Proceedings of the 2000 Hydrogen Program Review
NREL/CP-570-28890

ADVANCED THERMAL HYDROGEN COMPRESSION

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Abstract

Ergenics, Inc. has developed a novel thermal hydrogen compressor that may offer advantages for compressing hydrogen produced from renewable resources using advanced production techniques. Ergenics' thermal compressor is an absorption based system that uses the properties of reversible metal hydride alloys. Hydrogen is absorbed into an alloy bed at ambient temperature and is desorbed at elevated pressure when the bed is heated with hot water. Two recent innovations strongly suggest that thermal compressors can be used for non-pure hydrogen streams likely to result from advanced production methods. The first involves a combination of processes that permit the absorption of impure hydrogen streams by hydride alloys. The second is a modular alloy bed design that permits rapid hydrogen absorption kinetics, enabling a reduction in compressor size with an associated reduction in capital cost.

The long term goal of this project is to develop a thermal hydrogen compressor that operates in conjunction with advanced hydrogen production technologies and improves the efficiency and economics of the compression process.

Introduction

An important element of large scale hydrogen production, storage and utilization infrastructure is hydrogen compression. Ergenics is examining the application of advanced thermal hydrogen compression to hydrogen produced from renewable resources. The compressor would be used in conjunction with physical storage (e.g. storage as a high pressure gas) or other advanced storage system that requires hydrogen to be supplied at elevated pressure. The advanced thermal compressor can be powered by either waste heat from a hydrogen production process or solar hot water. It has overwhelming advantages compared to mechanical hydrogen compressors, including smaller size, lower capital, operating and maintenance costs, no rotating hydrogen seals, and nearly silent operation.

Ergenics, Inc. has been supplying thermal hydrogen compressors for pure hydrogen gas streams for more than 15 years. Recent developments in moisture tolerant metal hydride alloy storage systems strongly suggest that thermal compressors can be used for non-pure hydrogen streams likely to result from advanced production methods. Additional developments in rapid hydrogen absorption alloy bed design and modular construction now enable systems that can economically process the high flow rates associated with large-scale hydrogen production facilities.

In the thermal compressor, hydrogen is absorbed in a reversible metal hydride alloy at low pressure in a water-cooled container. The container is subsequently heated with hot water which releases the hydrogen at higher pressure. The pressure increases exponentially with increasing temperature, so large pressure increases can be affected with only moderate temperature increases. To obtain even higher pressures, several containers are connected in series, with each container using a different hydride alloy with successively higher operating pressures. Continuous compression is achieved with two identical containers in a parallel configuration; one container cooled by water absorbs hydrogen while the other is heated with hot water to release hydrogen at the same rate. The cool and hot water streams are periodically switched and simple check valves keep hydrogen moving through the compressor (Golben 1983).

The hydride alloys are active metal powders that are affected by gaseous impurities. Certain active gas species such as water vapor, oxygen and carbon monoxide can gradually poison the alloy, reducing its hydrogen sorption capabilities. Inert species such as noble gases and nitrogen can blanket the alloy, slowing hydrogen absorption until the blanket is swept away. Ergenics pioneered research into alloy poisons in the early 1980s. In the early 1990s, corrosion resistant alloys were developed for nickel-metal hydride batteries. In connection with its recent metal-hydrogen battery development, Ergenics has invented and patented a process that enables hydride alloys to store hydrogen saturated with water vapor. Related processes and alloying techniques can eliminate performance degradation from other active gas species.

The work completed to date includes three elements:

- We classified the hydrogen composition and operating conditions expected to result from various advanced production techniques to determine which processes would be good candidates for thermal compression.
- We identified three techniques that can mitigate the effect that impurities have on thermal compressor operation.

- We prepared a preliminary design for a 3,600 psia, 2,000 scfh refueling station thermal compressor, compared the thermal compressor with a mechanical compressor and performed a hazardous operation analysis.

Discussion

Hydrogen Composition Expected From Advanced Production Processes

The advanced hydrogen production processes analyzed for this work were selected from projects funded by the DOE Hydrogen Program in 1999. Production processes included:

- algal hydrogen production (photobiological)
- biomass via fast pyrolysis
- biomass in supercritical water
- plasma catalytic reforming of natural gas
- PEM electrolysis
- photoelectrochemical direct conversion
- sodium borohydride production

Information about hydrogen compositions attained to date and the availability of waste or solar heat was gathered from the Proceedings of the 1999 U.S. DOE Hydrogen Program Review. Where necessary, follow up calls were made to the principal investigators for clarification or updated information.

Hydrogen impurities include air, H_20, N_2, O_2, CO, CO_2, and CH_4 over wide concentration ranges. Production pressures range from atmospheric to very high. For example, a hydrogen compressor will not be required for biomass in supercritical water because the process produces hydrogen near supercritical (water) pressure. The availability of waste heat or solar heat is application specific.

Table 1 presents a summary of hydrogen compositions, conditions, availability of heat and conclusions about which processes are candidates that can take advantage of the benefits of thermal compression.

Table 1. Hydrogen Quality and System Compatibility Summary

H_2 Production Process	**H_2 Purity**	**Waste Heat**	**H_2 Pressure**	**Comments**
Algal H_2 Production (Photobiological)	H_2: >90% N_2: <10% Air: trace	Solar	Atmos-Pheric	Good Application for Thermal Compression
Hydrogen from Biomass via Fast Pyrolysis/Catalytic Steam Reforming	H_2: 60-70% CO_2: 20-30% CO: 5%	Yes	Moderate	Good Application for Thermal Compression
PEM H_2 Electrolyser	H_2: >99% H_2O: sat.	Mod.	Moderate	Will need heat assist
Plasma Catalytic Reforming of Natural Gas	H_2: 25-38% CO_2: 5-8% CO:8-17% CH_4:2-12%	Yes	Moderate	Incomplete Data
Biomass in Supercritical Water	H_2:.57mf CO_2:0.34mf CO:0.03mf CH_4:0.06mf (see below)	Yes	High	No need for Compressor
Supercritical Water Pyrolysis (Purification for Biomass SCW)	H_2: 9mf CO_2: 5mf CO: 0.25mf	Yes	High	No need for Compressor
Photoelectrochemical Based Direct Conversion Systems for H_2 Production	H_2: >99%	Solar	Atmos-pheric	Good Application for Thermal Compression
Sodium Borohydride	H_2: >99% H_2O: sat.	Mod.	Moderate	Will need heat assist

Thermal Compressor Purification Processes

Impurities interact with hydride alloys with varying effects (Sandrock 1984). *Poisoning* results in a rapid decrease in hydrogen capacity with cycling. Damage from poisoning tends to be localized on the alloy particle surface, so it is often possible to restore performance with little, if any, loss in capacity. *Retardation* is manifested by a reduction in absorption kinetics without loss in ultimate capacity. With enough time, full capacity can be achieved. *Reaction* causes irreversible capacity loss through bulk corrosion of the alloy. Reaction results in the formation of very stable chemical compositions that do not reversibly hydride and cannot be easily returned to their original state.

Although hydrogen purification systems can be used to remove impurities, the purification systems themselves are often complex, expensive to maintain, and, for hydrogen produced at atmospheric pressure, would require their own motive force in the form of a mechanical compressor or blower. These disadvantages offset most benefits that could be derived from thermal compression.

It is possible to engineer alloys and containment systems that can withstand impurities without degradation. Ergenics has invented and patented a process that enables hydride alloys to store hydrogen saturated with water vapor (Golben 1999). This alone opens many new possibilities to apply hydride process technology to commercial hydrogen production. In addition, nickel-metal hydride battery alloy development by Ergenics and others stimulated a large body of research into the corrosion of hydride electrodes submersed in electrolytes. A number of corrosion inhibiting additives, such as cobalt and tin, have been identified for submersed alloys, and Ergenics has found these to have positive impact on gaseous systems as well.

Previously, reversible metal hydride alloys would sustain damage from hydrogen impurities at low levels of ~ 50 ppm. Ergenics has developed three processes, summarized in Table 2, that permit hydride alloy beds to tolerate higher levels of impurities, in some cases up to 10,000 ppm or more. Passive Purification is used for water vapor and oxygen, Elevated Temperature Desorption is used for CO and CO_2, and Automatic Venting can clear inert gas blanketing caused by N_2 and CH_4. The advanced thermal hydrogen compressor will include the three purification processes.

Table 2 – Thermal Compressor Purification Processes

Impurity	**Process**	**Comments**
H_2O, O_2	Passive Purification	Hydride Heat Exchanger in-situ process prevents retardation and poisoning. Removes O_2 from hydrogen.
CO, CO_2	Elevated Temperature Desorption	Over 115°C desorption removes CO impurities from alloy surface.
N_2, CH_4	Automatic Venting	Clears inert gas blanketing and removes impurity from hydrogen.

Miniature Modular Hydride Heat Exchangers

Thermal hydrogen compressors produced to date are a superior alternative to diaphragm compressors when there is a source of hot water. However, they have been limited to applications with relatively low flow rates (400 scfh) due to heat transfer limitations associated with large alloy beds. Another important innovation from Ergenics will permit economical scale up to production-sized units competitively superior to piston compressors. Ergenics has developed and patented an advanced hydride bed design with rapid heat transfer capabilities. The hydride bed is essentially a miniature high surface area hydride heat exchanger, which permits the construction of large compressors of small size and cost. The small hydride beds can be thermally cycled at a rapid rate (<1 minute) in order to process high hydrogen flow rates. The unique hydride heat exchanger design is modular and lends itself to high volume, low cost production.

Thermal Compressor For A Hydrogen Service Station

Design

A thermal compressor sized for duty at a hydrogen service station to refuel vehicles has been preliminarily designed and compared with a mechanical compressor. The compressor employs the three purification processes and the miniature hydride heat exchanger design. A detailed Piping and Instrumentation Diagram and a Layout Drawing were prepared for cost estimating purposes. The layout appears in Figure 1.

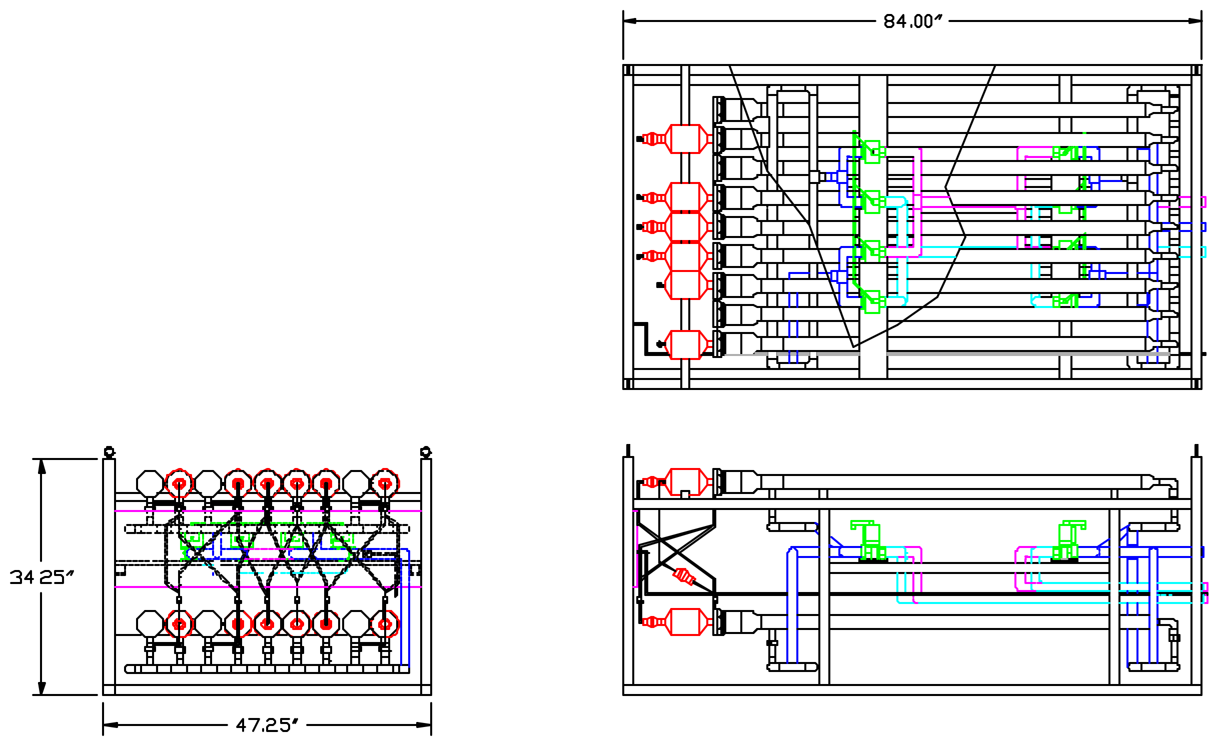

Figure 1 - Advanced Thermal Compressor Layout

Economic Analysis

An economic analysis comparing a thermal compressor with a mechanical compressor was performed and is summarized in Table 3. Assumptions used for the analysis are:

- Operating Conditions: 2,000 scfh, Inlet P=100 psia, Outlet P=3,600 psia

- Capital costs: Mechanical compressor quotation; Thermal compressor detailed cost estimate.
- Operating Costs: Power @ $0.10/kWh, Waste heat @ $0.00
- Maintenance Costs: Mechanical compressor annual rebuild; Thermal compressor valve replacement every other year

Table 3. Comparison of Advanced Thermal and Mechanical Hydrogen Compressors

	Thermal Compressor	**Mechanical Compressor**
Hydrogen Flow	2,000 scfh	2,000 scfh
Inlet Pressure	100 psia	100 psia
Outlet Pressure	3,600 psia	3,600 psia
Number of Stages	5	3
Weight	100 kg	3,600 kg
Volume	400 liters	6,000 liters
Hot Water Flow (waste heat)	50 gpm @ 90 C	-
Heat Energy Required	240 kBTU/h	-
Cooling Water Flow	50 gpm @ 30 C	20 gpm @ 30 C
Electrical Power	500 watts	20,000 watts
Estimated Capital Cost	$130,000	$145,000
Annual Power Cost (2,000 h/y, $0.10/kWh)	$100	$4,000
Annual Maintenance Cost	$1,000	$8,000

Safety Analysis

The compressor system was subjected to a complete Hazardous Operation Review in conjunction with a major supplier of hydrogen. The review divided the compressor system into six nodes and each node was reviewed for startup, normal operation, shutdown, failure modes, controls, design pressure, pressure relief, and materials.

Conclusions

Thermal hydrogen compression appears to offer significant advantages over mechanical compression for large scale hydrogen production from renewable resources.

Future Work

In order to validate the conclusions reached to date, we plan to construct and demonstrate a single stage thermal compressor that employs miniature hydride heat exchangers and an associated test apparatus that will verify thermal compressor performance while processing hydrogen with impure gas species. The test apparatus will be flexible enough to vary inlet impurity levels to determine threshold contamination levels (levels at which compressor performance is affected). Three purification technologies will be demonstrated: passive purification for oxygen and water, inert gas purification, and elevated temperature desorption for CO and CO_2.

In the case of impurities that can adversely affect fuel cell operation (e.g. nitrogen, CO), outlet hydrogen purity will be monitored to verify the degree to which a thermal compressor can perform the dual function of compressing and purifying hydrogen. This will allow the evaluation of trade-offs between hydrogen purity and compressor and fuel cell operating efficiencies necessary for the design and integration of full-scale systems

Acknowledgement

This material is based on work partially funded by the United States Department Of Energy's Hydrogen Program under Cooperative Agreement No. DE-FC36-99GO10448.

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