An Integrated Hydrogen Storage and Delivery Approach Using Organic Liquid-Phase Carriers

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\textbf{ABSTRACT:}

Hydrogen storage system development is a key enabling technology for the widespread introduction of hydrogen fuel cells. We have developed novel liquid-phase materials that undergo catalytic hydrogenation at the hydrogen production location, and are readily dehydrogenated at the point of use. This material-based hydrogen storage approach provides a liquid fuel paradigm where the consumer and other participants within the supply chain never come into contact with gaseous or liquid hydrogen. In addition to removing hydrogen from the supply chain, this approach provides the opportunity to build on the current liquid fuel infrastructure for a smooth fuel transition. Technical details of the approach, additional advantages over other hydrogen storage technologies, and remaining challenges will be covered.

\textbf{KEYWORDS}: hydrogen storage, dehydrogenation, liquid-phase carrier

\textbf{Introduction}

Hydrogen storage is one of the key technical barriers to the use of hydrogen as an energy carrier. Air Products and Chemicals Inc.’s (APCI) Corporate Science and Technology Center has been developing a hydrogen storage approach using organic liquid-phase carriers for several years, primarily in partnership with the U.S. Department of Energy’s Hydrogen, Fuel Cells & Infrastructure Technologies Program (U.S. DOE). This concept provides an integrated hydrogen delivery and storage approach that we believe provide some unique benefits to overcome those technical barriers.

APCI’s combination of industrial gases and specialty chemicals businesses is unique in the industry. Our growth platforms in hydrogen and energy markets and performance materials provide us the technical and market knowledge important for hydrogen storage development. We are the world leader in industrial hydrogen supply and own, operate and distribute around the world. Our business model for materials growth is centered around environmentally-friendly products that are based on competencies in materials and surface science, and feature value, innovation and global optimization.

APCI started participating in hydrogen fuelling in the early 1990s. In addition to supplying hydrogen, we have made significant contributions to technology advancements including mobile fuelling, underground liquid storage, dispensing, onsite generation and storage. Besides the United States, we have hydrogen fuelling projects in Europe, Japan, Korea, Singapore and India. Within Europe, project sites include United Kingdom, France, Germany, Holland, Spain, Italy, Greece, and Portugal.
Our hydrogen storage approach is to utilize an organic liquid carrier that can be reversibly hydrogenated and dehydrogenated. The carrier is capable of providing both the delivery and storage of hydrogen without introducing the hydrogen molecule to the supply chain. The carrier molecule is hydrogenated at the location where hydrogen is manufactured. Since it is a liquid at ambient conditions, it can be transported such as by truck or pipeline like gasoline as well as contained in similar storage tanks. The hydrogen is removed from the carrier by catalytic dehydrogenation at the point of use. The carrier can then be returned to the hydrogen production site to be regenerated with hydrogen.

**Hydrogen Storage Comparison**

In order to help explain our hydrogen storage approach, we’ll review other primary storage methods being developed: physical storage, physical adsorption (physisorption) and chemisorption. Physical methods involve containment of the hydrogen molecule in a vessel as either a cryogenic liquid or a compressed gas. These are the traditional methods used for industrial hydrogen delivery and storage. Cryogenic liquid hydrogen is delivered at conditions of approximately -425ºF and 100 psig, while gaseous hydrogen is stored onboard vehicles at 350 or 700 barg with even higher pressures required for fast-fill dispensing. Significant improvements are being made to improve storage densities and improve inherent safety and handling for these physical methodologies, but it is uncertain they will be able to meet the ultimate consumer requirements for commercial vehicles.

Physical adsorption methods rely on the adsorption of the hydrogen molecule to high surface area materials. These are generally solid materials such as activated carbons, carbon nanotubes and zeolites. In order for the hydrogen to be usable, the adsorption must be reversible under specific conditions of temperature and pressure. Currently, there are no known materials that contain adequate amounts of hydrogen at near-ambient temperature and low pressures. A great deal of research is currently underway to improve the hydrogen storage densities in materials that demonstrate hydrogen physisorption.

Lastly are the chemisorption methods. In these storage methods, the hydrogen molecule is no longer intact. That is, hydrogen is bonded to other atoms within the material. A catalyst is generally required to break those metal-hydrogen bonds to allow the hydrogen molecule to form. Ideal materials should be reversible and not require large quantities of energy to reform the hydrogen molecule. Examples of chemisorption methods include:

- Metal hydrides (FeTi, LaNi₅)
- Advanced hydrides (NaAlH₄)
- Chemical hydrides (NaBH₄/H₂O)

Chemisorption methods are, therefore, an indirect storage solution since they don’t contain the intact hydrogen molecule.

Similar to some of the experimental chemical hydrides, the approach we are suggesting involves the delivery of the hydrogen to the vehicle refuelling location in addition to the hydrogen storage onboard the vehicle. To illustrate, we’ll compare the various types of chemisorption methods. Table 1 covers regeneration conditions for the hydrogen charge and Table 2 covers hydrogen release. The comparisons provided in these tables represent “typical” molecules. The approach we are proposing is designated separately in the table as “liquid carrier” since it has distinct differences from the other methods.
Table 1. Chemisorption Comparison – Regeneration Conditions

<table>
<thead>
<tr>
<th></th>
<th>Regeneration</th>
<th>Fuelling Process</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Hydride (solid)</td>
<td>Onboard, reversible with H₂</td>
<td>Gaseous hydrogen on, waste heat removal, potentially long time to fill</td>
<td>Independent</td>
</tr>
<tr>
<td>Advanced Hydride (solid)</td>
<td>Onboard, reversible with H₂</td>
<td>Gaseous hydrogen on, waste heat removal, potentially long time to fill</td>
<td>Independent</td>
</tr>
<tr>
<td>Chemical Hydride (liquid)</td>
<td>Offboard, Multi-step chemical processing or direct electrochemical synthesis.</td>
<td>“Fresh” carrier and potentially reactant on, “spent” off, fast fill</td>
<td>Carrier and reagent</td>
</tr>
<tr>
<td>Organic Liquid Carrier</td>
<td>Offboard, Regenerated easily with H₂ alone using commercial hydrogenation technology.</td>
<td>“Fresh” carrier on, “spent” off, fast fill</td>
<td>Carrier</td>
</tr>
</tbody>
</table>

For metal hydrides and advanced hydrides, regeneration (charging with hydrogen) is performed onboard the vehicle. In these refuelling approaches, the fuelling process requires getting the gaseous hydrogen to the onboard storage tank and removal of heat that is liberated during the regeneration (heat of formation of the metal hydrides). Note that gaseous hydrogen is therefore required for the regeneration. The delivery system is largely independent of the specific material that is used for storage onboard the vehicle; however, the hydrogen molecule remains part of the transfer for fuelling of the vehicle.

Chemical hydride methods including our liquid carrier concept allow for the delivery of the hydrogen and carrier throughout the entire supply chain. The benefit of this method is that the hydrogen molecule can be removed from the entire delivery chain, and the regeneration of the material can be efficiently handled off-board the vehicle, reversible with hydrogen gas. The new challenge this approach introduces is the return of the spent carrier material into the supply chain. We’ll discuss this more later.

Table 2. Chemisorption Comparison – Release Conditions

<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
<th>Energy</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Hydride (solid)</td>
<td>M-H → M + H₂</td>
<td>Endothermic, but some reversible at ambient temperature</td>
<td>Equilibrium controlled - Temperature and/ or pressure swing mode</td>
</tr>
<tr>
<td>Advanced Hydride (solid)</td>
<td>M-H → M + H₂</td>
<td>Endothermic, utilization of waste heat necessary</td>
<td>Equilibrium controlled - Temperature and/ or pressure swing mode</td>
</tr>
<tr>
<td>Chemical Hydride (liquid)</td>
<td>MHₓ + H₂O → M(OH)ₓ + H₂</td>
<td>Exothermic, generation of H₂ and heat is spontaneous</td>
<td>Spontaneous with introduction of reagent and/or catalyst at ambient temperature</td>
</tr>
<tr>
<td></td>
<td>Reagent such as water required</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic Liquid Carrier</td>
<td>F*H₂ → S + H₂</td>
<td>Endothermic, utilization of waste heat necessary</td>
<td>Spontaneous upon heating in presence of catalyst.</td>
</tr>
<tr>
<td></td>
<td>F = hydrogenated S = dehydrogenated</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The hydrogen release conditions are shown in Table 2. This discussion will center on the difference between a typical chemical hydride and the liquid carrier concept, although the metal and advanced hydrides
are included for completeness. In addition to the potential differentiation that the reversible liquid carrier does not require a reagent, it also offers a more attractive energy profile for utilization onboard a vehicle. Typical chemical hydride methods involve the spontaneous release of heat with the generation of hydrogen. Onboard a fuel cell powered vehicle, the dissipation of waste heat of the fuel cell is already an engineering challenge that adds cost to the system. A reversible organic liquid carrier requires heat for release of the hydrogen. Ideally, a portion of the waste heat from the fuel cell can be recovered by the hydrogen storage system to release the hydrogen.

**Selection Criteria for the Organic Liquid Carrier**

Air Products’ approach for identification of organic liquid carriers suitable for hydrogen storage is to search known molecules first for feasible energetics, and then further improve storage density. Additional criteria include:

- Optimal heat of hydrogenation to allow use of waste heat for dehydrogenation
- Low volatility (b.p. > 250°C)
- Reversibility with no significant degradation
- Low toxicity and environmental impact
- Manufacture of the liquid carriers from low cost, natural source raw materials.
- Liquid state, all stages of hydrogenation/dehydrogenation
- High weight and volume storage densities

Chemical compounds that exhibit reversible hydrogenation and dehydrogenation (e.g. cyclohexane, decalin) have been investigated previously by a number of research groups [1-6] and other approaches to hydrogen evolution from organic compounds have been explored [7]. However, our selection criteria are centered around the need to dehydrogenate at lower temperatures relative to these prior art temperatures, and preferably below the temperature of PEM fuel cell waste heat.

One key to finding an ideal material is understanding enthalpy changes upon hydrogenation. Figure 1 shows enthalpy ranges for various hydrogen storage technologies. Materials that have low enthalpies for hydrogen storage are generally physical adsorption methods with hydrogen containment in a porous solid. At the far left, adsorption will be weak and not desirable since only low quantities may be contained at ambient temperature. Strong physical adsorption approaches 7 to 8 kcal/mol H2. The weak to moderate chemisorption range indicated represent the primary target range for our organic liquid carrier selection criteria.

**Figure 1. Enthalpy Ranges for Various H2 Storage Technologies (kcal/mol H2)**

![Figure 1](image1.png)

Relative to the weak to moderate chemisorption range in Figure 1, materials with higher enthalpies will generally require higher temperatures to dehydrogenate, and those with lower enthalpies may no longer have an ability to be hydrogenated. Figure 2 is a plot of the calculated standard enthalpies of hydrogenation for three structural classes of polyaromatic hydrocarbons as a function of the number of fused aromatic rings. The simplest molecule, benzene, is the far left molecule in Curve I. Note that only the very large fused multi-ring aromatic systems are in the desirable enthalpy range as shown in Figure 1. Unfortunately, these molecules aren’t liquid at near-ambient temperatures, let alone approaching the potential to achieve most of our other criteria.

Figure 3 is a plot of the calculated standard enthalpies of hydrogenation for two isostructural series of polyaromatic hydrocarbons, with and without nitrogen substitution, as a function of the number of fused
aromatic rings. The substitution of nitrogen in the ring can greatly lower the enthalpy with much smaller molecules. Curves I & II and III & IV are direct comparisons of the profound difference in enthalpy with nitrogen substitution.

Figure 2. Enthalpies of Hydrogenation as function of fused aromatic rings

![Figure 2](image)

Figure 3. Enthalpies of Hydrogenation as function of N substitution

![Figure 3](image)

Figure 4 shows examples of temperatures that have been determined for 95% conversion to the dehydrogenated form under 1 atmosphere hydrogen pressure based on calculations and experimental data. There is a wide range of chemical diversity and potential molecules that are being investigated. Note in the figure the lowering of dehydrogenation temperature by about 150º C with the nitrogen substitution from benzene to pyrazine (C₆H₅N₂).
Using the guidance from the calculated heats of hydrogenation of nitrogen-containing aromatic molecules (Figures 3,4), we have investigated reversible hydrogenation of a number of nitrogen-containing aromatic molecules [8]. Several promising organic liquid carrier prototypes have been developed and these have been used for a parallel study that is focused in development of new, high activity dehydrogenation catalysts.

N-ethylcarbazole can be hydrogenated with high selectivity under typical industrial hydrogenation conditions (130-200 °C, 500-1200 psi H₂) using standard types of hydrogenation catalysts. The theoretical hydrogen capacity of N-ethylcarbazole is 5.7 wt. % and 54 g H₂/L. The resulting perhydro-N-ethylcarbazole can be selectively dehydrogenated under 1 bar hydrogen pressure (Figure 5). The hydrogen release is characterized by recording the flow of hydrogen from the test reactor as the temperature of the reactor is increased from 100-200 °C. We have recently developed catalysts at Air Products that demonstrate high activity with 10 times less active metal than comparable commercial catalysts.

One criterion for a successful organic liquid carrier prototype is stability over cycles of hydrogenation and dehydrogenation. We have demonstrated that N-ethylcarbazole can be reversibly hydrogenated and dehydrogenated with no degradation of the liquid carrier (Figure 6).
Our cycling studies continue to demonstrate that liquid carriers can be reversibly hydrogenated over a number of cycles with little/no degradation in the hydrogen capacity or rate of hydrogenation and dehydrogenation. Figure 6 details the results observed for N-ethylcarbazole over the first 3.5 cycles under the hydrogenation and dehydrogenation conditions described on the figure.

In order to reach the hydrogen storage density targets necessary for commercialization of hydrogen powered vehicles, organic liquid carriers with higher gravimetric and volumetric storage densities must be discovered. We have recently discovered several new organic liquid carrier prototypes with theoretical gravimetric capacities of up to 7.2 wt. % H₂ and volumetric capacities of up to 69 g H₂/L (Figure 7).
Impurities in hydrogen are a concern for the operation of the fuel cell. Depending on the method of production, hydrogen can have various impurities of concern such as sulfur compounds and carbon monoxide. By using dehydrogenation at the point of use, we are able to generate an extremely high purity level. An initial set of tests during the dehydrogenation of perhydro-N-ethylcarbazole shown in Table 3 indicated the presence of some methane and ethane in the product stream, but typical impurities of concern have not been detected. Subsequent work has determined that these alkanes may have come from a contaminant in the liquid carrier. We also performed accelerated lifetime testing by holding N-ethylcarbazole for 400 hours at simulated dehydrogenation reactor conditions where multiple fully- and partially-dehydrogenated intermediates were present. Chemical testing of the N-ethylcarbazole showed very low levels of degradation after the lifetime testing. This test suggests that the liquid carrier will be stable under dehydrogenation conditions for many cycles of use.

Table 3. Hydrogen Purity from Continuous Flow Dehydrogenation Experiments

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole %</th>
</tr>
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<tbody>
<tr>
<td>Hydrogen</td>
<td>99.9+</td>
</tr>
<tr>
<td>Methane</td>
<td>0.0013%</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.0083%</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>ND</td>
</tr>
<tr>
<td>N containing compounds</td>
<td>ND</td>
</tr>
<tr>
<td>C3’s</td>
<td>ND</td>
</tr>
<tr>
<td>C4’s</td>
<td>ND</td>
</tr>
<tr>
<td>C5’s</td>
<td>ND</td>
</tr>
<tr>
<td>C6’s</td>
<td>ND</td>
</tr>
</tbody>
</table>
**Organic Liquid Carrier Approach**

Advantages of the organic liquid carrier approach over other hydrogen storage methods include:

- Maximum utilization of the existing liquid fuel infrastructure
- Provide energy efficient solution
- Provide practical, feasible, simple solution
- Fuelling using liquid with improved safety characteristics vs. gasoline

Gasoline, as the incumbent fuel, is the benchmark target for comparison. The gasoline delivery approach is depicted in Figure 8. One key to the efficiency in the delivery approach of gasoline is that it is a liquid at atmospheric conditions. It provides an integrated delivery and storage approach, and is completely consumed within the engine of the vehicle. We overlook the fact that it releases undesirable emissions (NOₓ, SOₓ, volatile organic chemicals, CO₂), is flammable, is carcinogenic, and is destructive to the environment including soil and groundwater if accidentally released.

**Figure 8. Gasoline Delivery Approach**

![Gasoline Delivery Approach Diagram]

The organic liquid carrier delivery approach is depicted in Figure 9. Differences from the gasoline delivery approach are marked in red. One primary difference with the carrier approach is that the carrier requires a return trip. However, we envision that the infrastructure will be developed so that two-way hauling can take place simultaneously. Therefore, the impact on capital, footprint, and time will be minimized.

Utilizing this method, the carrier would be regenerated at the same location of hydrogen production. Hydrogen production is independent of the carrier and could be produced by either renewable methods or hydrocarbon based sources. It could take place at a large central location such as a refinery today. In fact, refineries are one of the largest captive users of hydrogen today, where it is produced and consumed onsite. Hydrogenation is also one of the processing steps used in a refinery.

Energy efficiency is maximized by this approach when compared to other chemisorption methods. Since the hydrogenation is exothermic there is an opportunity to capture some value from the released heat such as steam generation for other chemical processes (eg. hydrogen production) or electricity generation. Dehydrogenation does require energy in the form of heat to allow the generation of hydrogen, but this is done at the point of use. Since the fuel cell generates waste heat that must be removed, our ideal carrier will be capable of utilizing the waste heat without requirement for additional energy or temperature upgrading.

Future fuel cell membranes that operate at higher temperatures than today’s proton exchange membrane (PEM) fuel cells could be important to the success of this approach.
Figure 10 depicts examples for cryogenic liquid delivery by truck and high pressure gas delivery by pipeline. These are the current methods used for the lowest cost hydrogen delivery for commercial higher volume applications. The organic liquid carrier approach provides a much simpler concept than physical distribution methods compared to gasoline. The equipment and delivery systems are more complex and require a larger footprint, particularly with incorporation of code and standards safety requirements.

**Figure 10. Delivery Approach for Physical Storage Method**

The system onboard the vehicle combines a storage tank with the system required to remove the hydrogen from the carrier, see Figure 11. A single storage tank could contain all of the liquid carrier, both the fresh and spent carrier, with the use of a flexible barrier to minimize the volume required. As an example, a vehicle would require a 18.9 gallon carrier capacity to carry 5 kg of available hydrogen at a content of 7 weight percent and density of 1.0 g/cc.

**Figure 11. Storage Approach Onboard a Fuel Cell Vehicle**

Equipment on the vehicle would pass fresh carrier over a catalyst and combine it with waste heat from the fuel cell. This dehydrogenation reaction would generate hydrogen for the fuel cell and return spent carrier to the storage tank. As mentioned earlier, the aggressive target of using heat from the fuel cell to facilitate the dehydrogenation helps maximize the energy efficiency of the system. In doing so, it also reduces the radiator requirement for the vehicle. Work is progressing on the catalytic converter that is key to understanding the hydrogen storage system requirements onboard the vehicle.
Summary

The organic liquid carrier approach allows for both the delivery and storage of hydrogen without introducing the hydrogen molecule to the supply chain by using a reversible hydrogenation of an organic liquid carrier. Potential benefits for the use of this carrier approach include:

- Utilization of the existing liquid fuels infrastructure
- Maximum energy efficiency
- Simplicity of supply
- Improved environmental, health and safety considerations

Towards enabling this organic liquid carrier approach, a number of liquid carrier prototypes have been developed with hydrogen capacity of up to 7.2 wt. % and 69 g H$_2$/L. These carriers have lower heats of hydrogenation than organic liquid carriers previously investigated by other research groups (e.g. cyclohexane, decalin). The lower heats of hydrogenation allow the dehydrogenation to occur at relatively low temperatures with the ultimate goal of performing dehydrogenation at below PEM fuel waste heat temperatures.

The stability of N-ethylcarbazole under repeated hydrogenation/dehydrogenation and accelerated lifetime testing has been demonstrated as well as high levels of hydrogen purity from the liquid carrier dehydrogenation. Dehydrogenation catalysts that show significantly higher activity than commercial catalysts have been developed.

Remaining Challenges

Ongoing technical and evaluation challenges for the organic liquid carrier approach that are currently being addressed include:

1. Development and testing of new organic liquid carriers and catalysts. We have successfully increased the gravimetric and volumetric capacity of our liquid carriers with recently discovered prototype carriers such as 4,7-phenanthroline. We must establish that the new higher-capacity carriers demonstrate the same stability under repeated cycles of hydrogenation and dehydrogenation as previously observed with N-ethylcarbazole. In addition, we are continuing to explore strategies for lowering the dehydrogenation temperatures of the liquid carriers with the ultimate goal of performing dehydrogenation at temperatures below the operating temperature of PEM fuel cells. This will require identification and testing of new carriers with heats of hydrogenation at the low end of the desired 10-13 kcal/mol H$_2$ range. Also required is the continued development of dehydrogenation catalysts that demonstrate adequate dehydrogenation rates at these very mild temperatures.

2. Demonstration of onboard storage system including dehydrogenation reactor. With funding from the U.S. DOE and in partnership with Pacific Northwest National Laboratory (Richland, WA), we have developed a research and development program designed to develop new reactor technologies for efficient liquid-phase dehydrogenation of organic liquid carriers. In the same research program, we intend to collaborate with United Technologies Research Corporation (East Hartford, CT) to study the integration of an organic liquid carrier hydrogen storage system with PEM fuel cells designed for vehicular applications.

3. Economic evaluation of the organic liquid carrier approach. We have initiated a preliminary evaluation that will explore the costs associated with hydrogen storage and delivery using liquid carriers for hydrogen.

References


