Abstract

TIAX has finalized an analysis of small-scale purification technologies suitable for hydrogen fueling stations. In this project, professionals at TIAX identified and analyzed three technologies not currently supported by DOE that have some promise as hydrogen purification methods for hydrogen fueling stations. The technologies selected for detailed evaluation in this study were amorphous membranes without noble metals (Zr-Ni alloy), dry fluorinated metal hydrides and the application of this fluorinated metal hydride in a slurry.

The detailed study was performed in the context of hydrogen fueling station hydrogen production and storage technologies. The analysis considered the technology R&D status, current and potential performance and cost, and possible development paths. Alternative fueling station scenarios were developed and compared on the basis of cost, performance and overall system efficiency to each other and baseline technologies such as small-scale pressure swing adsorption purification and central production options.

Results indicate that energy use for hydrogen purification with fluorinated metal hydrides could be lower if low-quality reforming techniques are used (such as an autothermal reformer or hydrogen production from renewables such as biomass), while small-scale PSA purification appears to result in the lowest well-to-tank energy use when coupled with steam reforming. Additionally, fueling costs using fluorinated metal hydride slurry purification appear to be generally lower than PSA options, except if the hydride is also used to store hydrogen (this would of course provide additional safety and size benefits). While fluorinated metal hydrides would appear to provide significant improvements in cost over the current state-of-the-art, considerable further development will be required to prove its feasibility and optimize its implementation.
Introduction

There is increasing interest in the development of small-scale (<1 million SCFD) hydrogen fueling stations to support direct hydrogen fuel cell vehicles when and if these vehicles capture a significant fraction of the U.S. passenger vehicle fleet. Considerable attention from DOE and others has been focused on small-scale hydrogen generation to minimize the cost of efficient decentralized hydrogen production, thus avoiding the cost of hydrogen transportation from central hydrogen production facilities. However, the critical step of purification and system integration has not received as much attention, although it has considerable impact on the efficiency and cost of hydrogen production. This relatively limited attention to small-scale purification and system integration may eventually result in barriers to broad implementation of hydrogen as a fuel in the future. That is why, though DOE funds the development of some hydrogen purification technologies, DOE wants to better understand what other options may be under development that they are not currently funding.

A hydrogen fueling station with on-site reformer-based production will require hydrogen purification, storage, and dispensing, along with the necessary safety and control components. Small, natural gas-based reformers, could be used to generate hydrogen rich reformate streams at small-scale fueling stations servicing hydrogen fuel cell vehicles. Purification is an essential step to remove impurities in the reformate that may poison the storage unit or fuel cell, and to remove non-hydrogen species that can dramatically increase the size of the on-site and on-board storage systems.

This paper represents a final progress report for this project. DOE has not yet reviewed the final analysis.

Approach

We have reviewed three small-scale purification technologies not being funded by DOE. For the analysis, we considered the integration of these purification technologies for on-site hydrogen production at vehicle refueling stations. Both a larger (690 kg H$_2$ per day) and a smaller (69 kg H$_2$ per day) refueling station capacity were analyzed. The analysis included assessments of technical maturity and risks, performance, cost, and a comparison to baseline technologies, as well as the identification of key barriers, and an evaluation of possible development paths. For the performance and cost analysis, we developed detailed flowsheet models for each of the options considered, which included steam reformers as well as autothermal reformers. These flowsheet models were used to estimate the conditions, flowrates, power requirements, and heat duties needed for sizing the equipment. Based on the equipment sizes so calculated, we then obtained cost estimates from quotes and from bottom-up cost models developed by the professionals at TIAX under other programs.

Purification Technology Selection

For the selection of the purification methods to be studied in detail, we first generated a list of potential purification technologies based on literature information and discussions with DOE and others. A rigorous screening was conducted based on the expected applicability of the options to distributed hydrogen production and on whether DOE already supports the option (options already supported were outside of this scope of the work). The selected technologies were also expected to have good potential to reduce cost and improve performance on the system level. The options selected for detailed evaluation were:
• **Non-palladium metal membranes.** Non-palladium metal membranes are a potential low-cost alternative to palladium-based membranes currently in use. Japanese researchers have promising results from amorphous alloy membranes without noble metals (Zr-Ni). Alloys without noble metals may be two orders of magnitude cheaper than palladium-based materials on a weight basis (Hara 2000).

• **Fluorinated metal hydrides (dry).** If properly protected from certain impurities, metal hydrides could purify reformate steams at much lower pressure than conventional technology. Forming a porous fluoride film on the surface of metal hydride particles is a promising way to protect the metal hydride from poisoning by non-hydrogen species that are less likely to penetrate through the fluoride film than hydrogen molecules (particularly carbon monoxide and water). Combining this low pressure purification with hydrogen storage in the same metal hydride has the potential to simplify system integration and improve efficiency and cost for fueling metal hydride vehicles.

• **Metal hydride slurries.** Utilizing fluorinated metal hydrides in slurries could improve system integration even further. The metal hydride slurry is pumpable, allowing for its use as a medium for hydrogen purification, storage and transportation simultaneously. Slurry systems also have faster absorption/desorption times than dry metal hydrides allowing them to be used for purification only with CH\textsubscript{2} storage and dispensing. The fast absorption/desorption time also reduces the amount of metal hydride material required for purification, thus minimizing capital cost of the purification process.

On-site production with small-scale pressure swing adsorption (PSA) purification and central production with delivered hydrogen/on-site dispensing were chosen as the baseline technologies for comparison. Central hydrogen production options investigated include compressed hydrogen (CH\textsubscript{2}) delivery via tube trailer, CH\textsubscript{2} delivery via an existing hydrogen pipeline, and liquid hydrogen (LH\textsubscript{2}) production and delivery via LH\textsubscript{2} tanker truck. A list of the on-site production scenarios is presented in Table 1.

### System Integration

Optimum system configurations were determined and system models were developed for each scenario. In all cases, purification off-gas (containing un-recovered hydrogen) is recycled for use in the reformer to drive the steam reforming reaction and/or preheat gases.

In addition to evaluating two types of on-site hydrogen production: steam reforming (SR) and autothermal reforming (ATR); two design pressures were also investigated: high-pressure (10 atm, 150 psia) reformers designed specifically for hydrogen production, and low-pressure (1-3 atm, 15-44 psia) fuel cell reformers designed for distributed fuel cell power systems or on-board reforming fuel cell vehicles. Reformers for distributed fuel cell power systems will likely be steam reformers and deliver reformate at around atmospheric pressure, although slightly higher pressures can have some advantages. Reformers for on-board reforming based fuel cell vehicles will likely be autothermal reformers and deliver reformate at around 3 atm (44 psia), although lower pressure can have some advantages. Either of the low-pressure reformers should be much cheaper than reformers designed specifically for hydrogen production due to the relatively high manufacturing volumes projected for reformate based distributed fuel cell power systems and fuel cell vehicles. However, operating low-pressure reformers with conventional purification systems will require very large reformate compressors, adding significant cost and parasitic power (decreasing system efficiency). For example, a reformate compressor can use as much as 5% of the hydrogen energy content for electric power to increase reformate pressure from 3 to 10 atm (44-150 psia), assuming reformate from an ATR
and 70% adiabatic compressor efficiency. When typical power plant efficiencies are taken into account, this electric load can significantly increase overall primary energy use.

### Table 1. Scenarios for Detailed Analysis

<table>
<thead>
<tr>
<th></th>
<th><strong>cH₂ FCV (5,000 psi) Fueling</strong></th>
<th></th>
<th><strong>MH FCV (100 psi) Fueling</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>On-site Production</strong></td>
<td>PSA (Baseline)</td>
<td>Steam Reformer</td>
<td>Steam Reformer</td>
</tr>
<tr>
<td><strong>Purification Technology</strong></td>
<td>High Pressure cH₂</td>
<td>Autothermal Reformer</td>
<td>PSA (Baseline)</td>
</tr>
<tr>
<td><strong>On-site Storage</strong></td>
<td>Zr-based Membrane</td>
<td>Steam Reformer</td>
<td>Low Pressure cH₂</td>
</tr>
<tr>
<td></td>
<td>High Pressure cH₂</td>
<td>Autothermal Reformer</td>
<td>Zr-based Membrane</td>
</tr>
<tr>
<td></td>
<td>Fluorinated Metal Hydride Slurry</td>
<td>Steam Reformer</td>
<td>Low Pressure MH</td>
</tr>
<tr>
<td></td>
<td>High Pressure cH₂</td>
<td>Autothermal Reformer</td>
<td>Fluorinated Metal Hydride</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Steam Reformer</td>
<td>Low Pressure MH Slurry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Autothermal Reformer</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- FI MH in slurry form was selected for cH₂ FCV fueling due to the higher absorption/desorption rates over dry FI MHs. This combination with autothermal reformers could also provide system benefits.
- cH₂ FCV = Compressed hydrogen fuel cell vehicle utilizing high-pressure on-board storage at 340 atm (5,000 psia).
- MH FCV = Metal hydride fuel cell vehicle utilizing low-pressure metal hydride on-board storage at 5 atm (70 psia).

Four types of on-site storage were investigated: high-pressure (240 atm, 3600 psia maximum) compressed hydrogen (cH₂) steel tanks, low-pressure (9 atm, 130 psia maximum) cH₂ steel tanks, low-pressure metal hydride (MH) beds, and low-pressure MH slurry systems. High-pressure cH₂ on-site storage was selected for all purification options when fueling cH₂ vehicles. Hydrogen boost compressors are assumed to be used to fuel cH₂ vehicles for 340 atm (5,000 psia) on-board storage. Other on-site storage pressure ratings are possible, but 240 atm (3600 psia) storage has capital cost and size advantages over lower pressure storage, and energy cost and efficiency advantages over higher pressure storage.

Low-pressure cH₂ storage was assumed for MH vehicle fueling with PSA and membrane purification. Primary compression is required for the membrane case, but not the PSA case where the purification outlet pressure is equal to the maximum storage pressure. Boost compression is required for both cases when the storage pressure drops below the assumed MH vehicle fueling pressure of 5 atm (70 psia). We assumed combining purification with on-site storage would be simplest for the MH and MH slurry cases when fueling MH vehicles. However, MH slurry purification with low-pressure cH₂ storage could have some cost advantages over combined MH purification and storage. This case will be investigated in the next phase of work.
On-site and on-board storage were assumed to be separate for all cases in this analysis because switching heavy MH or bulky \( \text{CH}_2 \) containers could be unwieldy and would introduce considerable complexity into the fueling and charging process. Slurries, on the other hand, could be easily transported from on-site to on-board storage so that on-site hydrogen desorption is not required, but weight and volumetric densities are likely to be too low for on-board vehicle storage.

**Cost and Performance Modeling**

Overall system efficiencies were determined based on integrated system modeling using thermodynamic software with inputs from developers and prior internal analyses. Figure 1 shows the thermodynamic modeling role in determining system efficiency and hydrogen price.

![Thermodynamic Model Diagram](image)

**Figure 1. Approach for Determining Efficiency and Price**

Overall hydrogen costs were determined based on estimated equipment costs, energy costs, and additional conventional economic assumptions. Equipment costs for individual components were estimated based on vendor quotes, bottom-up manufacturing cost analysis, or prior internal analyses. In some cases, progress ratios were applied to vendor quotes to obtain costs at high manufacturer production volumes. For most equipment, production volumes of 100 units/year were assumed. Higher production volumes were used for estimating low-pressure reformer costs, assuming a synergy between reformers manufactured for reformate based fuel cell systems and those manufactured for hydrogen production. Twenty-four vendors provided input to this analysis to date.

**Discussion**

**Amorphous Membranes without Noble Metals**

Amorphous membranes without noble metals are still in the very early research and development stage (Hara 2000). Japanese researchers were contacted to obtain the current
performance of their amorphous Zr_{36}Ni_{64} alloy membrane for hydrogen separation. We developed long-term performance assumptions based on discussions with these developers (personal communication with Pr. S. Har a, National Institute of Materials and Chemical Research, Tsukuba, Japan) and comparative analysis. The long-term assumptions were made considering the membranes’ intrinsic material properties such as mechanical properties and metal hydride formation conditions. Table 2 shows the current and long-term performance assumptions along with the current performance of conventional palladium-based membranes.

### Table 2. Membrane Performance Assumptions

<table>
<thead>
<tr>
<th>Membrane Purification Performance Assumptions</th>
<th>Units</th>
<th>Pd-Ag Current</th>
<th>Zr-Ni Current</th>
<th>Zr-Ni Future</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temperature</td>
<td>ºC</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Inlet Pressure</td>
<td>atm</td>
<td>15</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>H₂ Outlet Pressure</td>
<td>atm</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Membrane Thickness</td>
<td>µm</td>
<td>30</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>Permeability at 350°C</td>
<td>10⁻³mol m s Pa⁻¹</td>
<td>15</td>
<td>1.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Permeability Reduction due to CO</td>
<td>%</td>
<td>5</td>
<td>NA</td>
<td>10</td>
</tr>
<tr>
<td>Hydrogen Recovery from SR Reformate</td>
<td>%</td>
<td>92</td>
<td>53</td>
<td>86</td>
</tr>
</tbody>
</table>

Note: all membranes are 100% selective to hydrogen.

In order to achieve these long-term performance goals, a significant improvement in operating pressure difference across the membrane is necessary (see Figure 2). Note that the hydrogen recovery is also a function of reformate composition. Reformate from steam reforming natural gas gives higher hydrogen recovery than reformate from autothermal reforming natural gas.

It is believed that operating pressure for Zr-Ni amorphous membranes is limited by crystallization process conditions and not by mechanical properties of the material (Ritchie 2000; Ismail 2001). Amorphous Zr-Ni-based membranes show mechanical properties, such as tensile strength, hardness and Young’s modulus, comparable or superior to those of conventional metal-based membrane materials (Davis 1999). The current low operating pressure difference for Zr-Ni membranes is due to crystallization of the membrane material at the assumed temperature and pressure. Crystallization of amorphous materials in the presence of hydrogen is caused by metal hydride formation at certain conditions and leads to a dramatic loss in hydrogen permeability. Metal hydride formation conditions strongly depend on the alloy composition and, thus, can be tailored by modifying membrane material composition such as optimizing component ratios and/or adding small amounts of other metals.

Even if the future performance projections can be met, there is still considerable technology development risk involved in the development and commercialization of purification systems based on these membrane materials (as compared to the risks associated even with palladium-containing metal membranes).
Notes:
Maximum achievable membrane hydrogen recovery assuming equilibrium conditions.
Assumes no permeability reduction due to CO.
Feed stream from SR is 73.5% vol. hydrogen (after HTS); ATR is 45.0% vol. hydrogen (after HTS).

Figure 2. Membrane Recovery as a Function of Pressure

Fluorinated Metal Hydrides (Dry)

If successful, the use of metal hydride-based purification technology could significantly reduce the pressure requirements for the raw hydrogen stream, as well as the compression requirements for the purified hydrogen stream. Hydride-based systems could work at low-pressure and possibly even be used to pressurize the hydrogen partially, prior to the final compression stages (Golben 1999; Vanhanen 1999). Conventional purification technologies (PSA, membranes) require high reformate pressures (>10 atm, 150 psia) to obtain acceptable hydrogen recovery. This high-pressure requirement can increase cost and compressor parasitic power especially if low-pressure reformers, developed and manufactured for reformate based fuel cell systems, are available.

However, hydrogen absorption requires cooling, supplied by radiators and a cooling medium, and desorption requires heating. Heat for the dehydration reaction during desorption is significant and requires the use of an auxiliary burner (or, alternatively, electric heaters). In addition, we assume that most of the reformer waste heat from the tailgas burner is stored and used to supplement the auxiliary burner. For the autothermal reformer cases, most of the heat required for desorption is supplied by the reformer waste heat; but for the steam reformer cases, a significant amount of natural gas is needed in the auxiliary burner to generate the necessary heat.

If protected from certain impurities, metal hydriding alloys could provide highly selective and efficient hydrogen purification at low-pressure, permitting the use of potentially low-cost reformers without expensive and power intensive reformate compressors, as well as the use of more dilute hydrogen streams produced from renewable resources such as biomass. Japanese
researchers claim that fluorination permits hydriding alloys to tolerate high levels of impurities, and have carried out promising initial feasibility experiments (Liu 1995; Wang 1995). The working hypothesis is that hydrogen molecules could easily penetrate a porous fluoride top layer through microcracks, while larger molecules (impurities) could not. However, the fluoride coating is not infinitely selective to hydrogen, so the hydriding alloy is still poisoned by impurities even if treated. The four basic intermetallic impurity interactions and their effects are listed in Table 3. The quantitative effects on metal hydride performance depend on the impurity nature, fluorination treatment method, and impurity concentration in the bulk gas.

Table 3. Metal Hydride Impurity Interactions

<table>
<thead>
<tr>
<th>Impurity Interactions</th>
<th>Effect</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poisoning</td>
<td>Rapid loss of hydrogen capacity with cycling, caused by impurities strongly or irreversibly adsorbed on the surface active sites</td>
<td>H₂S, CH₃SH</td>
</tr>
<tr>
<td>Retardation</td>
<td>Reduction in absorption /desorption kinetics without significant loss in the ultimate capacity, caused by impurities reversibly adsorbed on the surface active sites</td>
<td>CO, CO₂, NH₃</td>
</tr>
<tr>
<td>Reaction</td>
<td>Bulk corrosion leading to irreversible capacity loss</td>
<td>O₂, H₂O</td>
</tr>
<tr>
<td>Innocuous</td>
<td>Loss in absorption kinetics due to surface blanketing</td>
<td>N₂, CH₄</td>
</tr>
</tbody>
</table>

Assuming sufficient sulfur removal prior to reforming, the main impurities of concern in reformate streams are carbon dioxide (CO₂), carbon monoxide (CO), and water (H₂O). We assumed the levels of these impurities found in reformate would not significantly affect hydride performance even after thousands of cycles. This assumption is based on developers’ claims of respective impurity tolerances of 20% and 3,000 ppm (dry volume) for carbon dioxide and carbon monoxide, and no effect of water on the fluorinated metal hydride (personal communication with Pr. S Suda, Kogakuin University, Tokyo, Japan; personal communication with K. Kobayashi, Japan Metals and Chemicals Co., Ltd., Japan). No conclusive tests have been carried out to demonstrate that fluorination alone can provide this level of tolerance but no information to the contrary was available either.

Japanese academic researchers developed a metal hydride fluorination technique involving metal hydride treatment with fluorine salt in aqueous media (Sun 1999; Liu 1995). A Japanese materials company is developing a fluorination process that does not require use of an aqueous system or, consequently, an expensive waste-water treatment system (personal communication with F. Liu, former Kogakuin University, Tokyo, Japan; personal communication with K. Kobayashi, Japan Metals and Chemicals, Japan). The proposed technology employs a fluorotreatment in the gas phase, similar to other fluorination processes currently employed in the chemical industry.
Metal hydrides are being considered for on-site and on-board storage, due in large part to their potential safety advantage over compressed and liquid hydrogen storage. The disadvantage to metal hydrides is their high cost and low storage density (1-5% wt). Weight is not a major concern for on-site storage, but cost is. Fluorinating the metal hydrides could provide purification at a relatively small additional cost, making the metal hydride system more cost competitive overall. Combining storage and purification has the additional advantage of long residence times. Innocuous and other non-hydrogen species may significantly reduce hydrogen absorption kinetics, but, assuming residence times during hydrogenation long enough to reach equilibrium between hydrogen in the gas and solid phases, we have estimated the hydrogen recovery to be limited by system equilibrium only. Figure 3 shows the hydrogen recovery versus system pressure.

![Fluorinated Metal Hydride Recovery as a Function of Pressure](image)

**Figure 3. Fluorinated Metal Hydride Recovery as a Function of Pressure**

**Fluorinated Metal Hydride Slurries**

Metal hydride slurries consist of metal hydrides suspended in a liquid material, such as an oil. These slurries can be stored and pumped like a viscous liquid, simplifying and speeding handling and heat transfer. However, slurries suffer from the same high cost as dry metal hydrides and have even lower weight and volume density. Still, with improvements in metal hydride technology, slurries could become a very attractive option, at least for on-site purification.

The performance assumptions for the fluorinated metal hydride slurries, such as hydrogen capacity and hydrogenation/dehydrogenation thermodynamics, are essentially the same as for the dry fluorinated metal hydrides. Experimental and pilot scale work with slurries in the
Netherlands has shown that the oil has no noticeable effect on various hydrides (Holstvoogd 1989).

Metal hydride slurry hydrogen purification technology was developed for large-scale applications, such as hydrogen for ammonia plants (Zwart 1989). The technology did not find an industrial application due to high product cost in comparison with large-scale membranes and PSA hydrogen separation. However, metal hydride slurries may present significant advantages in small-scale applications where the majority of the cost is in the metal hydride material, which scales well with size.

No fuel cell vehicles have demonstrated this technology for on-board storage. Even if the application for on-board storage would be un-attractive, its use for off-board purification and perhaps storage could offer considerable handling, thermal integration, and control benefits over dry hydride systems.

Metal hydride slurry purification combined with high-pressure $\text{CH}_2$ storage and dispensing for $\text{CH}_2$ vehicles was also investigated. These options have both the advantages of high hydrogen recovery by using FI MH purification and lower capital costs by using $\text{CH}_2$ tanks instead of expensive metal hydride material.

**Hydrogen Recovery Assumptions**

Hydrogen recovery was estimated for each purification technology and inlet condition. To maintain reasonable hydrogen recovery, it was assumed that reformate compression to 10 atm (150 psia) would be necessary for PSA and membrane purification options combined with low-pressure reformers. Fluorinated metal hydride purification options could maintain reasonable recovery at low inlet pressure, so reformate compression was not assumed. Reformate compression for these options would increase purification hydrogen recovery, but overall system efficiency was found to decrease due to the high reformate compression power requirements. No reformate compression was assumed for any of the high-pressure (10 atm, 150 psia) reformer cases.

Demonstrated performance and our assumptions for inlet and outlet pressures, operating temperature, and hydrogen recovery are shown in Table 3. Hydrogen recovery for the PSA case was based on vendor quotes for typical ATR and SR impurity concentrations. Zr-based membrane recovery was estimated based on current and estimated membrane performance characteristics, hydrogen pressure gradient across the membrane, and assumed permeability decrease due to CO presence in the feed stream. Fluorinated metal hydride recovery was estimated based on the operating conditions and metal hydride cycling hydrogen capacity.

**Results**

**System Efficiency**

Overall primary energy use shows efficiencies are higher for low-pressure MH vehicle fueling (Figure 5) versus high-pressure $\text{CH}_2$ vehicle fueling (Figure 4). However, the primary energy use shown here doesn’t take into account the on-board efficiencies that should be lower for the MH vehicles due to the increased weight of the on-board metal hydride storage. It is more useful to compare separately the $\text{CH}_2$ and MH vehicle fueling options.
Table 3. Demonstrated and Assumed Purification Performance

<table>
<thead>
<tr>
<th>Purification Attributes</th>
<th>Units</th>
<th>Small-scale PSA</th>
<th>Zr-based Membranes</th>
<th>Fluorinated MH3,4</th>
<th>Fluorinated MH Slurry1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet pressure</td>
<td>atm</td>
<td>10-20</td>
<td>3</td>
<td>15 (initial)</td>
<td>NA</td>
</tr>
<tr>
<td>H₂ Outlet pressure</td>
<td>atm</td>
<td>9-19</td>
<td>~1</td>
<td>1</td>
<td>NA</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>°C</td>
<td>0-50</td>
<td>250-350</td>
<td>60, 80</td>
<td>NA</td>
</tr>
<tr>
<td>Hydrogen recovery3</td>
<td>%</td>
<td>70-90</td>
<td>40-60</td>
<td>85</td>
<td>NA</td>
</tr>
</tbody>
</table>

Assumed Performance

| Inlet pressure          | atm   | 10             | 10                   | 1.5-10           | 1.5-10                |
| H₂ Outlet pressure      | atm   | 9              | ~1                   | 5                | 5                     |
| Operating temperature   | °C    | 40             | 350                  | 40-110           | 40-110                |
| Hydrogen recovery3      | %     | 70-76          | 78-86                | 65-94            | 64-92                 |

1 Based on the material and processes investigated in this study. Attributes vary significantly with material.
2 Current performance with 2 atm (30 psia) pressure difference across the membrane. Hydrogen recovery increases with increasing pressure difference.
3 Varies depending on inlet pressure and reformate composition (SR versus ATR).

Figure 4. Primary Energy Use for cH₂ Vehicle Fueling Stations
For CH₂ vehicle fueling (Figure 4), PSA purification with a high-pressure steam reformer gives the lowest primary energy use of all the options. Despite higher purification hydrogen recovery, the membrane option has higher primary energy requirements than the PSA when used with a steam reformer due to the additional power required for compressing hydrogen at the membrane exit pressure (~1 atm, 15 psia) compared to PSA exit pressure (~9 atm, 130 psia). In a steam reformer, not much is gained by increasing hydrogen recovery beyond ~80% because the steam reformer can use the un-recovered hydrogen to provide heat for the steam reforming reaction. However, with an autothermal reformer, purification off-gasses are not used as effectively so membrane purification results in nearly the same or lower overall energy use than the PSA. FL MH slurries can reduce power plant related energy use, especially with low pressure reformers, but overall energy use is not reduced, despite improved hydrogen recovery, due to the need to supply additional heat for the dehydration reaction. FL MH slurries were not evaluated with autothermal reformer production but would likely be more competitive with PSA purification for those cases because most of the heat for the dehydration reaction can be supplied by the autothermal reformer waste heat.

![Graph showing primary energy use for MH vehicle fueling stations.](image)

**Figure 5. Primary Energy Use for MH Vehicle Fueling Stations**

For MH vehicle fueling (Figure 5), PSA purification with a high-pressure steam reformer once again gives the lowest primary energy use of all the options. However, when autothermal reformers are used, FL MH options use far less primary energy than PSA or membrane options because hydrogen recovery is high and the reformer waste heat can be used to supply almost all the heat required for the dehydration reaction.
General Trends:

- Steam reformer based systems have lower primary energy use than autothermal reformer systems due in part because steam reformers can utilize the purification off-gases more effectively.
- PSA purification with a high-pressure steam reformer gives the lowest primary energy use.
- PSA and membrane purification for use with low pressure reformers tend to have higher power-based primary energy use due to the need for compression prior to purification.
- Membrane power requirements are always highest because additional primary hydrogen compression is required.
- Despite high hydrogen recovery, Fl MH purification options for use with steam reformers have high natural gas-based primary energy use due to the need for an auxiliary burner.
- Autothermal reformers have enough waste heat to significantly reduce or eliminate an auxiliary burner, provided the waste heat can be stored and used as needed during fueling.

Hydrogen Cost

Overall hydrogen costs are lower for low-pressure MH vehicle fueling (Figure 7) versus high-pressure CH₂ vehicle fueling (Figure 6). However, the hydrogen costs don’t take into account the potentially lower MH vehicle fuel economy or potentially higher vehicle cost (due to higher on-board storage cost). Once again, it is more useful to compare separately the CH₂ and MH vehicle fueling options.

![Figure 6: Hydrogen Cost for CH₂ Vehicle – 690 kg/day Capacity](image-url)

Notes:
Purification category includes reformate compressor costs for low-pressure reformers with PSA and membrane purification.
Cost categories include energy, maintenance, and capital recovery costs.
“Other” costs include labor, rent, utilities, profit, and capital recovery for site preparation and central controls and safety.

Figure 6: Hydrogen Cost for CH₂ Vehicle – 690 kg/day Capacity
For cH₂ vehicle fueling (Figure 6), Fl MH slurry purification with a low-pressure steam reformer gives the lowest hydrogen cost of all the on-site production options. Purification costs are lowest for the membrane with a high-pressure steam reformer, but compression costs are much higher due to the low purification outlet pressure, requiring more power and compression stages. Despite lower purification costs, high-pressure steam reformers result in slightly higher hydrogen cost than the low-pressure production options due to higher reformer capital cost. High-pressure autothermal reformers, on the other hand, result in approximately the same cost as the low-pressure options because purification costs are much higher. PSA and membrane purification costs are significantly higher when used with a low-pressure reformer versus a high-pressure reformer due to the need for a reformate compressor to bring the inlet pressure up to 10 atm (150 psia). The reformate compressor size and energy requirements are highest for the autothermal reformer cases due to the higher reformate flowrate. Purification costs are only slightly higher for the Fl MH case because reformate compression is not required (although purification hydrogen recovery is reduced).

The hydrogen costs assuming lower capacity (69 kg H₂ per day) stations are 50-90% more expensive than the high capacity station costs, but the same general trends are found. However, Fl MH purification scales down in size better than the other purification options, making it the lowest cost option for use with both low-pressure and high-pressure steam reformers.

Central plant production with tube trailer delivery gave the highest hydrogen cost of all the options due to the high transportation cost (tube trailers were assumed to be rented and left at the station for on-site storage). However, capital cost (both central and on-site) is lowest per kg hydrogen per day (not shown), making it an attractive option during the early years of FCV introduction when fueling station utilization factors are low. Central liquid hydrogen production and delivery was the cheapest option, despite higher production costs, due to low transportation and compression costs (most compression is accomplished through pumps and evaporators instead of gas compressors). However, energy use (not shown) is about 50% higher than on-site options. The pipeline delivery case is another low cost option (the lowest cost for small capacity stations), but is only applicable to areas with an existing pipeline network.

For MH vehicle fueling (Figure 7), PSA purification with a low-pressure steam reformer gives the lowest hydrogen cost of all the options. The combined Fl MH purification and storage options (dry and slurry) are too costly to compete with PSA and membrane purification using steam reformers, but are cheaper when autothermal reformers are used because, unlike PSAs and membranes, Fl MH systems are projected to have very similar cost regardless of reformate composition. Slurries are cheaper than the dry Fl MH options due to the assumption that less MH material is needed in the slurry cases. We assume dry MH storage requires an extra (or buffer) MH bed so that the reformer can continuously charge one bed even at the end of the day when the last vehicle is being fueled. The continuous nature of the slurry system allows for simultaneous absorption and desorption without the need for a buffer.

The hydrogen costs assuming lower capacity (69 kg H₂ per day) stations are, once again, 50-90% more expensive than the high capacity station costs. Combined Fl MH slurry purification and storage becomes the lowest cost hydrogen option for every reformer type because the MH options scale down better than PSA or membrane based purification with cH₂ storage.
Notes:
Purification category includes reformate compressor costs for low-pressure reformers with PSA and membrane purification. Cost categories include energy, maintenance, and capital recovery costs. “Other” costs include labor, rent, utilities, profit, and capital recovery for site preparation and central controls and safety.

Figure 7: Hydrogen Cost for MH Vehicle – 690 kg/day Capacity

**General Trends:**

- If low-pressure steam reformers are manufactured in relatively high volumes (10,000 units/yr) and used for on-site hydrogen production, PSA or Fl MH slurry purification systems result in the cheapest hydrogen cost options.
- Despite higher capital costs, high-pressure autothermal reformers result in approximately the same hydrogen cost as the low-pressure options because purification costs are much higher.
- Purification costs are lowest for membrane purification with a high-pressure steam reformer, but compression costs are much higher resulting in a higher hydrogen cost than PSA based purification.
- PSA and membrane purification costs are significantly higher when used with a low-pressure reformer versus a high-pressure reformer due to the need for a reformate compressor.
- Unlike PSAs and membranes, Fl MH systems are projected to have very similar cost regardless of reformate composition.
- The hydrogen costs assuming lower capacity (69 kg H₂ per day) stations are 50-90% more expensive than the high capacity station costs.
- Fl MH purification scales down in size better than the other purification options, making it a more attractive technology at small fueling stations.
Conclusions

Our analysis indicates that the use of fluorinated metal hydrides in slurry form could reduce overall hydrogen cost, especially if the slurry is used for purification only. Slurries could also provide benefits in terms of hydrogen transmission to decentralized fuel cell power systems in a mini hydrogen grid. However, some technology development will be required to optimize the slurry system, and significant development will be required to develop a stable and effective fluorinated metal hydride that can be produced cost-effectively.

If non-palladium metal membranes could be further developed to operate with reasonable fluxes and at higher pressures, they could provide a very competitive alternative to PSA-based separation and purification systems. However, no purification technology was found to use less primary energy than the baseline PSA system, unless autothermal reformers are assumed to be used.

Based on these results, we will make recommendations to DOE regarding the viability of each option, and regarding appropriate R&D activities to further their development.

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References


