquid carrier approach for delivering hydrogen has been completed. Based upon our analysis, we consider the economics to be favorable, in the range of \$0.85 – \$4.50/kg of H₂ delivery cost using N-ethylcarbazole as a test molecule. Additional work tailoring the characteristics of the carrier material and catalyst system should allow the cost of delivered hydrogen to fall in the lower end of this scale and thus should compare favorably to the DOE targets.



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 funding issues in previous years, the subcontracts were not executed with PNNL, UTRC, and BMW until late FY 2008/early FY 2009. Therefore, the reported results from these subcontractors 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 a 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 (H₂-ICE). 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 hydrogenated N-ethylcarbazole for testing. The team estimates that about 150 gallons of material will be needed for the entire project. We have located a supplier for N-ethylcarbazole offering a commercial-

scale supply. This new raw material was tested in both 50 ml and 1 liter reactors. The material from the new supplier hydrogenates faster than the standard material. We found that material from our initial supplier contained a small amount of chloride, which slowed down the reaction.

A single lot of 200 kg of N-ethylcarbazole has been purchased from the supplier and we have begun a campaign to hydrogenate the entire lot, thereby building an inventory of liquid carrier that should support the reactor testing for the duration of the project.

Task 2. Dehydrogenation Reactor Development and Systems Integration Modeling

PNNL: Testing was started in the first quarter of FY 2009 on compact microchannel dehydrogenation reactors that are able to achieve high catalyst productivity in the process of generating hydrogen from liquid organic hydrogen carriers (LOHCs). A method was developed for coating Pt/Al₂O₃ (or Pd/Al₂O₃) catalyst on porous substrates for testing in a single-channel microchannel reactor. Uniform coating of the wick structure at a loading of 10 mg/cm² with good adhesion was achieved. Temperature programmed reduction was performed on the calcined slurry of Pt/Al₂O₃ catalyst in order to determine the reduction temperature needed to fully reduce the Pt. The results indicated that reduction at 200-220°C is sufficient to reduce the catalyst.

A single-channel test reactor was selected and an apparatus was built for testing catalytic structures. The reactor was intended to perform phase separation and produce separate liquid effluent and hydrogen gas streams. Consequently, initial tests were conducted at room temperature with the hydrogen carrier liquid and nitrogen to determine the operation conditions under which complete phase separation could be maintained. Flow-through tests with the initial catalyst structure were conducted with perhydro-N-ethylcarbazole flowing at 0.1 ml/min and 20 sccm N₂ flow.

Benchmark experiments were conducted to evaluate the performance of the microchannel reactor setup during the dehydrogenation of perhydro-N-ethylcarbazole. The experiments were performed at a liquid flowrate of 0.1 ml/min at 215°C. The conversion obtained was about 18%, and the H₂ flowrate was 14 sccm. In these initial experiments, there was entrainment of liquid in the hydrogen gas and vice versa, indicating the catalyst structure was not effectively releasing the hydrogen being generated, which also resulted in inefficient use of the catalyst.

Additional testing of a single-channel test reactor encountered unexpected difficulties in maintaining good segregation of the liquid in the wicks. Although the perhydro-N-ethylcarbazole remained in the wick while

flowing through the reactor at low temperature (e.g., 25°C), as shown on the left of Figure 1, droplets formed in the vapor space when the temperature was increased to the range typically required to release hydrogen, as shown on the right of the figure. The explanation that was eventually supported by testing was that heating from the bottom with the sapphire window on top – even with the window covered in insulation – creates temperature gradients sufficient to cause Marangoni instability in the vapor-liquid interface. This instability causes stable droplets to form in the vapor space. The temperature gradients have been dissipated by heating the window, and the reactor can now be operated with good phase separation at temperature.

Performance targets have been set for the single-channel reactor shown in Figure 1. The objective is to generate 0.65 slpm of H₂ targeting a catalyst loading of 1 mg Pt/cm². So far, wick structures have been developed with 24-40% of the target catalyst loading. A series of experiments has been performed with the single-channel proof-of-principle reactor operated at 210-225°C. Various wicks have been used over a range of liquid feed rates and suction pressures on the wick structure. The total hydrogen production has been typically at 2% of target or less, and the catalyst productivity has been at 12% or less. Liquid conversion has also been in the 1.5-5% range. Volatilization of the liquid is a plausible explanation for the low productivity and low conversion. In several experiments, particularly at the lower liquid feed rates and higher suction pressures on the wick, the wicks appear to be dry, even though the siphon on the wick is maintained. The test stand was originally set up to collect both the liquid and vapor streams in the same vessel, which precluded knowing what fraction of the liquid is volatilized. After the test apparatus was modified, a recent test revealed that 70% of the liquid is being condensed from the vapor stream. Steps are now being taken to suppress volatilization. Concepts are also being developed to convert the vapor to generate additional hydrogen. Initial testing of these concepts has yielded promising results.

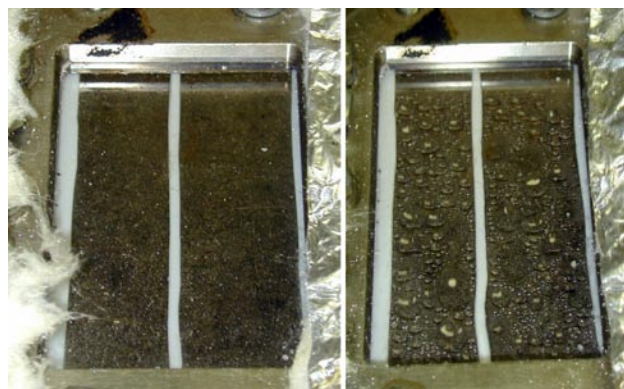


FIGURE 1. Microchannel reactor with sapphire window illustrating droplet formation when increasing from 25°C (left) to 210°C (right).

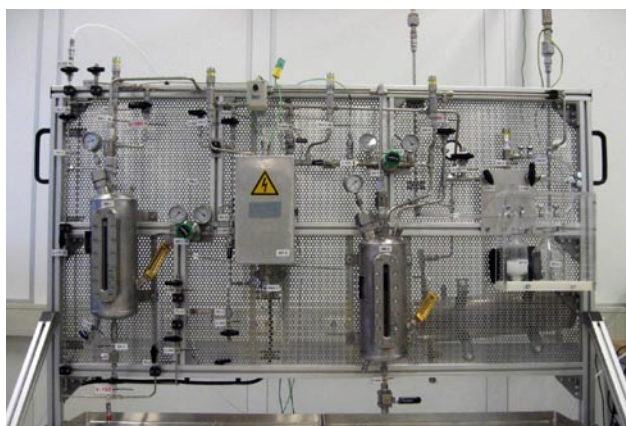


FIGURE 2. Reactor Testing Apparatus Constructed in BMW Laboratories

BMW: BMW has successfully finished the initial set up of an apparatus for testing microchannel reactors (Figure 2). The test rig consists of a combination of off-the-shelf Swagelok parts in combination with purpose-built components. As measurement hardware, existing test equipment for automotive test drives is used. National Instruments' DIAdem and ETAS INCA are used as software. The first hydrogen was generated using a packed-bed reactor supplied by Air Products. After initial testing of the system, a planned upgrade added test equipment such as flow meters, temperature controllers and pressure gauges. Additionally, there are plans for in situ direct gas analysis of the produced hydrogen. BMW has transferred the existing spreadsheet-based calculations to 1-dimensional simulation software Matlab-Simulink and added Air Products' kinetic modeling data to the model.

BMW has supplied operating characteristics of an H₂-ICE, and based on these data, the team has reached agreement on a set of specifications for the laboratory reactors. Measurements of basic material properties at BMW's chemistry lab have been finished.

UTRC: UTRC has obtained and reviewed models for fuel cell-based systems from UTRC and UTC Power, namely:

- UTRC system model for an on-board complex compound hydride based hydrogen storage system coupled to a proton exchange membrane fuel cell (PEMFC). For on-board hydrogen generation, the operation temperature of a PEMFC is too low for integration with the LOHC dehydrogenation reaction, but it could be used for preheating the carrier, including producing and maintaining a liquid state.
- UTC Power steady-state system configuration and model results for phosphoric acid fuel cell stationary plants running on reformed natural gas and other fuels.

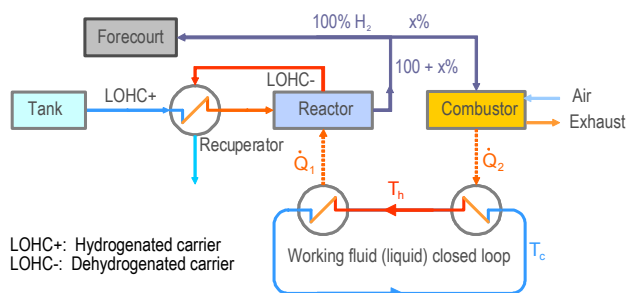


FIGURE 3. Preliminary Baseline System Model for Liquid Carrier Dehydrogenation

- UTRC steady-state model for an SOFC stationary plant running on reformed natural gas.

A preliminary baseline system configuration was constructed (Figure 3). For this system, the energy of the dehydrogenation process is obtained by burning a fraction of the produced hydrogen. A heat transfer fluid is used to convey that additional energy back to the dehydrogenation reactor in a manner which would produce a high degree of temperature uniformity. This preliminary configuration is similar to a subsystem of a layout studied by Argonne National Laboratory [1]. This system was subsequently identified and will be used as a guideline in the near term. A change being considered is the addition of a loop for preheating the liquid carrier using the coolant exiting the fuel cell stack.

As a stepping stone to full integration of a model of the dehydrogenation reactor with a stationary SOFC power plant, a pre-existing UTRC system model of a coal gas-fueled SOFC plant with heat reutilization was modified to run on hydrogen as fuel. The previous system model was designed to prevent coking by imposing a certain steam-to-carbon ratio at the anode entrance. In the modified model the anode recycle ratio replaces the steam-to-carbon constraint, allowing hydrogen operation using a relatively cool fuel inlet (<150°C). An effect of the transition to pure hydrogen fuel is that the net-endothermic process of steam reforming plus water-gas shift at the cell is now absent. The loss of this cooling process is compensated by increased cathode flow rate.

Air Products: Continuing work at Air Products uses CFD to understand the multiphase flow conditions in catalyst-coated microreactors. Previously, we calculated that for the dehydrogenation rates necessary to achieve complete dehydrogenation, the gas flow is very high, and a layer of hydrogen is found near the catalyst walls. This layer of gas prevents the liquid reactant from contacting the catalyst on the walls, thereby causing low catalyst efficiency. This phenomenon of gas building on the walls occurs because the gas-to-liquid volumetric ratio is very high, and the hydrogen flow has considerable

momentum because of the high velocity. The modeling results show that gas is found at the wall and that the strong gas flow creates a liquid recirculation within the micro channel, which can lead to reverse flow at the exit. This secondary flow was unexpected. The liquid flow tends to eliminate any mass transfer resistance in the liquid; however, the gas flow at the wall leads to catalysis inefficiency, as discussed previously.

Kinetic models are needed to assess the performance of wash-coated and other types of catalysts, as well as judge the efficiency of the new reactor designs. Therefore, kinetic models for both Pt and Pd catalysts have been developed. The kinetic model for the Pd catalyst was improved from previous models by considering the first two steps of the dehydrogenation reactions as irreversible and the final step as reversible. For the Pt catalyst, all three reactions were modeled as irreversible. We were able to obtain good fits to the data from previously reported large-scale batch experiments (Figure 4).

Microchannel reactor testing was accomplished by engineering an annular reactor from 5/8 inch diameter iron/chromium metal tubing and inserting a 3/8 inch diameter thermocouple into the center of the tube. The resulting annulus was 0.7 mm in width with a diameter of 10.9 mm. The catalyst wash coat was located on the inside of the outer tube. The reactor length was 12 inches for testing of Pd catalyst and 10 inches for the Pt catalyst.

Two sets of experiments were performed for the reactor with the Pd catalyst. In the first set of experiments, the feed flow rate was varied, and the hydrogen flow rate was noted. Reactor performance was similar to previous single channel reactor experiments. Repeat runs at the same feed rate showed no evidence of earlier catalyst flaking problems found with a stainless steel, alumina-coated reactor. The second set of experiments was performed to see if mass transfer issues were present. Typically this test involves changing the amount of catalyst in the reactor. In our case, the reactor tube was cut in half, providing two 6-inch-long reactors. Each of the two reactors had half the catalyst of the previous reactor. The kinetic model discussed above was used to analyze the data. Typical results from both sets of experiments are shown in Table 1.

Results for the shorter reactor are the average of the results for the two halves of the larger reactor. The results of these individual, half-length reactors were similar, indicating that a stable catalyst coating had been achieved. Previously reported batch reactor experiments have shown a productivity of about 2 gm H₂/gm Pd/min in the range of 40-90% conversion. However, because the run was not isothermal, the only way to compare the catalyst efficiency was to use a kinetic rate model. For a feed rate of 0.25 ml/mi, a flow rate of hydrogen was 39 sccm using the full-length reactor. The

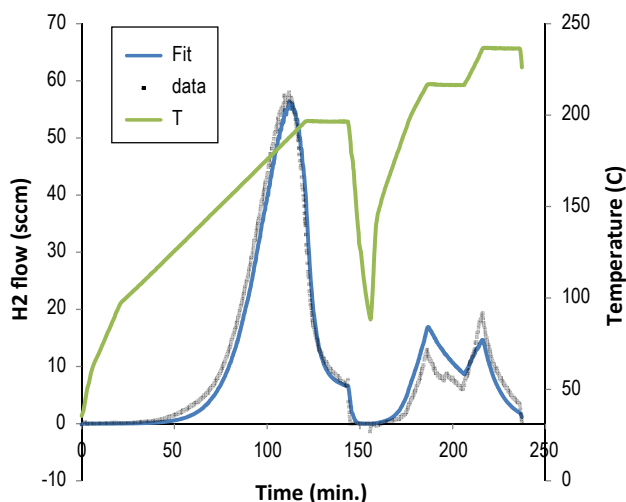


FIGURE 4. Figure showing data collected using an annular microchannel reactor with Pt catalyst and the fit to a kinetic expression developed using batch reactor dehydrogenation.

simulation shows that this flow rate could be achieved by ~0.44 milligrams of Pd at 100% efficiency. The full-length reactor contained approximately 4 mg of catalyst. Thus, catalyst efficiency was only about 11%.

TABLE 1. Reactor Experiment Results

Reactor Length (cm)	Liquid Feed Rate (cc/min)	H ₂ Flow Rate (sccm)	Conversion %	Rate/gm Pd (gm H ₂ /gm Pd/min)	Temp. (°C)
30.5	0.10	23	38	0.5	248
30.5	0.25	38	25	0.8	252
30.5	0.40	50	20	1.1	251
30.5	1.00	75	12	1.7	256
15.25	0.11	21	34	0.9	248
15.25	0.25	26	17	1.2	248
15.25	0.40	33	14	1.5	248
15.25	1.00	55	9	2.5	253

Catalyst efficiency is a function of the catalyst manufacturing variables, e.g., dispersion, and hydrodynamic effects. If all of the efficiency loss is due to manufacturing, we would expect that the half-length reactor would have about half the effective catalyst, i.e., 0.22 mg effective catalyst, and the hydrogen flow rate would be about 19 sccm. However, the measured flow rate for the half-length reactor was 26 sccm. Thus, catalyst efficiency is higher for the shorter reactor than for the longer reactor. Clearly, flow effects must be important in determining catalyst efficiency as well as manufacturing effects. Thus, the experimental evidence seems to agree with the CFD prediction that the high flow of hydrogen decreases flow efficiency.

Task 3. Hydrogen Delivery Economics

A detailed economic analysis was completed in the third quarter of FY 2009 and has been submitted as a report to DOE. Based upon our analysis, we consider the H₂ liquid carrier economics to be favorable, in the range of \$0.85 – \$4.50/kg H₂ 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. To be specific, we recommend lowering liquid carrier cost to under \$10/gallon, lowering carrier melting point, reaching catalyst productivity targets exceeding 1,000,000 kg liquid carrier processed/kg catalyst metal (close to existing hydro-desulfurization catalysts), reducing carrier loss rate to less than 2% per year and investing in understanding cost-performance issues around fuel cell reactor heat integration to enhance predictability. Dehydrogenation reactors need to be investigated further alongside their integration performance with the fuel cell over dynamic conditions encountered on-board automobiles. Performing more analyses around these factors will eliminate significant uncertainties surrounding the liquid carrier concept.

Conclusions and Future Directions

- Initial results from the development of microchannel reactors have confirmed that effective gas/liquid separation is critical to achieving high conversion of the hydrogenated liquid carrier.
- Experimental results and CFD modeling has suggested that high gas flow rates represent a challenge due to drying of catalyst surfaces. While the first generation of microchannel reactors developed at PNNL has largely overcome these issues, the vaporization of the hydrogenated liquid carrier has presented new challenges. Two new types of microchannel reactors will be evaluated in the remainder of FY 2009 to address low conversion due to the liquid carrier vaporization.
- Ramping up of reactor testing capability at BMW has been completed. Final testing of the testing apparatus will be completed using annular tube microchannel reactors. The testing of proof-of-principle reactors constructed at PNNL is expected to commence within FY 2009.
- Additional high-level system evaluation of reactor systems with H₂-ICEs will be performed.
- Complete N-Ethyl Carbazole-specific elements for the system modeling library.
- Develop a high-level model module to represent reactor performance.
- Perform steady-state evaluation of at least two system configurations.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent 7,485,161; Dehydrogenation of liquid fuel in microchannel catalytic reactor (issued Feb. 3, 2009).

FY 2009 Publications/Presentations

1. Potentiale von alternativen Wasserstoff-Speicherungstechnologien (“Potential of alternative Hydrogen Storage Technologies”), von Wild, Jürgen et al., 6. VDI-Tagung “Innovative Fahrzeugantriebe”, November 6th and 7th 2008, Dresden, Germany, published in: “VDI-Berichte/VDI-Tagungsbände, Sachgebiet: Fahrzeug- und Verkehrstechnik,” Volume Nr. 2030, 520 pages, year 2008, Title: “Innovative Fahrzeugantriebe 2008 inkl. CD-ROM”, ISBN: 978-3-18-092030-6.
2. “Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen”, Bernie Toseland and Alan Cooper, U.S. Department of Energy HFCIT Annual Merit Review, May 2009.

References

1. “System Level Analysis of Hydrogen Storage Options”, Ahluwalia, R.K. et al., 2007 DOE H₂ Program Review, May 2007.